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THE FUTURE OF THE ITALIAN GEOSCIENCES OF THE FUTURE

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Nelle pagine seguenti vengono riportati gli abstract presentati in alcune sessioni selezionate del primo congresso congiunto SGI-SIMP "The Future of the Italian Geosciences – The Italian Geosciences of the Future".

Sono state selezionate le sessioni che si ritiene possano interessare maggiormente i Soci SIMP, in particolare quelle in cui uno dei convener è socio della SIMP o afferisce ad uno dei settori scientifico-disciplinari di ambito SIMP (GEO/06, GEO/07, GEO/08, GEO/09). È stata inoltre inserita la sessione poster "Le Geoscienze a scuola".

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PLENARY LECTURES

Back to Exploration with geological drivers: New frontiers of the last decade

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Keywords: Deep water exploration, Frontier Basins, Play Openers, Pre-salt, Abrupt Margins, East Africa, Levantine Basin, Play based exploration, Conjugate Margins.

Exploration trends have always been linked to the oil price. The last decade has been dominated by two main phenomena: the exploration and exploitation of Unconventional reservoirs and the deep water conventional exploration.

The oil Industry put priority on investing in new Plays Concept and new basins pushing conventional exploration spend to grow 4 times since early 2000. Limits have been pushed forward towards Ultra Deep waters, pre/sub salt Plays, subtle traps, harsh environments. Besides technology, sound geology and the capability to innovatively describe the subsurface and associates Petroleum Systems proven to be key to success in exploration and new venture activities.

Reserves discovered in the period 2004 – 2013 are almost three times the amount of reserves exploration brought to replacement during previous decades (Biteau et al., 2014). Most of these reserves comes from new Plays and frontier basins in deep waters that gained a primary role in reserve replacement eclipsing the golden exploration targets of the 80's and 90's. The last decade exploration arena has been characterized by fast movers International Independents and NOC's (National Oil Companies) opening Plays and Majors fast reloading their Portfolios on these new exploration frontiers while the Supermajors partially loose their grip on exploration arena. Few majors Integrated have been successful, among these eni, especially in the last few years. Moreover eni results have been achieved only based on conventional exploration, thus re-enforcing the central role of geology, geophysics and exploration technology in our organization. Being Play Openers (e.g. Anadarko/eni in east Africa) has been the key to be successful: coming first on under-explored areas, with new ideas to exploit new play concepts has proven the right attitude to access the bests assets at the best contractual conditions. The barycentre of eni activity rapidly shifted towards new basins and countries (e.g Mozambique, Ghana, Cyprus, Myanmar, Greenland) with new geological challenges.

Breakthrough events of the last 10 years exploration are: the emergency of the pre-salt play in south Atlantic deep waters; Cretaceous turbidites Play on Abrupt Margins (e.g. Equatorial Transform Margin); Rovuma and Tanzania Tertiary and Cretaceous clastic Play and Levantine Basin pre-salt clastic Play.

The Atlantic Margins have increasingly established their role of global "sweet spot" for the oil search, while east Africa and Levantine have delivered gas.

The opening of *Pre-Salt Carbonates oil Play* of Santos Basin has added over 30 billion barrels of oil since 2006 accounting almost 60% of the total volumes discovered in the decade. Spectacular interest rose for trying to export on the West African margin the Santos Play (Lottaroli et al., 2013). In this perspective, the Kwanza Basin (South Angola) gained most of the attention promising to be the focus of future pre-salt exploration.

In 2007 the discovery of the Jubilee Field unlocked the exploration potential of the *Cretaceous deep water Play* in offshore Ghana. The Zaedyus discovery in French Guyana, extending the successful play to the South American, have contributed to increasing the focus on exploration along the entire margin. Recent drilling activity turned out in light and shadows and so far the oil sweet spot of the margin seems restricted to the Ghana/Ivory Coast Tano Basin but the evolution of abrupt margins is still poorly known and the deposition of organic facies (source rocks) still away to be understood.

The entire Deep water tract of *East Africa* was hardly considered an area holding some exploration potential since the drilling of the first Anadarko well in Mozambique in 2010. Enormous volumes of Gas have been discovered in Mozambique/Tanzania (Rovuma Basin) in the last 2 years. Eni, alone, proven in excess of 15 bbnoe with 12 wells in Area 4 in Mozambique. Exceptional quality reservoirs have been encountered increasingly fitting the innovative and poorly documented model of a prevalent interaction of turbidite turbulent flow and bottom-current motion, with winnowing and redistribution of the finer materials deflected within sediment drifts (Fonnesu & Orsi, 2013).

In the past two years, the *eastern Mediterranean* has been transformed from an industry backwater, to one of the world's most exciting exploration plays. The catalyst for the transformation was the discovery of the giant Tamar gas field, in offshore northern Israel in 2009, followed by other significant discoveries in the surroundings made by Noble Energy. Since then the whole Levant Basin has witnessed a proliferation of bid rounds, well beyond the Israeli sector, in offshore Cyprus, Lebanon and Syria with increasing expectations and different Companies exposures.

Exploration drivers have radically changed in the last decade and results have been far better than the previous. The recent successes overturned most of the geological and exploration paradigms we brought from previous activity.

Non marine carbonates were almost completely disregarded under the reservoir perspective before the Santos pre-salt successes.

Being located down-dip from productive Tertiary Delta System and the presence of a mobile substratum (Salt/Shale) was considered a key driver for exploring deep-water Plays based on 1980/2000 historical record (Pettingill & Weimer 2003). None of these elements is present in the emerging deep-water provinces of the last decade (e.g Mozambique, Ghana).

Pure stratigraphic traps are having an increasing role in this new exploration phase while has been long disregarded, mainly when not DHI (Direct Hydrocarbon Indicators) supported.

Turbiditic reservoirs have been proven far away from main traditionally envisaged entry points in some basins (e.g Levantine). As well interaction between down-current evolution and bottom currents overprint gain new insights (e.g. Rovuma Basin).

Large accumulations of biogenic gas seem an overcome contradiction after the Levantine results.

Plate tectonics and geodynamic have been brought back to the base of exploration workflow. The conjugate margin perspective has been exported from the pre-salt of South Atlantic to the entire Atlantic and also to different Plays. Large scale paleogeographic and geodynamic reconstruction and the basic importance of a regional, Play based, approach are today largely agreed as basics in exploration.

Apparently there is still wide space to “invent” in exploration and probably, more than economical and commercial drivers, the geological “thinking” will be, also in the next future, the more powerful tool for success.

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Insights into the Geological Carbon Cycle from subduction to erosion

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Keywords: carbon, subduction, erosion, graphitic carbons, carbonates.

Carbon is ubiquitous on Earth from the deepest levels to the atmosphere, and is recycled between the different terrestrial enveloppes on various timescales and lengthscales. There is considerable ongoing research effort dedicated to the long-term carbon cycle, for instance regarding the Deep Earth to assess the carbon content in the Earth's mantle and core, but also to identify and quantify the contribution of various carbon carriers (diamond, carbonates, fluids, minerals…). Interaction between the solid Earth and the exosphere (atmosphere, hydrosphere and biosphere) is also matter of active research. Recent advances include mapping of non-volcanic CO_2 degassing at different scales in active orogenic belts, or the characterization of synthesis pathways for organic molecules during alteration of the oceanic crust. Altogether, we do have a broad view of the geological carbon cycle, which is the basis for complex models of the global carbon cycle (e.g. Berner 2003). However, if the major carbon terrestrial reservoirs are identified, their respective contributions are not well quantified, and the detailed picture for the fluxes between these reservoirs remains barely known.

This lecture will be focused on the carbon cycle in the Earth's lithosphere. This is a key segment of the geological carbon cycle at the interface between the exosphere and the solid Earth (Hayes and Waldbauer 2006), and where carbon is exchanged between the biomass and the mineral world. Also, there are two carbon subcycles in the Lithosphere, organic versus inorganic cycles, which broadly corresponds to the distinction between reduced versus oxidized carbon. Interactions between the two subcycles are largely unknown, although they may have profound implications for buffering redox conditions, or controlling the speciation of deep fluids. This means that an in-depth characterization of the carbon carriers by means of petrological and mineralogical investigations is required to complement and interpret geochemical data. Main lithospheric fluxes are identified : on one side, carbon is incorporated into the Lithosphere through burial of organic carbon as well as formation of carbonates in sediments or during weathering of the oceanic lithosphere. On the other side, carbon is released from the Lithosphere through degassing, erosion of continental surfaces or subduction to the deep Earth. The broad picture seems relatively simple (Gaillardet & Galy 2008), but field and experimental studies reveal that the reality is indeed much more complex, and that it depends on many local parameters.

A first example of this natural complexity will be discussed and regards the fate of carbonates during subduction based on field studies in high-pressure metamorphism settings. It has been recently proposed that carbonates can be dissolved due to intense fluid-rock interactions during subduction, and that the carbon-bearing fluids can migrate into the mantle wedge and ultimately could feed CO_2 degassing in Arc volcanism (Frezzotti et al. 2011 ; Ague & Nicolescu 2014). On the other hand, based on a similar approach, calcite reduction in metasediments at the contact with serpentinites has been evidenced and yielded wollastonite and graphite which can be highly refractory and could transfer carbon to the deep Earth instead of feeding the mantle wedge (Galvez et al. 2013). There might be other processes yet to be found, and the global respective contributions of devolatilization, dissolution or reduction of carbonates during subduction have now to be established. Another example regards the carbon budget during erosion of continental surfaces. A major point is then the fate of modern carbon deriving from the biomass (e.g. Galy et al. 2007): burial in sediments, or oxidation and release as CO_2 to the atmosphere? Also, the fate of carbonates and rock-derived organic carbon during continental erosion as well as the CO_2 consumption for silicates weathering have to be considered for a complete budget on various timescales. This is a complex factory that depends highly on the scale and dynamics of the erosion system, and that will be discussed in light of recent studies in active small-scale (Taiwan) and large-scale (Himalayas, Andes) systems.

The geological carbon cycle is a global issue that have implications for the geological cycle of many other elements like water, trace elements, sulfur or nitrogen. As such, it must be considered with a global approach involving geochemistry (isotopic, organic, bulk chemistry…) but also petrology, mineralogy, biology and thermodynamics among others. Tracking carbon reservoirs and fluxes in the solid Earth also requires investigations down to the finest observation scale (e.g. Wu & Buseck, 2013), as carbon may be present even when non expected, and therefore carbon may be widespread in deep geological settings as it is at the Earth's surface.

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Paleomagnetism in Italy: contributions to tectonics, stratigraphy, and timescale

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Keywords: Adria, apparent polar wander, palinspastic reconstructions, magnetic stratigraphy, timescales

Fifty years since the first paleomagnetic work in Italy, it's apparent that paleomagnetism in Italy has been transformational in three aspects of geologic research.

(1) In the 1960s, it was first realized that the Southern Alps of northern Italy possess Early Permian paleomagnetic declinations deviating from coeval directions from non-Alpine Europe by ~50° (Van Hilten, 1962). It was then realized that Southern Alpine data agree with coeval directions from Africa (Zijderveld et al., 1970), a coherence that was later proven valid also for the Mesozoic (e.g., Channell, 1996). Recent analyses of paleomagnetic data from Italy (Muttoni et al., 2013) support the concept of "Adria as a promontory of the Africa plate" (Channell et al., 1979), a concept that can be traced back to the classic work of Argand (1924). The corollary from this work is a "Pangea B" configuration for Atlantic-bordering continents in Early Permian, a conclusion that remains unpopular particularly amongst field geologists.

(2) Palinspastic reconstruction of the Sicilian and Apenninic fold-and-thrust belts has helped to reveal the paleogeography of these "African" Mesozoic continental margins prior to deformation, and has emphasized thrust-sheet rotation and oroclinal bending associated with the Tyrrhenian extension and its propagation northward into Tuscany, driving thrusting that largely postdates the initial collision of the Sardinia/Corsica island arc with the Sicilian/Apenninic "African" continental margin. The origin of the subducting slab beneath the Tyrrhenian Sea remains enigmatic because of the external/internal polarity of the "African" margin in this region (ocean to the west), uncertainties concerning the crustal basement in the Ionian Sea, and the necessity for continuity of the Sicilian Mesozoic continental margin into the Southern Apennines until deposition of the Oligocene to Early Miocene Numidian Flysch.

(3) The Upper Cretaceous magnetic polarity stratigraphy from the Gubbio section (Lowrie and Alvarez, 1977) was matched to marine magnetic anomalies (MMAs) and combined with the foraminiferal biostratigraphies (Premoli-Silva, 1977) to provide correlation of geologic stage boundaries to the emerging MMA-based geomagnetic polarity timescale (GPTS). This work spawned the correlation of the Cretaceous and Cenozoic GPTS to foraminiferal and nannofossil zones and hence to stage boundaries, both from marine cores recovered through ocean drilling for late Cenozoic time, and in land sections (largely from Italy) for the early Cenozoic and Cretaceous. The strong legacy of both micropaleontological and magnetostratigraphic research in Italy has resulted in the GPTS becoming central to geologic timescales for the last 160 Myr. The GPTS now provides linkage among biostratigraphies, chemostratigraphies, radiometric ages and astrochronologies; and has resulted in radical improvement in the resolution of time in Earth history.

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Deep drilling in the ocean crust : where are we, and what's next ?

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Keywords: Ocean drilling, International Ocean Discovery Program, IODP, ocean crust, mid-ocean ridges, Mohole to the mantle.

This lecture will draw from the latest results from Integrated Ocean Drilling Program (IODP) drilling expeditions in both fast-spread and slow-spread ocean crust, highlighting scientific questions related to accretion processes at mid-ocean ridges. In 2004-2005, IODP Expeditions 304 and 305 (Ildefonse et al., 2007; Blackman et al., 2011) illustrated the role of detachment faulting and associated hydrothermal alteration, together with localized and protracted magmatic construction recorded in the footwall of these faults, possibly involving recycling of mantle rocks (Drouin et al., 2010), in building crust in volcanic-poor regions of slow-spreading ridges. In fast-spread crust, observations from the lower crust gabbros are essential to test models on crustal accretion and cooling. IODP Expedition 345 at Hess Deep (Dec 2012 – Feb 2013) drilled and sampled for the fast time the layered primitive gabbros of fast-spread crust (Gillis et al., 2014). The preliminary results will be summarized. At site 1256, in intact East Pacific superfast spread crust, operations during IODP Expedition 335 in 2011 (Teagle et al., 2012) proved challenging throughout, and the lower crustal gabbros are yet to be recovered. The material recovered from the complex dike-gabbro transition zone document evolving geological conditions and the coupling between temporally and spatially intercalated intrusive, hydrothermal, contact-metamorphic, partial melting, and retrogressive processes at the interface between the magma chamber and the hydrothermal system. I will also shed light on some of the next challenges for scientific drilling in the ocean lithosphere, exemplified by the shallow coring project on the Atlantis Massif oceanic core complex on the Mid-Atlantic Ridge (http://www.iodp.org/doc_download/3299-758-full2cover), the "SloMo" project at the Southwest Indian Ridge (http://www.iodp.org/doc_download/3557-800-mdp), and the "MoHole to the Mantle" project (http://mohole.org), which aims to reach and sample the uppermost mantle beneath the Pacific fast-spread crust.

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One hundred years of mineral crystal chemistry

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Keywords: X-ray diffraction, Laue and Bragg interpretation, Crystal structures, Barlow contribution, Ionic radii, Goldschmidt rules, Pauling stability rules, Classification schemes, Polymorphic relationships and polymorphic transformations, Modular crystal chemistry, Crystal structure prediction, Automated electron diffraction tomography.

After the experience of Friedrich and Knipping suggested and interpreted by Laue, the young Bragg correctly explained the results of the Munich discovery and showed how to use X-rays to determine the arrangement of atoms in crystals and, in few years, actually derived the structures of several inorganic compounds. From then on it was possible to do something which had been conjectured about in the past several hundred years (Kepler, Huygens, Dalton, Barlow) without conclusive proof: namely to study the relationships between the chemical compositions of crystals and their atomic arrangements in space and their physical properties.

The comparison of the structural data permitted to Bragg to assert that crystals are composed of 'inelastic spheres in contact' and that 'it is possible to assign to the sphere representing an atom… a constant diameter.' This assertion marks the beginning of the modern crystal chemistry. The development of these concepts by Goldschmidt led to the first reliable list of ionic radii, to the rules relating ionic size and atomic structure and to the relationship between radius ration and coordination number. Shortly thereafter, Pauling, using a different approach through wave mechanics, produced a similar list of radii, the well known table of ionic radii of Pauling, who – at the same time - proposed the rules for the stability of ionic compounds, based on the concept of coordination polyhedrons as building elementary modules of inorganic compounds.

The stability rules of Pauling, as well as the conception, formulated by Bragg, of the structures of complex oxides as characterized by 'close packing' of oxygen anions, were the main guiding lines in the 'trial and error' procedures to determine the atomic arrangements in minerals and in inorganic compounds in general.

The increasing number of known structures raised the need for proper classification schemes, largely based on elementary structural units and the various ways of their connection. Machatschki, an outstanding coworker of Goldschmidt and Bragg, applied the Goldschmidt's ideas on crystal chemistry to the problem of silicate structures, demolishing current theories of silicate structures based on hypothetical silicic acids and established the concept of the silicon tetrahedral coordination by oxygen anions as the basic structural unit in silicates. The brilliant idea of Machatschki was then developed by L. Bragg, who sketched a reliable classification of the structures of silicate minerals, a classification which was subsequently updated and completed by F. Liebau.

At the same time the wide basis of structural data and the increased precision and accuracy of those data stimulated the revision of the old compilations of ionic radii (new compilation by Shannon and Prewitt), as well as a re-formulation of the Pauling's rule of valence bond balance (Baur; Donnay and Allmann; Brown and Shannon).

Examples are presented of the application of the crystal chemical tools to some important mineralogical, geochemical and geophysical problems: patterns of element distribution and partition; polymorphism in serpentine minerals; polymorphic transformations in the transition zone; spin pairing in the lower mantle.

An explosive growth of structural knowledge in the last decades of the twentieth century was stimulated by the new techniques of data collection, the high speed of computing and the advent of direct methods of structure solution, which resulted not only in an enormous increase in the number of known structures, but also in unraveling very complex arrangements. This increasing structural knowledge accompanied and stimulated the development of a new way to look at the arrangements of inorganic compounds, based on their modular aspects, from OD (order-disorder) theory (Dornberger-Schiff), particularly useful in dealing with polytypic families, to polysomatism and polysomatic series (Thompson), to the other types of approach to modularity.

The concept of assembling different, geometrically compatible modules, mainly structural layers, to build up complex structures has been very productive; in fact it not only consented a deep knowledge of the structural relationships inside wide families of natural and synthetic compounds, but also favored the solution of complex structural problems and permitted careful previsions of new possible structural arrangements.

Few lines of future developments of the crystal chemical study of minerals are briefly presented and discussed: 'synergy' between mineralogists and material chemists; computational simulations of structural arrangements; new possibility of automated electron diffraction tomography; ultra-intense pulses of radiation obtained with the new source, the x-ray free-electron laser (FEL).

SESSIONE S10

Geomaterials and their likes: from Nature to technology and manufacturing

CONVENORS

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The "Modica" stone: study of salt damage and assessment of efficacy of different consolidants

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The deterioration of a stone material is strictly related to its pore structure that affects the interaction between surface and environmental agents, especially water that transports large amounts of salts into the stone. Indeed, salt crystallization, is one of the most dangerous weathering agents in porous building materials (Belfiore et al., 2012; La Russa et al., 2013). This damage depends on numerous factors: type and quantity of salt in the stone, the shape of crystals, the super saturation of the salt, the pore size and the force of repulsion between salt and the walls of the pores (Scherer, 2004; La Russa et al., 2013), characteristics of porous network and environmental conditions. Specifically, pore size distribution is considered as a principal factor controlling the uptake and transport of liquid within a stone, because it determines the degree of damage of a rock subjected to salt crystallization attack (Yu and Oguchi, 2010). In particular, the crystallization pressure of salt crystals, growing in confined pores, is found to be the main cause for damage (Steiger, 2005; La Russa et al., 2013). The conservation of such degraded stone is an important step in the field of restoration; therefore, an essential aim of the scientist is the correct choice of conservation strategies to be applied to each case study. Specifically, the consolidation of degraded stone materials represents a crucial issue in the field of restoration of cultural heritage: is used to improve the cohesion of weathered stone when serious decay patterns and in-depth cohesion loss are present, consequently increasing the mechanical strength of the rock. This contribution presents the results of a laboratory experimentation carried out on a limestone largely used in the Sicilian Baroque architecture, namely the *Modica stone* (Belfiore et al., 2012). Several specimens, collected from a historical quarry nearby the city of Modica were artificially degraded by salt crystallization tests (EN 12370, 2001). Then, degraded samples were treated with three different consolidating products: i) a suspension of nanolime in isopropyl alcohol, ii) a suspension of nanosilica in water, iii) ethyl silicate dispersed in white spirit. A systematic approach, including thin section observations mercury intrusion porosimetry (MIP), colorimetric analysis, peeling tests (ISO 11664-4:2008, 2008; Drdàcky el al., 2012), point load test (ASTM D 5731, 2002) and scanning electron microscopy (SEM) analysis, was used to evaluate the correlation between salt crystallization and both microstructural and chromatic variations of the examined limestone as well as the efficacy of treatments. The consolidating behaviour of the tested products was also appraised by repeating salt crystallization tests after consolidation, in order to assess the resistance of treated stone against the crystallization pressure. Results showed that some treatments, although inducing an enhancement of stone cohesion, lead to an increase of the crystallization pressure, which could generate dangerous susceptibility to degradation.

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Structural relaxation along solid solutions: from the crystal field theory to the polyhedral bond valence approach

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Keywords: Structural relaxation, crystal field strength, polyhedral bond valence.

The degree of structural relaxation due to the isovalent substitution of cations along a solid solution can be evaluated by means of the structural relaxation coefficient, ε. This coefficient, defined as the measure of the mismatch between *average* and *local* bond distances at the crystallographic site where the substitution takes place, can vary between 0 and 1 (Urusov, 1992), i.e. from absent to total relaxation. Electronic absorption spectroscopy is one of the most common technique used in mineralogy to obtain local bond distances. Deconvolution of electronic spectra allows to calculate the crystal field strength ($10Dq$) that, according to the crystal field theory, is proportional to the inverse fifth power of the mean distances from XRD (Langer, 2001). In a recent work (Ardit et al., 2014) it is unequivocally demonstrated, at least for Al↔Cr substitutions at octahedral site, that ε inversely scales with the absolute difference between crystal field strengths of solid solution end-members. On the other hand, it is not always possible to obtain a complete solid solution, and the linear extrapolation of structural and optical parameters up to one of the end-members may lead to incorrect values. In light of this, a new approach based on the bond-valence method (Brown, 2002) has been developed to evaluate the lattice strain associated to different local arrangement of ligands at a coordination site (Dondi et al., 2014). In detail, it has been demonstrated that the $\mathrm{BVsum_{obs}}/\ \mathrm{BVsum_{calc}}$ ratio linearly scales with $10Dq$ (i.e. with the local bond distances of the involved crystallographic site). This ratio entails the observed bond-valence sum of polyhedra which share the oxygens coordinating a doped site ($\mathrm{BVsum_{obs}}$) with respect to the bond-valence sum calculated from ideal bond distances for each polyhedron ($\mathrm{BVsum_{calc}}$). In this contribution, the aspects of above will be discussed through different case studies (i.e. the effect of Cr^{3+} and Co^{2+} at octahedral and tetrahedral sites, respectively) and by a comparison of structures having a different atomic arrangement (i.e. the case of II-Na$M$$P_2O_7$ pyrophosphates).

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Non-destructive methods for stone materials characterization

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Keywords: Image Analysism, Non destructive method, stone materials.

Technical properties of stone materials are strongly dependent on their textural organization: in this note we present some application of image analysis techniques developed at the DST of Pisa to solve petrologic problems in basic research fields, but of potential commercial interest. Both methods collect data on the smooth surface of a slab and are not destructive, not requirying the preparation of thin sections.

Petrr® is a technique which can be applied to coloured stones, like granites, in which each mineral phase has a distinguishable colour. *Panoptes*® applies to materials in which grains have identical optical properties. Both methods have been patented.

Petrr® is based on a cursory method which provides a quantitative modal analysis that derives from comparison of RGB spectra of whole rocks and single minerals. The test can be applied to diverse fields ranging from the certification of the colour of a composite material, to archeometry and study of the modality of fracturation upon load. *Panoptes*® is a sophisticated technique that applies the Snell law to detect grain boundaries in monomineralic rocks, allowing the accurate spatial determination of structural surfaces and the related Grain Size Distribution. We show an application related to the non destructive determination of the yield strength upon compression and flexure and a method for the individuation of blocks that may undergo spontaneous fracturing.

Radiometric characterization of building materials from Eastern Sicily

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Keywords: Building materials, radioactive nuclides, Eastern Sicily.

Regulation no. 305/2011 of the European Parliament and of the Council of March 9, 2011 sets the conditions for the commercialization of construction materials. According to the provisions of the Directive 2013/59/EURATOM of the European Council of December 5, 2013, which lays down basic safety standards for the protection against dangers arising from the exposure to ionizing radiations, it is recommended to develop a measurement protocol to be followed in radiometric characterization of building materials such as mortars, cements and stone materials. In particular, the accurate determination of the radionuclides U238, Th232 and K40 occurring in building materials is of primary importance. Eastern Sicily, chosen as the pilot site for the testing phase, is characterized by the presence of rocks that are frequently used as building materials which, for simplicity, can be grouped into three main geological domains: volcanic, sedimentary and crystalline basement. The diverse nature of the rocks of the three domains is reflected in their different compositional features in terms of major and trace element concentrations, also affecting the primary abundances of radioactive nuclides (for example, various isotopes of U, Th, K, Rn etc.). A simplified analysis of the geological context of eastern Sicily suggests that the basement rocks are potentially the richest in radionuclides (U <5 ppm, Th <23 ppm), followed by those belonging to the volcanic domain (U < 3 ppm, Th <17 ppm) and finally by the sedimentary ones (U <2.5 ppm, Th <8 ppm). The rocks of each of the three identified geological domains may also exhibit a compositional variability depending on structural and textural features such as grain size, mineral habit, shape and preferred orientation. In addition to these intrinsic rock features, other physical characteristics, such as the presence of porosity, open or closed, as well as the pore size may also exert an important control in determining the selective enrichment or depletion of specific elements. Although the extent and effectiveness of different processes in producing compositional anomalies in various types of rocks is not well known in quantitative terms, these anomalies appear to be very frequent in systems subjected to intense active tectonics responsible for fracturing processes at different scales (from micro-fracturing up to regional scale fault systems). The knowledge of how the chemical-physical characteristics of rocks of different nature may influence the production of such anomalies is today still rather limited. The presence of rocks with a wide spectrum of chemical and physical characteristics and the complex structural framework of eastern Sicily give therefore the possibility to investigate factors involved in the generation of anomalous concentrations of radioactive isotopes in rock types commonly used as building materials.

Synthetic magnetic zeolites from waste materials: fly ash and red mud

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Keywords: fly ash, red mud, magnetic zeolites.

A new method is proposed to synthesise magnetic zeolites with suitable magnetic properties without the addition of iron oxide magnetic nanoparticles. The precursors employed for the synthesis are two waste materials, i.e. red mud (RM) and fly ash (FA), which are abundant, easy to recover and inexpensive. In addition, large amounts of FA and RM are deposited in landfills resulting in an increasing environmental problem.

The two waste materials were chosen because they both contain iron-based oxides, which are the most common magnetic materials used to induce magnetic properties in zeolites. RM is a waste material formed during the production of alumina when the bauxite ores are subjected to caustic leaching. RM are mineralogically characterised by the presence of iron oxides (i.e., primarily hematite and goethite with a minor boehmite component), while aluminium hydroxides, calcium oxides, titanium oxides, aluminosilicate minerals and sodalite occur as traces. However, the RM mineralogical composition varies due to the differences in the bauxite ores and the refining processes employed. The use of this waste material for zeolite synthesis has not been previously reported. FA is a by-product of thermal power plants and is used in concrete and cement manufacturing. FA is primarily composed of amorphous aluminosilicate and minerals, such as quartz and mullite. In addition, hematite, magnetite and carbon may also be present. More than half of FA is disposed of in landfills but in the last few years, much research has been focused on its use in solutions to environmental problems (Belviso et al., 2014) as well as for the synthesis of zeolites (Belviso et al., 2012).

The structural, microstructural and magnetic properties of precursors and synthetic zeolites formed from these two waste materials were investigated. Different types of zeolites were obtained for different FA/RM percentages and all of them possess sufficiently high magnetic moments to enable their easy separation from the solution using an external magnet. Therefore, the time consuming and expensive high performance centrifugation processes, which are typically employed to recover zeolites, can be eliminated.

The absorbance properties of the synthetic zeolites were determined by RO16.

Due to their properties, the synthetic newly-formed minerals can be used to solve water pollution problems and after their action they can be easily removed from solution.

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Silicate glasses recycling: optimization of the procedure for tobermorite synthesis

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Keywords: Tobermorite, Synthesis, Recycling.

Tobermorite identifies a group of layered-like calcium silicate hydrated minerals, with general formula $Ca_5Si_6O_{16}(OH)_2 \cdot 4(H_2O)$, composed by the three polytypes plombierite, tobermorite and riversideite, which differ for the baseline periodicity (approximately 14.0, 11.3 and 9.30 Å, respectively) that is in relation with the different content of water molecules. Here, we aim at finding a system to recovery silicate glass from recycling through economically advantageous and ecologically sustainable synthesis of tobermorite.

Preliminary synthesis trials suggested the introduction of additives to enrich the calcium content and optimize the composition of the glass powder.

Different synthesis trials were performed varying: i) the ratio (weight/volume) between suitably corrected starting material and the alkaline solution simulating the hydrothermal environment; ii) the concentration of the alkaline solution; iii) the interaction time between the starting material and alkaline solution; iv) the reaction temperature; v) the reaction environment (open container or bomb); vi) the interaction mode (static or dynamic).

The main phases formed in all the synthesis trials are tobermorite 11Å in varying proportions depending on the treatment used and calcite. The quantitative mineralogical analysis of each phase was obtained using the Rietveld-RIR method and the employed structural models for the quantitative refinement are those definied by Battocchio et al. (2012), Bonaccorsi et al. (2005) and Merlinoet et al. (2001). The degree of crystallinity of tobermorite was evaluated according to the method proposed by Coleman (2005) which takes into account the shape of the peaks of the reflections (002), (220) and (222).

The main conclusions of this work are that at constant temperature of synthesis, the amount of formed tobermorite and its crystallinity increases when increasing the time of interaction. In 48 hours of interaction we obtained a compound characterized by the presence of about 60 w/w% of tobermorite. In all the tests, notwithstanding the synthesis conditions employed, the total amount of calcite that forms is almost constant and slightly higher than the starting quantity present in the glass. So the synthesis of tobermorite is an usefull process in recycling waste glasses.

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Reactivity of fillosilicates kaolinite and montmorillonite towards μ-oxo complex of Fe(III) with phenantroline

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Keywords: montmorillonite, iron, phenantroline.

In the last decades many efforts have been devoted to functionalize clay minerals to impart them with specific properties, driven by the nature of the functionalising species and/or synergic effect resulting from the interaction. The best example of this trend is the synthesis and exploitation of pillared clays, organoclays, and clay mineral-polymer nanocomposites (Bergaya and Lagaly, 2011). In fact, clay minerals are particularly suited to host molecules able to exert a desired function: they are natural (not toxic), stable, biocompatible, available both as crystals and polydispersed powders. This is why the possibility to immobilize onto clays molecules having smart properties is still a goal of several current research, given the wide range of clay-functionalising molecules and properties that can be obtained.

The literature on Fe(III)-pillared clays is often lacking of a detailed description of the resulting structure; moreover, the loading of the materials starts from a mixture of iron species which makes heterogeneous also the iron speciation inside the mineral, dealing with partly hydrolyzed Fe(III) solutions. Here, we immobilize in a stable form a m-oxo Fe(III)-phenantroline complex ($[(OH_2)_3(phen)Fe^{III}OFe^{III}(phen)(OH_2)_3](SO_4)_2$ (phen= 1,10-phenanthroline) onto kaolinite and montmorillonite with the aim of obtaining stable Fe(III)-modified materials in which the iron species present in the surface and/or in the interlayer of the clay minerals is clearly and univocally identified. We obtain this goal introducing onto clays an iron solution in which the Fe(III) is complexed by a phenantroline ligand: the complexation prevents Fe(III) precipitation and allows to work at weakly acid and neutral pH values in acetate buffer solution. The obtained Fe(III)-modified kaolinite and montmorillonite were analyzed through DR-UV-Vis, TG-mass and elementar analysis techniques which provides a full characterization of the obtained materials including the immobilized iron species. Preliminary results showing that the Fe(III)-phenantroline modified montmorillonite acts as a catalyst for the oxidation of guaiacol in the presence of hydrogen peroxide are also presented.

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Characterization of CaO-based Sorbents for CO_2 capture: Sorbent Morphology and Reaction Kinetics

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Keywords: Carbon Capture and Storage(CCS), thermo-gravimetric analysis (TGA), in-situ X-Ray Diffraction XRD.

Among greenhouse gas emissions, anthropogenic CO_2 is widely recognized as the major contributor to global warming and climate change effects. Carbon dioxide emissions have rapidly increased due to the technological and industrial development and in the last decade the reduction of the CO_2 emitted by power generation industry (mainly the power plants based on fossil fuel combustion and coal gasification) has become an important worldwide scientific goal.Among the Carbon Capture and Storage (CCS) technologies, a promising cost effective CO_2 capture technique involves the utilization of calcium based solid sorbents. This approach exploits the reaction of calcium oxide (CaO) with CO_2 to form calcium carbonate ($CaCO_3$) under operative conditions not reachable with other CCS technologies, namely at high temperatures. The carbonation reaction (CaO (s) + CO_2 (g) ßà $CaCO_3$ (s)) is reversible and hence this technology should be based on cyclic stages of carbonation and of calcination. However, it is well known that CaO-based sorbents are usually subjected to a marked decay in the CO_2 capture capacity after multiple calcination-carbonation cycles, and this loss-in-capacity is believed to be caused by the sintering and the loss of the available pore volume of the sorbent particles.In order to improve the capture capacity of CaO-based sorbents, it is important to deeply understand the mechanism of calcium oxide carbonation and the kinetics controlling this gas-solid reaction. The purpose of this project is to investigate the relationship between sorbent morphology (before carbonation) and carbonation kinetics. In the present work, calcium oxide carbonation kinetics was followed by means of thermo-gravimetric analysis (TGA), mainly using CaO samples previously obtained by several ex-situ calcination stages conducted in a muffle. A characterization of each sample (before the carbonation stage) was carried out utilizing BJH and BET methods for pore size distributions and specific surface areas estimation. X ray powder diffraction technique was used to collect specific information about the initial CaO crystallite size. Finally, the carbonation kinetic constants (intrinsic kinetic constant and diffusivity through the product layer) were obtained by fitting of TGA data at different temperatures and were correlated with the starting CaO crystallite size and the sorbent structural parameters (porosity, specific surface, "structural parameter"). Additionally, the evolution of the CaO sorbent crystallite size during the calcination was monitored using in-situ X ray diffraction (XRD), at different calcination temperatures and with different atmospheres.

LightWeight Aggregates from industrial and c&D waste recycling: new perspectives for environment safeguard and energy saving

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Keywords: Recycling, waste management, lightweight aggregates, energy efficiency.

Recent advancements in R&D of LightWeight Aggregates (LWA) are overviewed. Aggregates are natural or artificial cohesionless materials constituted by elements with different grain size. LWA must possess: i) a mass/volume ratio not higher than 2000 kg/m^3 for each single particle; ii) a bulk unit weight not higher than 1200 kg/m^3 (EN 13055-1). LWA historically used in architecture are natural products such as pumices, diatomites, etc. During the fifties, the growing market demand enhanced the production of new LWA obtained by the expansion by heating at high temperatures of some natural materials such as clays, vermiculite and perlite. Reference parameters necessary to achieve an expansion are the SiO_2:Al_2O_3 ratio and the fluxing oxides (Fe_2O_3+MgO+CaO+Na_2O+K_2O); actually, these factors are not sufficient to determine the real expansion of the material for which it is necessary the occurrence of gas developing substances at raw materials' softening temperature. Recent investigations demonstrate that it is possible to produce LWA by using other natural materials such as tuffs, ignimbrites and zeolitized epiclastites as well as industrial wastes and recycled materials (Kazantseva, 1997; de Gennaro, 2004; 2007; 2009). Promising results were obtained with porcelain stoneware and ornamental stone polishing muds which contain small amounts of abrasive (max 3%wt SiC) that is the expanding agent necessary for the bloating. Good results were obtained also by mixing these muds with zeolite-rich rocks: the LWA obtained show similar or even better features that those currently marketed and provide a good prospect for the production of lightweight structural concretes. The proposed process also accounts for environmental positive benefits as these wastes of the ceramic or stone industry (tuffs included) have no current applications and need to be landfill disposed. Glass is also a recycled material useful for the production of expanded aggregates with good technical properties in the cement industry (Ducman et al., 2002; Lebullenger et al., 2010). Expanding agents are calcium carbonate or chalk, sodium sulphate, mixture of iron oxide with carbon, silicium carbide and nitride compounds. Other industrial wastes tested in the LWA production are the fly ashes and sewage sludge from wastewater treatment plant (Cheeseman & Virdi, 2005; Ramamurthy et al., 2006). A further application sector is the manufacturing of lightweight cement-based insulating panels, to improve the energetic efficiency of buildings.

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Nucleation of CAS by thermal treatment of Cs-clinoptilolite

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Keywords: $CsAlSi_5O_{12}$, clinoptilolite, nuclear waste.

Clinoptilolite is a zeolite highly selective toward cesium cation, thus is employed for the decontamination of radioactive wastewater to remove Cs radioisotopes (Armbruster, 2001). Heating is one of the methods tested to prevent cesium release from spent clinoptilolite. Due to the high thermal resistance of this zeolite in Cs-form, temperatures up to 1000-1100 °C have been required to attain an almost complete cesium immobilization inside materials prevailingly amorphous (Komarneni & Roy, 1981; Cappelletti et al., 2011). On the other hand, crystalline Cs-bearing phases like $CsAlSi_5O_{12}$ (CAS) have been often indicated as potential host for cesium radioisotopes (Gatta et al., 2008). This paper shows the possibility to obtain CAS by thermal treatment of a Cs-clinoptilolite.

Following a procedure already tested (Brundu et al., 2008), a powder containing about 90 wt.% of clinoptilolite has been prepared with the same Sardinian zeolite-rich rock used by Cappelletti et al. (2011) (QXRPD analysis: Siemens D5000 diffractometer; Bruker Topas software). Clinoptilolite has been initially Na-exchanged (10 cycles in 1M NaCl solution; s/l = 30 g/l) then conducted in Cs-form (5 cycles; 0.5M CsCl). Chemical analyses (ICP-MS) of Na- and Cs-exchanged materials have been performed at Actlabs (Ontario, Canada).

Taking advantage of a TA-Instrument Q600, amounts of about 15 mg have been heated up to 1300 °C (10 °C/min; air flow 100 ml/min; no isothermal step at 1300 °C). Several experiments have been performed by varying the cooling time and/or by re-heating samples already treated. Tests have been repeated to check the results. Heated samples has been investigated with a Bruker D2 diffractometer using a zero-background sample holder. So far, the best CAS pattern is related to the material that followed the path: RT→1300°→RT (fast cooling)→1300°→RT (cooling: 10 °C/min). Basically, this sample has a structure totally crystalline.

The ideal reaction $Cs_6Al_6Si_{30}O_{72}\cdot nH_2O \rightarrow 6CsAlSi_5O_{12} + nH_2O\uparrow$ summarizes the transformation of Cs-clinoptilolite.

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Characterization of the pore system of commercial bricks: a new perspective combining 2D and 3D imaging and traditional methods

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Keywords: Porosity, Computed micro-tomography, Image analysis.

During the firing process of bricks, mineralogical and textural changes transform the base clay into an artificial aggregate, characterized by significant porosity. Pore morphology, pore-size distribution and interconnection model influence the physical properties and represent important parameters to evaluate the predicting durability of bricks. Indeed, the porosity is the principal factor of connection between building materials and environment and entails the capacity of water storage and circulation and therefore, in combination with crystallization of soluble salts or stress due to freeze-thaw cycles, determines the decay behaviour. Four commercial bricks used also in restoration, with different compositions and firing temperatures, have been here analysed. Mineralogy and chemistry were studied by Field Emission Scanning Electron Microscopy (FESEM), X-ray Fluorescence (XRF) and X-ray Powder Diffraction (XRPD). Decay accelerated ageing tests were carried out to evaluate their resistance to frost and salt crystallization (UNI EN 12371, UNI EN 12370), while ultrasound was measured to check the elastic-mechanical characteristics and the structural anisotropy. The distribution of pore access size (in the 0.001–100 μm range) was determined by means of Mercury Intrusion Porosimetry (MIP). More information was defined measuring water absorption and drying according to the method described in UNI EN 772-7 normative. Capillarity rise, drying index, apparent and real densities, open porosity and degree of connection of pores were calculated. Size, morphology and texture of pore matrix (closed and open porosity) was detected by the 2D digital image analysis (DIA), carried out processing back-scattered images acquired by Scanning Electron Microscopy (SEM), and by 3D models, obtained from computed micro-tomography (μ-CT). The present work represents a preliminary study based on a multianalytical approach that combines various methods which investigate different size and aspects of the pore system, in order to draft a more complete knowledge of the porosity of bricks and optimize new mix designs to use in restoration and in modern buildings. This will represent a starting point to define a protocol for quantification and parameterization of morphological features of voids, through 2D and 3D digital image processing techniques in view of restricting and substituting the traditional method of mercury intrusion porosimetry.

Zn-biominerals: a perspective for environmental technologies to treat mine waters

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Keywords: bioremediation, bioremediation, sustainability.

Since life flourishing, biological processes have been producing a profound impact on the Earth's environment (Hazen et al. 2008). Often, biomineralization processes respond to processes of life adaptation to extreme environments. Science and technology have advanced to the point where their relationship can now be explored in interdisciplinary studies. Thus, Nature offers many examples of sustainable materials that can be used in environmental and material science technologies.

An extracellular Zn-biomineralization seasonally occurs in Naraculi river in the mine area of Ingurtosu (Sardinia, Italy). This biomineralization is made of hydrozincite and has relevant environmental implication for the abatement of Zn transported by river water. The cyanobacteria *Scytonema sp*. is responsible for the hydrozincite biomineralization. Several different factors affect the Naracauli biologically controlled mineralization, and bioremediation technology should be calibrated to optmize many of these factors. However, the Naracauli biomineralization occurs extracellularly, thus it is intrinsically a good candidate to be synthesized from Zn adsorption and nanocrystal nucleation onto a template.

In this work, biomineral hydrozincite is investigated in order to assess molecular mechanism ruling nucleation and growth. Wanty et al. (2013) found that Zn is adsorbed onto organic filaments, and hydrozincite nanocrystals there nucleate and aggregate to form (100) flattened mesocrystals. Biologically produced hydrozincite was sampled and then analyzed by various techniques. Focusing Ion Beam was used to cut oriented thin slices comprising both organic filaments and hydrozincite mesocrystals. The thin slices were then investigated by HR-TEM imaging finding that the organic filaments are substantially made of an amorphous phase. Then, organic molecules were extracted from the biomineralization material and analysed by H-NMR finding the lipidic composition. Actually, the ongoing research is aimed to fully characterize the *Scytonema sp*. produced template, and then nucleate hydrozincite from adsorption of Zn onto a corresponding synthetic template.

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Use and explotation of Piemonte dimension stone (NW Italy)

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Keywords: dimension stone, quarrying activity, Piemonte.

Stone materials represent the direct evidence of history and cultural heritage of important Italian areas. In particular, Piemonte region (NW Italy), thanks to the vicinity to the Alpine chain, shows a strong presence of local stones for the construction of buildings and infrastructures. Here stone has been widely exploited and used in the historical and contemporary buildings, monuments and urban art (Borghi et al., 2013), but also for local applications, such as rural buildings and villages (e.g. mountain huts, barns, pastures), street furniture, flooring, paving, stairs of local buildings (Dino & Cavallo, 2014). Piemonte valleys are characterized by the presence of quarrying activities (closed and still in progress) and of working plants, so that villages and towns present in Piemonte valleys widely employed, with different techniques, local stones. These rocks are mainly connected to siliceous materials such as granites (Montorfano and Baveno granites, above all), gneisses (beole and serizzi from Verbano – Cusio – Ossola area; Luserna stone, Malanaggio Stone, Villarfocchiardo Stone and Cumiana Stone from Cottian Valleys) and quartzite (*Bargiolina*), but also to marble (Palissandro from Crevoladossola, Candoglia and Ornavasso marbles) and biocalcarenites (Cantoni Stone). Local applications for rural villages, squares, city centres, etc.. have to be considered as "cultural heritage", because stones represent local history and culture and must be preserved as heritage stone. Therefore, such local infrastructures and buildings have to be restored in the right way, by employing stones correctly quarried, worked and certified.

In this context, the local authorities have to foresee for public works and buildings refurbishment, mainly in the city centres and rural villages, the application of local materials, which could be classified as heritage stones (Cooper et al. 2013). In that way not only the local peculiar heritage would be preserved but also local economy would be improved.

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Waste recycling: opportunities and challenges for earth sciences

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Keywords: critical raw materials, inertization, waste recycling, stability of mineral assemblages.

The Raw Materials Initiative undertaken by the European Commission sheds light and draw a renovated interest on recovery, reuse and recycling of waste materials. This action is relaunched by the Horizon 2020 programme, where waste recycling is one pillar of the climate and resources societal challanges. The main objectives of these policies are: a) recovery of critical raw materials from wastes (through urban mining and mineralurgical processing); b) paving the way toward a zero-waste society (cannibalistic approach to industrial manufacturing, construction and demolition, municipal solid wastes); c) exploiting novel processes and materials, especially in high throughput sectors (e.g., cements, ceramics, glasses, building materials). Opportunities and role of Earth Sciences in the field of waste valorization are envisaged by overviewing the main technological hindrances and open questions in the track of more efficient processes and safer products. Examples entail knowledge and experimental approach close to Geochemistry, Mineralogy and Petrology. Relevant tasks concern: tracing useful elements in waste deposits; efficiency of technologies for the recovery of critical raw materials; modelling ion mobility and interaction with minerals; behaviour of elements during processing and after transformation into products; effective incorporation of hazardous components and their inertization; phase transformations which waste materials undergo along the processing; crystal chemistry of phases in waste-bearing products; making sense of new parageneses in waste-based materials; stability of mineral assemblages during thermal cycles; role of amorphous and glassy phases; predictive models to improve the mix design.

Characterization of sustainable conglomeratic materials made with aggregates recycled from returned concrete

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Keywords: Sustainable concrete production, multi-analytical characterization, numerical modeling.

Nowadays, one of the main waste materials produced by the ready-mix concrete plants is constituted by returned concrete, the residual amount of fresh concrete not poured to the building site and returned to the production plant by the truck mixer. Recently, a new technology has been developed to convert such waste into sustainable concrete aggregates, based on the utilization of two types of additives - a super-absorbing polymer (SAP) and a set accelerator - that transform fresh concrete into a solid, granular material constituted by a core of original coarse aggregate surrounded by a composite shell of sand and hydrated cement. In the present contribution, the results of a series of characterization studies based on both experimental and modeling approaches are reported, to investigate the properties of such materials at the fresh and hardened state.

One of the key technological issues related to the treatment of returned concrete with this procedure is related to the definition of the right period of curing, to obtain a material with both granular characteristics and proper mechanical properties. For the purpose, a series of numerical simulation with the VCCTL software developed by NIST were performed, to define the proper curing intervals according to temperature and concrete type.

Furthermore, a series of studies have been performed to investigate the chemical, physical and microstructural properties of the obtained granular materials. The standard characterization tests (density and absorption measurements, abrasion and freeze/thaw resistance determination, soluble chlorides and sulfates quantification) confirmed that such materials are fully utilizable as concrete aggregates. Furthermore, micro-analyses by X-ray micro-tomography and scanning electron microscopy (SEM-EDS) allowed to define the microstructural and micro-chemical characteristics of such materials, characterized by high density of the cement pastes and extremely good interfacial properties between the aggregate core and the surrounding composite shell.

Finally, the effects of recycled aggregates addition into conglomeratic materials of different strengths have been investigated by means of uniaxial compression tests, absorption tests and SEM-EDS micro-analyses. For the purpose, two types of granular materials have been produced, from original low strength and high strength concretes, respectively. Then, the resulting aggregates have been used with a 30% by weight degree of substitution to produce three concretes characterized by different compressive strength classes (low, medium and high, respectively). The results indicate that in no case the properties and the nominal strength class of the concretes are downgraded by the aggregate substitution. Furthermore, the water permeability properties of the final concretes are always significantly improved by the addition of the recycled aggregates. Such improvements in the technological properties of concretes are justified by a substantial absence of interfacial transition zones (ITZ) between recycled aggregates and surrounding cementitious matrices, as showed by SEM-EDS analyses.

Breakdown of natural chrysotile and asbestos-containing waste by Self-propagating High temperature Synthesis (SHS)

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Keywords: Chrysotile, asbestos-containing waste, inertisation.

The Asbestos-Containing Waste (ACW) represents, beside the urban solid waste, the most conspicuous typology in our country and the first among toxic wastes. In the perspective of reducing the environmental issue and to explore recycling of the breakdown products, we experimented the use of Self-propagating High temperature Synthesis (SHS), exploiting the highly exothermic and fast self - propagating high temperature alumino-thermic reactions (Munir, 1988; Gaggero et al., 2010).

Experimental procedures typically referred to the SHS method were adopted, taking advantage of the energy release of the highly exothermic reactions ignited by a relative low heat source. Reactants were selected between different oxide - metal couples (Hem+Mg; Mgt+Mg; Hem+Al) liable to activate the aluminothermic reaction and to break down the chrysotile. The successful experiments are based on the couples Fe_2O_3 + Mg and Fe_3O_4 + Mg varying some parameters as chrysotile or ACW abundance (from 45% to 65% weight), size of the pellet (diameter 13 and 25 mm, height from 7 to 70 mm) and weight of samples (from 2 to 100 g).

The process occurred in a reaction chamber with Ar inflow at ambient pressure. Chrysotile-reactant pellets were placed inside the chamber under a W coil that transferred the ignition energy from a power supply, turned off as soon as the reaction was ignited (after about 7s). After ignition, the average loss of weight of the sample resulted c. 4% that normalized to the percent of chrysotile in the pellet corresponds to a variable weight loss between 10 and 12%, likely corresponding to the dehydroxilation of chrysotile. As the toxic action of asbestos resides in habit, composition and size, inertization requires the structural change of mineral fibre. Following the combustive reaction, all experiments demonstrated effective in destructing the fibrous habit of chrysotile, turning its composition to stubby olivine grains. The asbestos inertization is particularly advantaged by the SHS process in comparison with conventional thermal treatments, due to fast reaction time, low activation energy and simple instruments, that positively reflect into time and costs of the process. Finally, the product of this transformation is liable to be re-used as second material.

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Experimental method for the deep cleaning of soluble salts from mortars and lithic materials

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Keywords: Soluble salt extraction, mortars, frescos.

A common *in situ* alteration pattern in mortars and frescoes is the crystallization of soluble salts from solutions rising by capillarity or circulating in damp walls. If this pattern reveals overwhelming upon other environmental decay factors, the extraction of salts is the major restoration to operate on the artpiece to recover its pristine conditions after a preliminary assessment and mitigation of the causes of soaking.

An innovative method has been assessed to enhance the quality and durability of decontamination by soluble salts, compared with conventional application of sepiolite or cellulose wraps.

The conventional application of cellulose or sepiolite requires casting a more or less thick layer of wrap on the mortar, soaking with distilled water, and waiting until dry. The soluble salts are then trapped within the wrap. A set of artificial samples reproducing the stratigraphy of frescoes was contaminated with saline solution of known concentration. The extraction by the new method (UNIGE patent under filing) was demonstrated by trapping the salts within layers of Japanese paper juxtaposed to the mortar; the extraction was operated in a significantly shorter time than with wraps (some hours *vs*. 1-7 days). Two cycles of about 15 minutes are effective in deep cleaning from contaminants. The decontamination was proved by conducibility tests on the juxtaposed Japanese paper.

In addition, we established that a considerable amount of soluble salts could be further extracted even after the conventional treatment, demonstrating that traditional wraps operate just a shallow cleaning, and soluble salts are liable to emerge as efflorescence affecting the conservation after restoration.

The optimum cleaning is obtained by finishing the innovative extraction with sepiolite/cellulose wraps. The innovative method decreases the time for accurate cleaning before consolidation and protection.

MSWI residues as unconventional source of critical raw materials: understanding possible easy ways to evaluate their occurrence and to obtain added-value products

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Keywords: Critical raw materials, Waste, Substance flow analysis.

Critical raw materials (CM) are chemical elements and minerals such as Be, Co, Ga, Ge, In, Mg, Nb, Sb, Ta, W, Platinum Group Elements (PGE), Rare Earth Elements and Y (REY), fluorite, graphite, which are important for the technological development (European Commission, 2010) needed to achieve a low-carbon society.

Solid residues from Municipal Solid Waste Incinerators (MSWI) may represent an unconventional source of valuable chemical elements, as a continue flow stream (e.g.: Morf et al., 2012). In this contribution we will show that the CM content in bottom and fly ashes, which are the common MSWI outputs, and their estimated annual flow (t/a) are significant. Analyses were carried out by ICP-MS and XRF, reaching very low detection limits in order to evaluate the CM potential. Total CM (Ce, Co, Nb, Sb, Ta, W) in bottom ashes is 380 mg/kg; fly ashes contain 1022 mg/kg Sb, 49 mg/kg total other CM (Ce, Co, Nb, Ta, W). Bottom and fly ashes have an average concentration higher than 60 mg/kg SREY. The estimated substance flow shows that an hypothetical recovery is advantageous in bottom ashes for the most of the elements.

To further explore the CM potential of bottom ashes, we have considered the different granulometric fractions produced by simple gravitational sorting during their temporary storage as stockpiles. The substance flow analysis reveals that the bottom ash finer fraction (which forms the top layer) shows an overall enrichment in CM compared to the other coarser layers. The finer bottom ashes residing on the top of stockpiles, which can be sampled by simple visual inspection at the plant storage facility, seem to represent the most promising target for future recovery strategies. We are also investigating whether correlations with the mass specific magnetic susceptibility of the MSWI solid residues can be used as proxies for CM occurrence (and, hence, as a fast indicator of CM's relative availability). First results show that this parameter is related to the REE distribution.

On the short term, our data will help to bolster the attention on incinerated waste as an unconventional solution for raw materials supply. A comprehensive strategy has to be implemented to address the quantitative availability of CM through new prospecting technologies, as called for by the European Commission in its European Innovation Partnership in Raw Materials (EIP).

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Innovative, quantitative, *in situ* characterization of weathered building materials

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Keywords: Weathering, ablational decay, reproducible sampling.

The diagnostic of weathered rocks and mortars aims at deciphering processes that affect materials exposed under outdoor, indoor, buried environmental conditions, and at enucleating decay factors. However, the characterization of weathering intensity is mostly descriptive and non-quantitative (ICOMOS Glossary, 2008). The Fitzner indexes applied to arenites (Fitzner et al., 2002) and more recently to marbles (Scrivano et al., 2013) help the description. The current method of decay diagnostic (Drdàcky & Slìzkovà, 2014) was improved by a joint gravimetric + dynamometric measure of ablational decay products. It encompasses:

i) Preparation of stubs for SEM analysis with adherent conductive carbon tape (surface area 1.3 cm^2)
ii) Weighing of stub + tape + its plastic envelope at 0.001 g precision
iii) Connecting the stub to a pocket penetrometer
iv) Non invasive sampling of the incoherent dust applying a constant pressure of 2 kgf for 1 minute, then packing away the stub without loosing grains
v) Weighing of stub + tape + weathering products + their plastic envelope at 0.001 g precision
vi) Recast the weight of removed material
vii) Addressing the weathering products to electron microscopy and or microanalysis.

Our quantitative peeling test was applied on a cladded wall in the Staglieno Monumental Cemetery in Genoa. The wall is 96 m long and shows weathering gradients due to a neighbouring interred stream and to different insulation. Slabs of Verde Polcevera ophicalcite were tested in three different areas of the structure (samples c1-c5 collected to the E, samples c6-c10 at the centre, samples c11-c15 to the W). The results highlighted capillary rise up to 2 meters height (weight of samples: c3 = 0,009 g; c8 = 0,0224 g; c13 = 0,0063 g) and a more weathered central area (weight of samples: c6 = 0,0062 g, c7 = 0,0058 g, c8 = 0,0224 g, c9 = 0,0024 g, c10 = 0,0045 g). On the whole our protocol allows reproducible factual sampling. Moreover, if carried out on statistically significant population, the definition of Intensity of decay results categorized.

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Influence of minor elements on the clinkerization process

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Keywords: clinker, minor elements, in-situ high temperature X-ray powder diffraction.

Ordinary Portland cement clinker is nowadays usually produced by firing in a rotary kiln a blend of limestone and clay minerals up to 1400°C, where a melt is formed and clinkerization occurs (Taylor, 1990). This standard manufacturing process is very energy-consuming and pollutant, so the exploration of new techniques and methodologies is of primary importance, because of the growing knowledge in terms of environment preservation, paying particular attention to intensive quarrying of ore bodies and greenhouse gases emissions, together with a careful energy policy, oriented towards eco-saving and recycle. Usually, manufacturing 1000 kg of clinker requires 850000 kcal, 1700 kg of raw materials and emits 850 kg of pollutants, mainly carbon dioxide (van Oss & Padovani, 2003; Habert et al., 2009). A performed solution is represented by the use of wastes both as raw materials and alternative fuels, but this involves the occurrence of minor elements as impurities, which can enter the structure of main clinker phases.

Most common impurities are sulfur, magnesium and alkalis; individually, their behavior has been studied in details (Emanuelson et al., 2003), but a comprehensive and combined study lacks, even though they normally occur together at production plants. This research aims to study the behavior of the above-mentioned impurities together and their reciprocal interaction during the clinkerization process. Processing in situ High Temperature X-Ray Powder Diffraction (HT-XRPD) patterns, collected at different temperatures up to 1400°C, performing Rietveld refinement method will give a quantitative phase analysis, while observation and processing of scanning electron microscopy back scattered electrons images will make possible to determine porosity and cracks distribution in manufactured clinker.

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Alunite-bearing kaolin from Piloni di Torniella mine: a suitable raw material for the synthesis of metakaolin-based geopolymers?

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Keywords: Metakaolin-based geopolymer, alunite, texture.

Geopolymers are ceramic materials obtained at temperature lower than 150 °C by alkali activation of an aluminosilicate solid precursor of natural (*e.g.*, kaolin/metakaolin) or industrial (*e.g.*, fly ashes) origin. The increasing interest in these materials is related to their "eco-friendly" production process and good mechanical and chemical properties (see Duxson et al., 2007), which may vary depending on the kind of raw material and processing conditions.

Aim of this work is to investigate the possibility to employ low-quality natural kaolin, containing secondary minerals such as alunite, for geopolymer synthesis. Alunite is present in kaolin deposits deriving from trachyte, rhyolite, and similar potassium-rich volcanic rocks and normally hinders the use of these clays in the ceramic industry due to the release at about 600 °C of SO_x gases which damage furnaces refractories.

Geopolymers have been synthesized from kaolin from Piloni di Torniella mine, supplied by Eurit s.r.l. The kaolin is composed of about 55 *wt*% quartz and feldspar, 40 *wt*% kaolinite and 5 *wt*% alunite, and was activated at 550 °C for 3 hours. This condition have been chosen in order to prevent alunite desulphation, although at this temperature the dehydroxylation of kaolinite is not complete and hence it is expected that a lower amount of it can actually react with alkali.

The heated raw material and a sodium silicate solution have been mixed in stoichiometric amount to allow the following molar oxide ratios of synthesised samples: $SiO_2/Al_2O_3 = 4.6$ and $Al_2O_3/(Na_2O + K_2O) = 1$. Geopolymer maturation conditions of 52 °C for 19 hours have been chosen according to the results of a previous study, where the synthesis conditions have been evaluated by the Design of Experiment approach on geopolymers synthesised from alunite-free kaolin.

The synthetic conditions allowed to obtain geopolymer samples characterised by high thermal stability and good mechanical properties, showing compressive strength higher than 80 MPa. A multi-technique approach has been used to characterize the synthesized geopolymers: (i) compressive strength test has been used as a qualitative tool to assess the success of synthesis reaction; (ii) X-ray powder diffraction and Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) spectroscopy have been applied to investigate phase composition; (iii) optical and scanning electron microscopies have been used to study the textural features of geopolymers, at different lengths of scale; (iv) differential thermal analysis and gas pycnometry techniques have allowed to investigate the thermal stability and density of synthesised samples, respectively. The relationships among mineralogical, petrographic and physical features of geopolymers have been studied and related to sample strength. Furthermore, leaching tests have been carried out and the resulting materials have been characterised. The amount of sulphur in geopolymer samples has been measured, before and after the test, by using Scanning Electron Microscope - Energy Dispersive spectrometry technique. Inductively coupled plasma - optical emission spectroscopy has been used to evaluate the concentration of sulphate, related to alunite decomposition, in the leached solution.

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Host-guest and guest-guest interactions in a new perylene dye - Zeolite L composite

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Keywords: Zeolite L, perylene dye, ZL/tB-DXP composite, SR-XRPD, structure refinement, IR, UV-Vis.

In recent years dye-zeolite L (ZL) composites (Calzaferri, 2012; Devaux et al, 2013) attracted renewed interest in several fields. These materials, in fact, can mimic the biological blueprint of the natural photosynthesis, designing systems used in several applications as novel optical materials, with a large variety of different properties. They are employed as key components of promising devices to be used in technology for converting light into stored energy, in biology and diagnostics. Supramolecular organization inside the ZL nanochannels depends on the shape and size of the dye, on its orientation – in turn affected by zeolite geometric constrains – and on the extraframework content (e.g. cations, H_2O molecules). Due to the influence of the involved guest-guest and host-guest interactions on the optical properties of dye−ZL systems, the study of their structure is a prerequisite for advancing our knowledge of such materials. In this work we have studied the ZL/tB-DXP composite (Devaux et al, 2013), prepared by loading ZL with a dye belonging to the perylene family. Specifically, we investigated the influence of water molecules on the host−guest interactions through an integrated approach based on IR spectroscopy and Synchrotron Radiation X-ray Powder Diffraction (SR-XRPD). The ATR-IR and FTIR spectra collected on the hydrated and dehydrated form of the ZL/tB-DXP composite showed strong shifts of all the dye peaks with respect to those collected on the pure dye. Moreover, in the hydrated form the shift is significantly higher than in the dehydrated one, giving a clear indication that the water molecules present in the channels strongly affect host-guest and guest-guest interactions. The crucial role of water molecules was also confirmed by a general blue shift observed in the diffuse reflectance UV-Vis spectra collected upon water removal.

The SR-XRPD data showed a slight increase of the unit cell volume of the ZL/tB-DXP composite respect to the as-synthesized ZL. The structural refinement revealed the presence of about 0.25 tB-DXP molecules per unit cell, aligned along the main 12MR channel of ZL, and interacting with the framework oxygen atoms via hydrogen bonds mediated by water molecules. Concluding, both the results of the IR measurements and of the structural refinement highlight the effective influence of the water molecules on the optical properties of ZL/tB-DXP composite.

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Topotactic and reconstructive changes at high pressure and temperatures from Cs-natrolite to Cs-hexacelsian: potential nuclear waste disposal materials

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Keywords: Nuclear technology, Cs-zeolites, Cs-hexacelsian.

Synchrotron X-ray powder diffraction experiments have been performed on dehydrated Cs-exchanged natrolite in order to systematically investigate successive transitions under high pressures and temperatures. At pressures above 0.5(1) GPa using water as a pressure transmitting fluid and after heating to 100°C, dehydrated $Cs_{16}Al_{16}Si_{24}O_{80}$ (deh-Cs-NAT) transforms to a hydrated phase $Cs_{16}Al_{16}Si_{24}O_{80}\cdot 16H_2O$ (Cs-NAT-II), which has a ca. 13.9% larger unit-cell volume (Lee et al., 2011; Seoung et al., 2013). Further compression and heating to 1.5(1) GPa and 145 °C results in the transformation of Cs-NAT-II to $Cs_{16}Al_{16}Si_{32}O_{96}$ (anh-Cs-POL), a H_2O-free pollucite-like triclinic phase with a 15.6% smaller unit-cell volume per 80 framework oxygen atoms (O_f). At pressures and temperatures of 3.7(1) GPa and 180 °C, a new phase $Cs_{1.547}Al_{1.548}Si_{6.452}O_{16}$ (Cs-HEX) with a hexacelsian framework forms, which has a ca. 1.8% smaller unit-cell volume per $80O_f$. This phase can be recovered after pressure release. The structure of the recovered Cs-HEX has been refined in space group $P6_3/mcm$ with a = 5.3731(2) Å and c = 16.6834(8) Å, and also been confirmed by HAADF-STEM real space imaging. Similar to the hexacelsian feldspar (*i.e.*, $BaAl_2Si_2O_8$), Cs-HEX contains Cs^+ cations which act as bridges between the upper and lower layers composed of tetrahedra and are hexa-coordinated to the upper and lower 6-membered ring windows. These pressure- and temperature-induced reactions from a zeolite to a feldspar-like material are important constraints for the design of materials devoted to Cs^+ immobilization.

Lee Y., Lee Y. & Seoung D. 2010. Natrolite may not be a "soda-stone" anymore: Structural study of fully K-, Rb-, and Cs-exchanged natrolite. Am. Mineral., 95, 1636-1641.

Seoung D., Lee Y., Kao C.-C., Vogt T. & Lee Y. 2013. Super-Hydrated Zeolites: Pressure-Induced Hydration in Natrolites. Chem. Eur. J., 19, 10876-10883.

HP-induced confinement and polymerization of ethylene glycol in high-Si mordenite

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Keywords: Zeolite mordenite, High-pressure polymerization, synchrotron XRPD, pressure-induced molecular intrusion.

The confinement and the high-pressure (HP) induced polymerization of organic molecules into microporous solids can be of paramount technological interest. Pressure is the most efficient tool to reduce intermolecular distances, thereby permitting continuous tuning of the corresponding interactions and allowing the chemical reactions to occur without the use of catalysts. In this work, the penetration of guest molecules under HP into a high-silica mordenite (HS-MOR, (SiO2)48•5 H2O, SiO2/Al2O3 ~ 200, s.g. Cmcm) in its protonated form was investigated by in-situ synchrotron X-ray powder diffraction (XRPD) using (16:3:1) methanol:ethanol:water (m.e.w.), (3:1) water:ethanol (w.e.), ethylene glycol (e.g.) and resorcinol (res.) as penetrating pressure transmitting media (PTM). The HP synchrotron XRPD experiments were performed in DAC at SNBL1 (ESRF, Grenoble). The powder patterns were collected in the following pressure ranges: Pamb - 11.8 GPa, Pamb - 2 GPa, Pamb - 8.8 GPa and Pamb - 8.5 GPa for m.e.w., w.e., e.g., and res., respectively. Other patterns were measured upon decompression. The evolution of the structural features was followed by full profile Rietveld refinements. The general results of this study are the following:

i) penetration of guest species into the channels, even at very low P, has been observed for all the tested PTM;

ii) the P-induced effects are partially reversible upon decompression;

iii) In the P range Pamb-1.2 GPa, common to all the experiments, the volume contraction of HS-MOR compressed in e.g. (-1.47%) is higher than those registered in m.e.w., w.e. and res (-0.96%, -0.86% and -1.02%, respectively). However, on the overall investigated P range, the volume contraction undergone in e.g., m.e.w. and res. is rather similar. This suggests a slower penetration rate of the guest molecules when using ethylene glycol as PTM.

Of great interest is the formation, at about 1 GPa, of polymeric chains of ethylene glycol molecules (polyethylene glycol), running along the c-axis inside the 12-membered ring channels. An important aspect of this intrusion process is that it is partially irreversible upon pressure release. This HP-polymerization could represent a novel “green chemistry” route to industrial chemical synthesis, as the use of additional and polluting compounds is avoided (Santoro et al., 2013; Scelta et al., 2014).

Santoro M., Gorelli F. A., Bini R., Haines J. & van der Lee A. 2013. High-pressure synthesis of a polyethylene/zeolite nano-composite material. Nature Comm., 4, 2564-2569.

Scelta D., Ceppatelli M., Santoro M., Bini R., Gorelli F. A., Perucchi A., Mezouar M., van der Lee A. & Haines J. 2014. High Pressure Polymerization in a Confined Space: Conjugated Chain/Zeolite Nanocomposites. Chem. Mater., 26, 2249−2255.

Synthesis and colouring performance of the $CaCoSi_2O_6$ pyroxene ceramic pigment

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Keywords: Ceramic pigment, pyroxene, colouring performance.

The pink coloured pyroxene $CaCoSi_2O_6$ has been here synthesised as a possible ceramic pigment stable in very aggressive media like Ca and Zn-rich glazes and glassy coatings used in porous tiles. Pyroxenes was selected as a crystalline structure both for their six/eight-fold crystallographic sites where Co^{2+} ions can be accommodated, producing a pink colour and for the good stability to the alteration. The colour of the Co^{2+} compounds depends on the coordination geometry and the host lattice: if cobalt is in tetrahedral coordination the colour is deep blue while, if the coordination number is higher, six or eight, the hue swings to pink or violet (Mimani & Ghosh, 2000; Dondi et al. 2010). In ceramic science, the alternative Co-based pink colourant is frequently represented by the Co-olivine, but it does not remain stable in porcelainized glazes during firing (Llusar et al. 2001). Moreover, $CaCoSi_2O_6$ pyroxene has a minor cobalt content per formula units respect to the Co-olivine, promoting minimization of the production cost and toxicity. The syntheses were performed through solid state method, mixing up powders of Co_3O_4, $CaCO_3$ and amorphous SiO_2; different time and temperature of annealing were used to pinpoint the best synthesis condition for the formation of single phase $CaCoSi_2O_6$. The final product of the different annealing has been analysed by XRPD, SEM-EDS and the colour behaviour has been investigated (CIE-Lab). Syntheses made at temperature equal or lower than 1100°C produced a mixture of $CaCoSi_2O_6$ (pyroxene), $Ca_2CoSi_2O_7$ (Co-åkermanite), Co-olivine (Co_2SiO_4) and SiO_2 in different quantities. Co-åkermanite has one fourfold crystallographic site where Co^{2+} ions can be accommodated, thus ensuring its blue colour. The hiding power of blue Co in fourfold coordination is more intense than that in octahedral one; for this reason the presence of Co-åkermanite dominates the resulting colour, giving a deep blue hue even if it is present in small quantities. Increasing the temperature to 1150°C for about 24 hours, a single pyroxene phase with composition $CaCoSi_2O_6$ is obtained: the final colour is a bright pink (CIE L*=64, a*=23, b*=-9). Technological tests were done for the resulting pigment $CaCoSi_2O_6$ mixing them with glaze and glassy coating commonly used in the industrial tile making process. The final results showed that only in one case the $CaCoSi_2O_6$ withstands the corrosion by melted glaze and acts as a pigment giving a pale-pink colour (CIE L*=67, a*=8, b*=-14). In the other cases the chemical attack caused a gradual leaching of Co^{2+} that dissolves into the glass, thus imparting a deep blue colouring (dye behaviour).

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Effects of soda-lime-silica waste glass on mullite formation kinetics and micro-structures development in vitreous ceramics

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Keywords: soda-lime glass, sanitary-ware body, physical-mechanical features, kinetic analysis.

Several papers on the use of different waste glasses in industrial products have been presented proving that such refuses can be an alternative to the traditional raw materials (Bernardo et al., 2010). Among silica-rich wastes those from bottle banks have attracted much attention. Glass cullets (referred to as soda-lime or soda-lime-silica (SLS) glass) from urban waste consist mainly of silicon, sodium and calcium oxides. Thanks to its potential of low temperature viscous flow sintering, SLS glass can be considered as a good candidate for total, or partial, replacement of the natural fluxes (mainly Na-feldspar) in ceramic manufacturing. Souza et al., 2004 claimed that SLS glasses can substitute feldspar-based fluxes up to 5 wt% without affecting the technological features of the output but reducing the sintering temperature.

The use of SLS glass in the vitreous sanitary-ware ceramics provides an environmental safeguard by saving natural resources, and reducing the process energy consumption and CO_2 emissions. However it is still a matter of debate how SLS-glass affects the basic ceramic reaction kinetics. Much attention has been paid to porcelain-type technology, but comparatively little has been spent for vitreous sanitary-wares, which result from high-temperature treatments (~1230 °C) of the system clay-kaolinite-feldspar-quartz.

In the present paper, we discuss the introduction of SLS glass into the vitreous sanitary-ware ceramic phase-system in partial replacement of the traditional flux agent (Na-feldspar) focussing the attention on: (i) how SLS glass affects the sanitary-ware ceramic transformations at high temperature, in terms of mullite nucleation and growth; (ii) how SLS glass influences the micro-structures formation and the technological properties of the output, as a function of the firing time (t_f) and temperature (T_f).

The study was performed on samples with classical vitreous sanitary-ware compositions in which a fraction of feldspar is replaced by SLS glass. The mullite kinetics was investigated by isothermal runs using *in-situ* High Temperature X-Ray Powder Diffraction (HT-XRPD) and Scanning Electron Microscopy (SEM). Samples fired over a t_f-T_f grid to mimic a ceramic body were then studied by means of XRPD and technological testing to measure the properties relevant to vitreous sanitary-ware ceramic technology.

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Fuel-based pollutants removal from water: structural evidences of adsorption into high silica zeolites

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Keywords: Zeolites, fuel-based pollutants, adsorption.

Removal of fuel-based compounds from natural water is of considerable interest due to the harmful effects of these pollutants on the environment, even at very low concentration. Adsorption is a reliable technique to eliminate them from wastewaters due to the flexibility of the system, low energy and cheap operation costs (Braschi et al., 2012; Martucci et al., 2012; Pasti et al, 2012). The presence of natural organic matter can significantly affect organic pollutant adsorption by either competing for adsorption sites, or restricting access to (micro)pores.

In this work organophilic zeolites differing in topology, channel systems and free window apertures, and fuel-based-pollutants differing in chemical properties and molecular dimensions, were tested. Structural evidences of adsorption from dilute solutions into organophilic zeolite as well as the competitive role of humic monomers, the effect of the temperature in the adsorption processes will be discussed. The selected adsorbents were hydrophobic ZSM-5 and Y zeolites with high SiO_2/Al_2O_3. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction-GC. X-ray powders patterns were collected before and after adsorption on a Bruker D8 Advance diffractometer with SOL-X detector. Thermal analyse were performed in air up to 900°C at 10°C/min. Infrared spectra were collected on a Thermo Electron Corporation FT Nicolet 5700 Spectrometer. This combined diffractometric, thermogravimetric, chromatographic and spectroscopic study allowed us to: 1) measure the sorption capacity of zeolites weighed against organic pollutants dissolved in water; 2) characterise the structure after contaminants adsorption; 3) localise the organic species in the zeolite channel systems; 4) highlight the role of humic monomers in the pollutants removal; 5) probe the interaction between the adsorbate and the zeolite framework. The very favorable adsorption kinetics along with the highly irreversible adsorption into zeolite pores make these cheap and environmental friendly materials applicable for the treatment of water contaminated with fuel-based pollutants.

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Selective adsorption of biomolecules on mineral surfaces for nanotech applications

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Keywords: Chlorite, glycine, scanning probe microscopy.

Mineral surfaces are good candidates as substrates for biotechnological applications because they may present at the nanoscale a wide variety of physico-chemical properties and surface nanostructures that can be used to actively condense and manipulate biomolecules (Valdrè et al., 2012). Recent advancement in highly spatially resolved experimental and theoretical methodologies (e.g., scanning probe microscopy, SPM, and quantum mechanical simulations) has widened the possible investigations of biological/organic matter interaction with mineral substrates, enabling both controlled surface modifications at the nanoscale and detailed prediction and characterization of surface properties. SPM is one of the best-suited techniques for the investigation at a single-molecule level of bio-surface interactions. Recent availability of high performance computing has increased the possibility to study quantum mechanically the interaction phenomena, extending the number of atoms involved in the simulation. In this contribution we present a detailed study of the interaction at the single-molecule level of the amino acid glycine with the (001) crystallographic plane of chlorite. Single glycine molecules were experimentally observed to selectively adsorb and condense on the (001) brucite-like surface of a freshly cleaved chlorite. Chlorite surface potential was ascribed to drive single glycine molecules to align along crystal sub-nm edges. We simulated the glycine interaction with the brucite-like (001) surface using the DFT/B3LYP-D* functional and an all-electron basis set to aid the interpretation of the experimental results. In agreement to the SPM observations, the amino acid is strongly adsorbed by the mineral surface (binding energy of about -33 kJ/mol), with several hydrogen bonds established. The understanding and control of this kind of bio-mineral interaction is useful in specific applications, such as self-assembly, bio-nanopatterning and biomolecular arrays, and also in theories on prebiotic chemistry and origin of life (Hanczyc et al., 2007; Hazen et al., 2010; Valdrè et al., 2004).

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Hazen R.M. & Sverjensky D.A. 2010. Mineral surfaces, geochemical complexities, and the origins of life. Cold Spring Harbor Perspect. Biol., 2, a002162.
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Valdrè G., Moro D., Hounsome C.M. & Antognozzi M. 2012. SPM nanolithography of hydroxy-silicates. Nanotechnology, 23, 385301.

Polyphase ore deposition at the Montevecchio vein system, SW Sardinia

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Keywords: Sardinia, sphalerite, fluid inclusions.

Montevecchio is among the biggest Pb-Zn mining districts in Sardinia. The mineralization is hosted in a 10 km-long, NE-SW-trending set of hydrothemal veins emplaced along steep fractures parallel and radial to the contact of the late Variscan Arburese granitoid complex. Host rocks are Paleozoic low-grade metapelites and metavolcanics variably affected by contact metamorphism. The Montevecchio vein system was extensively exploited for Pb, Zn and Ag with Bi, Sb, Cu, Cd and Ge plus Co and Ni as byproducts, between 1848 and 1973 by means of a network of galleries extending for over 100 km [reviewed in Biddau & al. 2001). Reports about the detailed features of the Montevecchio veins are scarce and outdated. The mineralization was described as dominated by Ag-rich galena or Cd-rich sphalerite with minor tetrahedrite chalcopyrite, pyrite and accessory Ag-, Cd-, Co-Ni-rich sulfides and sulfosalts, in quartz, Fe-Mn-Mg-Ca carbonate and/or baryte gangue. Preliminary microthermometry revealed a complex history for the mineralization, with contrasting low-T (max 150°C) saline and high-T (>300°C) fluids reported in Boni & al.(2009). New micro-textural, chemical and thermometric studies on the Montevecchio veins confirm the complexity of the mineralization and suggest polyphase emplacement from epithermal to high-T, skarn deposition (with scheelite). Ore facies may be nominally “sphalerite only”, “galena only” or mixed. Coarse, zoned sphalerite exhibits chemical signatures where minor components (Fe, Cd, Mn, Ag, Sb, Ge, Cu, Pb) compete with Zn in the lattice according to variable patterns in different veins, not always compatible with what observed in literature. The controls on economic byproducts Cd, Ge and Ag are far from being obvious or clear. These metals may locally partition between sphalerite and sulfosalts during polyphase deposition, where sulfosalts are depending on galena abundance. In some cases sphalerite may be completely devoid of Cd and anomalously rich in Ag. Tetrahedrite composition ranges between Sb and As end-members, with Ag content depending on vein, assemblage and presence of Ag phases. In Cd-rich ore Cd-rich tetrahedrite inclusions in galena may occur. Galena is rich in sub-μ mono/polyphase sulfosalt blebs locally inducing selective low-T decomposition of galena close to unaltered sphalerite. Zn remobilization is however recorded by growth of late-stage Zn carbonate. The quartz, carbonate or baryte-bearing gangue assemblages equally show evidence of complex polyphase deposition.

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Synthesis and characterization of wollastonite-2M by using a diatomite precursor

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Keywords: diatomite, calcium silicate, wollastonite.

The calcium silicate wollastonite ($CaSiO_3$) presents two structurally quite different forms; the phase stable above 1150°C called pseudowollastonite or α-wollastonite and the phase stable below 1150°C called β-wollastonite (Hesse, 1984). Wollastonite 2M (Parawollastonite) represents a low temperature polytype with monoclinic symmetry.

Due to its acicular particle shape, whiteness, fluxing properties and absence of volatile components, wollastonites are in general applied with success in the fields of tile factories, paint, paper and vinyl tile manufactures and also as a substitute of asbestos (Justness, 2012). Synthesis of wollastonite is referred to the solid phase reaction method (Grigoryan et al., 2010), the hydrothermal process (Grigoryan et al., 2008), the sol-gel method (Villegas et al., 1988) and the molten salts technique (Trubnikov et al., 1989).

Solid phase reaction synthesis of wollastonite 2M by a natural rock precursor as source of amorphous silica and $CaCO_3$ has been here achieved. Chemical treatments were carried out on a diatomitic rock from Crotone (Calabria, Italy) in order to measure its reactive silica and $CaCO_3$ contents. Synthesis was performed at 1000º C, ambient pressure and for the duration of two hours, by the mixing of the diatomitic rock with a natural limestone as source of additive $CaCO_3$ and sodium carbonate as triggering agent.

Chemo-physical, crystallographical, morphological characterization and infrared and nuclear magnetic resonance (^{29}Si) experiments were carried out. Estimation of the amorphous phase in the synthesis powders was performed through the quantitative phase analysis using the combined Rietveld and reference intensity ratio methods, resulting in a final product of 95.2% wollastonite 2M.

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The effect of mineralizers on tridymite stabilization

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Keywords: mineralizers, silica polymorphs, energy efficiency.

The H-T silica polymorphs are known to be tridymite and cristobalite, crystallizing at 870 and 1470°C respectively, as reported in the stability diagram proposed by Fenner (Fenner, 1913). Nonetheless, there has been a lot of discussion over the last century about whether tridymite could or not be considered a stable phase in the pure silica system: when pure quartz is heated, the transformation that usually happens is the direct crystallization of cristobalite, without the intermediate formation of tridymite (Pagliari, 2013, just as an example). However, if any mineralizing agent is added to quartz, tridymite can stabilize and grow, helped by the presence of impurities, such as Na, Ca and K atoms, which accommodate in the large voids of the structure (Buerger, 1954; Flörke, 1956; Holmquist, 1958; Stevens, 1997). Some authors (Flörke, 1986; Stevens, 1997) proposed also that tridymite cannot nucleate if a cristobalite nucleus is first formed.

The present study is about the kinetics and mechanism of tridymite formation starting from pure quartz powders of different grain sizes (D50 of 24, 11 and 3 µm), mixed with 20% acqueous sodium or potassium hydroxide solution. After preliminary *ex-situ* experiments at 900, 1000, 1100 and 1200°C for 1 and 6 hours, necessary to give an idea of the tridymite formation temperature, isothermal analyses were carried out with a Philips X'Pert diffractometer equipped with the hot chamber Anton-Paar HTK 16 MSW. Data collections were performed at different temperatures, depending on the grain size of the starting quartz, and lasted about 10 hours, time required to tridymite to form completely.

Evaluations on the influence of grain size of the raw material, use of mineralizers, temperatures and dwell times of the firing process could be done. The main results are the following: (i) cristobalite crystallization is promoted by the presence of a mineralizer, which decreases the temperature of its formation (compare with Pagliari); (ii) smaller grain sizes of the starting quartz boost the reactions, as already found by Pagliari; (iii) tridymite forms just after a previous nucleation of cristobalite, in agreement with literature; (iv) quartz can be completely replaced by tridymite at 1200°C, avoiding the undesired α-β quartz transformation in the process of ceramic production. From the knowledge of these aspects, industries can obtain an important advice on how to improve their energy efficiency, so recommended nowadays.

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Crystal structure of the mineral-derived titanosilicate compound $BaTiSi_2O_7$

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Keywords: BTS2, titanium, photoluminescence, twinning, Rietveld.

Because of their optical, photo-luminescence (PL), and afterglow properties, barium titanosilicates are compounds of great interest for functional materials and light-emitting devices (Takahashi et al., 2012). Some of them are natural minerals (e.g. $Ba_2TiSi_2O_8$, mineral fresnoite and $BaTiSi_3O_9$, mineral benitoite), but others can be synthesised finding inspiration from natural analogues. In this work, the crystal structure of synthetic $BaTiSi_2O_7$ (BTS2), displaying peculiar orange PL emission, was solved for the first time from X-rays powder diffraction data. Results indicate that its structure is a distortion of the tetragonal form of the natural mineral suzukiite (?-$BaVSi_2O_7$) with Ti in place of V (Liu and Greedan, 1994). BTS2 has been synthesized through conventional solid state reaction methods. Although BTS2 crystals invariably show complex twinning patterns, the structure solution and Rietveld structure refinement were attempted using two synchrotron diffraction datasets. BTS2 was found an indivisible intergrowth of monoclinic and triclinic crystals. The monoclinic phase has space group $P2_1/n$ and unit cell a = 7.98355(31) Å, b = 10.00843(37) Å, c = 7.47952(27) Å, and beta = 100.321(3)° whereas the triclinic phase has space group P-1 and unit cell a = 7.99385(4) Å, b = 10.01017(5) Å, c = 7.47514(3) Å, alpha = 90.084(8)°, beta = 100.368(8)°, and gamma = 89.937(9)°. The structure models obtained from this study confirm the presence of 5-fold coordinated Ti-atoms in a distorted pyramidal configuration, supporting existing theories for the explanation of PL orange colour in BTS2 (Takahashi et al., 2006). This compound can be considered as an example of intelligent exploitation of primary georesouces for the realization of advanced technological materials in that its constituting elements are relatively abundant, and, unlike others PL synthetic compounds, no rare earth dopants are employed.

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Synthesis of microcrystalline hydroxylapatite and influence of the growth kinetics on the crystal growth morphology

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Keywords: Hydroxylapatite, growth morphology, twinning.

Microsized hydroxylapatite ($Ca_5(PO_4)_3(OH)$) was synthesized under mild hydrothermal conditions (T=220°C, autogenic pressure) by modifying the procedure proposed by Perloff and Posner (1956). The method involves the hydrolysis of a secondary calcium phosphate previously obtained (monetite, $CaHPO_4$) into a tertiary calcium ortophosphate (hydroxylapatite). Crystals grown in this way were measured by X-ray powder diffraction using a D5000 Siemens diffractometer. They correspond to the pure hydroxylapatite (PDF 00-009-0432, Hodge et al.1938), are morphologically monoclinic and show habit modifications strongly dependent on the growth rate and supersaturation of the system. In fact, smaller crystals exhibit an undeniable monoclinic morphology showing well developed forms belonging to some of the pinacoids expected from the ab-initio calculations about the equilibrium shape of the hydroxylapatite (Aquilano et al., 2014). The morphology becomes gradually more complicated when crystal size increases, because of the recurring twinning of the crystals. At a first glance, the biggest ones can be misinterpreted as hexagonal crystals because of their morphology, but a careful observation of the relative extension of the forms, of the orientation of the closing facets with respect to the "prisms" and of their surface character, will banish all doubts about their monoclinic symmetry. The final growth morphology differs significantly from the calculated equilibrium shape, but some of the expected forms can be found again, with a change in the relative size due to the growth regime in the presence of the solvent. This observation fits in with the hypothesis that the twinning of monoclinic hydroxylapatite polymorph could mime both structure and morphology of the hexagonal one engendering a mess of conjectures, found in literature, about twinning and symmetry of pure hydroxylapatite.

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Characterization of geo-inspired binding materials from heat treated cement asbestos

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Keywords: Cement-asbestos, magnesium cement, recycling.

According to recent European directives, the need for environmentally friendly alternative solutions to landfill disposal of hazardous wastes, such as asbestos-containing materials, prompts their recycling as secondary raw materials; this concept known as "end of waste", adopted by the European Commission on December 2005, regards under which conditions a waste could cease to be waste and could be regarded as a non-waste material. (Gualtieri et al., 2013). In this respect, this contribution describes recent results on the recycling of the high temperature products of cement-asbestos, in the formulation of magnesium phosphate cements (Viani & Gualtieri, 2014). This is an example of nature-inspired materials produced from recycled building materials; indeed, during thermal treatment, destruction of asbestos minerals and recrystallization processes leads to the formation of new phases that have their natural equivalents (Viani et al., 2013). The simultaneous formation of cementitious compounds represents a recycling opportunity for this class of hazardous wastes, bringing benefits in terms of energy requirements and preservation of natural resources in cement manufacturing.

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Occurrence of natural asbestos in the historical quarries where "greenstones" are exploited: the example of the Gimigliano-Mount Reventino Unit ophiolite terranes (Calabria, Southern Italy)

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Keywords: Asbestiform minerals, ophiolite terranes, Calabria (Italy).

In order to assess the occurrence of asbestiform minerals within the ophiolitic sequence of the Gimigliano-Mount Reventino Unit (Calabria, southern Italy), a detailed mineralogical and petrographic investigation by means of Polarized Light Microscopy, X-ray powder diffractometry, Scanning Electron Microscopy combined with Energy-Dispersive Spectrometry, and Thermo Gravimetry together with Differential Scanning Calorimetry has been carried out.

Indeed, the main lithotypes that constitute the ophiolite sequence (i.e. metabasites and serpentinites) are exploited and marketed for building and ornamental purposes since prehistorical times (Punturo et al., 2004); for this reason, attention focused on the historical quarries with the main aim to detect the presence of asbestiform fibres which may be harmful for human health.

Results showed that, among the asbestos minerals contained in metabasites, tremolite is the main constituent followed by actinolite; moreover, other fibrous amphiboles (not regulated by the Italian law) occurring are crossite, glaucophane, horneblende and gedrite. As far as serpentinites, chrysotile is the dominant asbestos phase (Bloise et al., 2014; Punturo et al., 2013).

Obtained results hold environmental implications, since they can be used in order to take decisions for the realization of health protecting measures (e. g. during the road yards and quarry excavations) and may also provide data for the compulsory Italian mapping of natural sites, since the selected sites are characterized by the presence of the asbestos commonly known as NOA (naturally occurring asbestos) as well as by the occurrence of other fibrous minerals (e.g., antigorite) that are non- asbestos classified and, therefore, not regulated by law (e.g. DM 18/03/2003).

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Temperature-induced transformations in ZSM-5 after 1,2-dichloroethane adsorption by "in situ" time resolved synchrotron powder diffraction

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Keywords: ZSM-5, 1,2-dichloroethane adsorption, "in situ" time resolved synchrotron powder diffraction.

The aim of this work is to investigate the structural modifications in ZSM-5 during desorption of 1,2-dichloroethane (DCE) by *'in situ'* time-resolved X-ray powder diffraction. DCE is an important environmental pollutant due to its high toxicity, inertness and widespread application in industry (Gavaskar et al. 1995). Recently, the effective adsorption of 1,2-dichloroethane from aqueous solutions onto highly siliceous ZSM-5 zeolite has been demonstrated by Pasti et al. (2012) by combining diffraction and gas chromatography.

In this work the step by step thermal desorption process of ZSM-5 organophilic zeolite (CBV28014, Zeolyst International, SiO_2/Al_2O_3 ~280) loaded with DCE has been studied "*in situ*" by synchrotron radiation powder diffraction. Time-resolved diffraction data were collected (temperature range 25°-600°C) at the ID31 beamline at ESRF (Grenoble), using a fixed wavelength of 0.40003(1) Å. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction -Gas Chromatography. Rietveld refinements were carried out on 19 consecutive powder patterns in the temperature range from 25°C to 600°C. The evolution of the structural features monitored by full profile Rietveld refinements reveals that a monoclinic ($P2_1/n$) to orthorhombic ($P2_12_12_1$) phase transition occured at 70°C (Figure 1).

The decomposition and expulsion of DCE was accompanied by changes in the unit-cell parameters, as well as in the channel apertures. Complete DCE degradation and expulsion was achieved upon heating at about 300 °C. This kind of information is crucial for designing and optimizing the regeneration treatment of zeolite used as adsorbents in water and wastewater remediation treatment technologies.

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Thermal infrared investigation applied to the physical and mechanical characterization of some natural materials

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Keywords: thermal infrared investigation, natural materials, physical and mechanical properties.

Thermographic investigation is a technique that allows to evaluate the temperature of surfaces by detecting the electromagnetic emissions of them (Tulipano L., 1976). This technique is based on the principle that any body with temperature, above absolute zero, emits electromagnetic radiation, which depend on the temperature of the body and the physical, chemical and geometrical properties of the surface. The goal of this paper was to evaluate potential applications of thermographic analysis to the characterization of natural materials, carried out at the scale of the laboratory sample (Gong W., 2011) We wanted, in fact, to give an evaluation on the possibility of use the observation and results obtained in laboratory, to study and interpret the termographic survey made at the scale of rock mass, considering and confronting mainly the values of thermal conductivity and dynamic elastic constant of the materials (He M.C. et alii, 2010). Initially they have been considered eight types of rock including: tuff, limestone, roman wall, basalt, sandstone. From these rocks they were obtained cylindrical specimens of various, but similar size, while it were evaluated, whith appropriate procedures, various physical and characteristics, like specific weight, porosity and imbibition coefficient, the compressive strength of the samples, estimated by the Schmidt's hammer and the value of modulus of elasticity, determined by the mechanical wave propagation test across the specimen, using the specific sensors and an oscilloscope. Using the infrared camera it has been detected the temperature of various samples in thermal equilibrium with the environment and it has been calculated the behaviour of materials in respect of emissivity. Later, the specimens have been analysed in respect of the thermal flow, heating any specimens from the bottom by an electrical resistivity plane.

The warm-up phase, lasting about an hour, has been monitored by the camera, and they have been taken every minute of termography. The thermal images obtained from all these tests have been developed using a specific software, inserting reference points and areas in the image, from which has been possible to extrapolate the temperature data needed for the development and study of physical phenomena analysed. Some interesting results coming from these investigations are presented and discussed in this paper.

Lithiophorite and other Mn phases in a Messinian alluvial deposit of Sardinia: first considerations on REE and trace elements uptake capability

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Keywords: Lithiophorite, Uptake, REE.

Mn oxides minerals are important scavengers of trace elements controlling the migration of heavy metals and radionuclides in the geosphere. In soils and laterites, as well as in other tropical sediments, Mn-bearing minerals commonly occur forming nodules, crusts, coatings on clasts, and/or Mn-rich horizons.

In northern Sardinia (western Italy) Mn oxides concentrations were found into Messinian alluvial conglomerates and residual clayey deposits. They occur as Mn-oxides and oxihydroxides locally forming the matrix of conglomerates, coatings covering the conglomerate clasts, and centimeter-size nodules scattered in the clays.

In this paper the preliminary data on mineralogical and chemical composition of Mn-oxides concentrations from the alluvial deposit of Scala Erre are provided with the aim to decipher the environmental conditions and chemical processes occurring during Mn oxides accumulation.

XRPD analysis showed that the main Mn phase of analysed samples is lithiophorite. Birnessite is also a significant component in most samples, whereas pyrolusite, todorokite, hollandite, and cryptomelane were detected in few samples only. Quartz, Fe-oxides and hydroxides (hematite and goethite), clay minerals (mainly kaolinite and scarce illite) and other phyllosilicates (muscovite and chlorite) complete the mineralogical association. ICP-MS and INAA analyses were performed on all samples showing a strong enrichment in transition metals, such as Co, Ni, Zn and Cu, a moderate enrichment in Ba, Y, U Pb and weak depletion in the other trace elements, compared to the GLOSS. Regarding the REE chondrite-normalised distribution patterns, some differences between nodules and the other Mn-rich samples were observed. Nodules are characterized by very high ÓREE values in the range of 1368.8 and 3398.5ppm; high values of LREE/HREE fractionation index (6.82<(La/Yb)ch<9.96); and strongly positive Ce anomalies (3.90)

Chemistry, particularly REE data, suggest possible different environmental conditions of precipitation. Ce anomalies are likely due to the presence of organic-rich and organic-poor fluids incoming during the formation of Mn phases, and the LREE/HREE fractionation was probably caused by a different geochemical behaviour of REE rather than a different REE uptake capability of Mn oxides.

Theoretical and experimental characterization of pure and defective hydroxylapatite for biomedical applications

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Keywords: Carbonated hydroxylapatite, surface electrostatic potential, vibrational properties.

In the biomedical field, much attention is paid on calcium apatites, because these minerals present many similarities with vertebrate bone tissues (Dorozhkin, 2009). In particular, the main component of the bone mineral phase is the hexagonal polymorph of hydroxylapatite [OHAp, space group $P6_3/m$], which presents both anionic and cationic substitutions to stabilize its structure. The most abundant defect in biological OHAp crystals is the carbonate ion (CO_3^{2-}), in a weight percentage ranging from 3% to 7%, depending on the function of the tissue and its age (Dorozhkin, 2009). The CO_3^{2-} may substitute both OH^- in the *c*-axis channel of apatite (type A) and the PO_4^{3-} group (type B), as confirmed by experimental (Fleet & Liu, 2003; Fleet & Liu, 2004) and theoretical studies (Ulian et al., 2013a; Ulian et al., 2013b; Ulian et al., 2014). Indeed, the normal modes of carbonate ion fall at different positions, according to the site occupied by the anion. In natural bone tissues, it is common to find both A and B defects at the same time. A deep knowledge of the hydroxylapatite surface biomimetic features is of utmost importance to understand organic biomolecular interactions. In our work, we studied by *ab initio* quantum mechanical approach the surface geometry, the vibrational (IR and Raman) features and the electrostatic potential of the (001) surfaces of both OHAp and defective carbonated hydroxylapatite (COHAp). Theoretical structural and spectroscopic data were compared to experimental XRD, IR and Raman ones with a very good agreement. These results can be very helpful to understand how the carbonate ion modulates the hexagonal OHAp features, information useful, for instance, to obtain more biocompatible materials for prosthetic implants.

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Glass forming ability of sub-alkaline silicate melts

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Keywords: silicate melts, nucleation, solidification, critical cooling rate, glass forming ability.

The glass forming ability (GFA) of natural silicate melts is still not well understood, although it is an important physico-chemical parameter to be accounted for in Earth and material sciences. In this study we quantified the GFA of natural sub-alkaline silicate melts *via* the experimental determination of critical cooling rate (*Rc*), i.e. the rate at which ≤ 2 area% of crystals solidify. To experimentally model the GFA, we used six melts (basalt, basaltic andesite, poor evolved andesite, evolved andesite, dacite and rhyolite) with compositions shifting systematically from basalt (B) to rhyolite (R) (B_{100}, $B_{80}R_{20}$, $B_{60}R_{40}$, $B_{40}R_{60}$, $B_{20}R_{80}$ and R_{100}; the numbers refer to proportions of B and R). The starting glasses were cooled from superliquidus temperature of 1300 °C down to 800 °C (quenching temperature) with six cooling rates of 9000, 1800, 180, 60, 7 and 1 °C/h .

The proportion of phases in each of the 51 run-products was determined from about 300 BS-SEM images at different magnifications. Identified phases are glass, clinopyroxene (cpx), spinel (sp), plagioclase (plg) and rarely a very low amount (< 1 area%) of olivine, orthopyroxene and melilite. In general the amount of crystals continuously decreases as the cooling rate increases. However, solidification behaviour does not invariably follow this trend as observed for one composition ($B_{80}R_{20}$). High cooling rates also promotes the formation of dendritic crystals. For a given composition, the first phase which nucleates and grows is Sp (high cooling rates), followed by cpx and ultimately plg (low cooling rates). Sp is the most ubiquitous crystalline phase albeit its amount is few unit of area%; cpx always occurs with sp and is abundant (up to 60 area%) at intermediate cooling rates and in more basaltic compositions; plg crystallizes only in the most mafic compositions.

The *Rc* values span 5 order of magnitude being < 0.001, 0.114, 17, 68, 145 and 150 °C/min for R_{100}, $B_{20}R_{80}$, $B_{40}R_{60}$, $B_{60}R_{40}$ and $B_{80}R_{20}$ and B_{100}, respectively; the variation of *Rc* can be modelled *via* the NBO/T (non bridging oxygen per tetrahedron) parameter by the following master sigmoidal equation: $Rc = a / 1+e^{-(NBO/T-xo/b)}$, where *a*, *b* and xo are fitting parameters equal to 165(5), 0.047(5) and 0.283(6). Similar to other glass-forming systems (network, metallic and molecular systems), the *Rc* trend of natural sub-alkaline silicate melts can also be predicted by the classical reduced glass transition parameter *T*rg (*T*rg = *T*g/*T*m, where *T*g is the temperature at 10^{12} Pas*s and *T*m the temperature of melting) *via* the equation $R\text{c} = 4.939\text{-}9 * T\text{rg}^{-41.69}$.

The results can be straightforward applied to retrieve solidification conditions of aphyric, degassed and oxidised lavas. In addition, the intricate relations between crystal content and kinetic conditions induced by cooling suggest that the solidification path at volcanic conditions can be also highly complex and strongly non-linear. Our equations can also be used to design glass-ceramics based on very abundant and low cost starting materials.

Quality control of a recrystallized Proterozoic limestone used for the industrial production of quicklime in a Twin Shaft Regenerative (TSR) kiln: a South African case study

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Keywords: South African Proterozoic limestone, quicklime production, quality control, lime reactivity.

The dark grey bedded limestone from the Ouplaas Mine in Daniëlskuil, South Africa, is currently used to feed both the new 560 tpd Twin Shaft Regenerative (TSR) kilns, recently installed at the local manufacturing lime plant by Cimprogetti Spa. In order to support the client for setting up the quality control of the lime, compositional and microstructural analyses of the limestone, coupled with the technological characterization of limes burnt in laboratory at different temperatures, have been performed (Vola & Sarandrea, 2014). Especially, samples from two different quarry benches (A & B) have been studied to evaluate their burning attitude, and quicklime reactivity. This limestone belongs to the Kogelbeen Fm. of the Campbellrand-Malmani Carbonate Platform, Transvaal Supergroup, which is approximately 2500 Myrs old. It presents characteristic microbial stromatolite laminations, composed of prevalent planar, small scale domal, multi-layered sheets of problematic microorganisms, mainly microbes, originally deposited in a marine shallow subtidal environment. The most of the microfacies are strongly recrystallized. Micro and speudosparites, with ghosts of peloids and mud intraclasts, are dominant with also abundant late diagenetic poikilotopic calcite cement, generally associated with burial diagenesis, mechanical compaction, and pressure solution that produced swarms of thick black stylolites rich of pyrite and graphite (kerogen). The quantitative phase analysis (XRD-QPA) permitted to identify the impurity content, which is mainly ascribed to clay minerals, i.e. illite and chlorite, microcrystalline quartz (chert), and, locally, fabric dolomite.

This limestone generally shows a sensitive burning attitude, and an overburning tendency at high temperature, so that the average slaking reactivity (EN 459-2) on limes burnt at 1050°C is very high (t_{60}= 1.3 min. and T_{max}= 72°C), but rapidly decreases at 1150°C (t_{60}= 7.5 min. and T_{max}= 68°C). Just two different layers of the quarry present significant exceptions, and one of them maintains an high reactivity also at 1150°C (t_{60}= 2.3 min. T_{max}= 67°C). The colour of the lime is mainly brown, due to the high content of manganese within the parental limestone. Light brown colour corresponds to soft-burnt limes, dark brown colour to medium-burnt limes, and dark-grey or black colours to hard-burnt limes. This information has been useful to control and setting up important kiln parameters, such as the heat distribution and the burning temperature of the plant. Considering the stratigraphic quarry log, and the reactivity of each layer, it was possible to calculate the average reactivity of each bench, and, subsequently, the expected reactivity of different mixtures feeding the kiln. The following scenarios have been reported: 1) A (100%): t_{60}= 6.5 min.; 2) A (50%) + B (50%): t_{60}= 7.3 min.; 3) B (100%): t_{60}= 8.3 min.

This study confirms that specific characteristics of the limestone, such as texture, degree of cementation, presence of dolomite, opaques, and clayey impurities, can significantly impact on quicklime reactivity, as well as, thermodynamic conditions of the process. Moreover, stratigraphic data, associated with laboratory tests, can be successfully adopted to select the best raw mix, reducing the impact of materials of a lesser quality.

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Improving cement sustainability by using nano-materials in clinker production

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Keywords: Clinker, nano-materials, CO2 emission, belite.

During the last few years, particular attention was given to reduce CO_2 emission from industrial processes. Cement industry is one of the most exposed CO_2 producers with more than 5-8% of the total antropogenic production of CO_2. Carbon dioxide originates (i) from the decarbonation of calcite ($CaCO_3$) during firing process and (ii) from energy consumption of rotary kilns during clinker burning. Many works recently dealt with belite-rich clinkers (Sui et al. 2004; Kacimi et. al. 2009) since their low clinkering temperature which reflects in a reduction of CO_2 emissions, in high late strength, in high flow ability and in a low heat of hydration. The present work wants to analyse techniques to further decrease the environmental cost of belite-rich clinkers production by adding nano-materials and by-products (blast furnace slags) to the raw mixture. Nano-CaO was synthesized by a precipitation method with the aid of ultrasonic irradiation using $CaCl_2$ as source (that is a by-product of industrial processes) and NaOH as precipitator. The $Ca(OH)_2$ nanoparticles were then converted in nano-CaO by calcination process. Four different burning temperatures were chosen for clinker production (1450°C, 1350°C, 1250°C and 1100°C). Clinkers after cooling were analysed by means of Field-Emission Scanning Electron Microscopy (FE-SEM) and X-ray Powder Diffraction (XRPD). The *Rietveld* refinement of collected data was performed by means of TOPAS Academic software (Cheary and Coelho 1992; Cheary et al. 2004). Results showed that T = 1100°C is the temperature limit for the firing process being the sample after cooling still dusting and not massive. Belite (C2S) is the most representative mineral phase in the clinkers being β-C2S in the range 20-50 wt%; whereas γ-C2S is absent from all the samples. Moreover, β-C2S increases as nano-CaO is added to the raw mixture at the expense of the second generation products, such as Fe-gehlenite (C2AS). Concluding, the optimum production process for belite-rich clinkers starts from nano-CaO enriched raw mixtures fired at approximately 1200°C. The result is a set of clinkers with β-C2S ~ 35 wt%, C3S < 3 wt%, Fe-C2AS ~ 0 wt%. The study of the effects of different nanomaterials, such as SiO_2, Al_2O_3 and Fe_2O_3, added to different clinker typologies, including standard Portland clinkers, is in progress.

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SESSIONE S11

Archaeometry and Cultural Heritage: the contribution of Geosciences

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Nanostructured coating and innovative organic-inorganic consolidant: efficiency tests on a calcarenite from Sabucina (Sicily)

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Keywords: TiO_2 coating, consolidant, Sabucina Stone.

Natural stones used in historical buildings often suffer the effects of weathering and degradation processes. In order to preserve and conserve natural building stones, in recent years suitable synthesized products have been deeply investigated. In the frame of the synthesis of innovative, cheap, eco-friendly, reversible, compatible and high activity products, nanostructured materials represent a cutting edge technology. In particular, TiO_2 nanoparticles are an efficient coating product in view of its self-cleaning photocatalytic action, as testified by the successfully results on Sicilian calcarenite (Bergamonti et al., 2013). However, surface coating could not be a complete solution for conservation purposes, especially when the structural, textural and porosimetric features of the stones require an integrated preservation and conservation effect both in terms of surface protection and of structural strengthening. Consolidant products are widely used in order to improve durability of building stones and the current researches are focused to test innovative products with high compatibility and low impact.

In this work we present the results obtained on the Sabucina stone, a calcarenite outcropping in Central Sicily and widely used as building and replacing stone, by applying coatings based on TiO_2 nanoparticles and hybrid organic-inorganic consolidant products also associated with hydrophobic coating.

Referring to TiO_2 nanostructured coating, we tested self-cleaning photocatalytic coatings obtained by sol–gel process at different pH values. Photocatalytic activity of the TiO_2 coatings on Sabucina stone was assessed under daylight and ultraviolet irradiation, monitoring methyl orange (MeO) and methylene blue (MB) dyes degradation as a function of time. To evaluate the effect of the treatment, colorimetric and water absorption tests were performed. Moreover, in order to verify the efficiency of coating in inhibiting degradation processes, aging tests have been carried out by evaluating stone resistance to salt crystallization.

In addition, a network based on aluminum and silicon oxides with epoxidic functional groups has been tested as consolidant product. In order to evaluate its effectiveness, colorimetric, water adsorption, compressive strength, aging tests and mercury porosimetry measurements have been performed.

Finally, the performance of an hydrophobic coating applied in association with the consolidant has been verified by colorimetric and water adsorption tests.

In conclusion, the obtained results show good photodegradation rates for titania nanosols and good protection properties, especially using the basic preparation. Referring to hybrid organic-inorganic strengthen product and hydrophobic coating, preliminary tests highlight promising applications to the preservation of calcarenites.

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An updated isotopic and petrographic reference database for white crystalline marbles used in antiquity

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Keywords: Ancient marbles, Petroarchaeometry, Isotopic composition, Reference Database, Provenance.

The identification of the quarry of provenance of ancient marble artefacts is, on one hand, of the utmost interest to archaeologists and art historians, on other hand, one of the most debated problem of petroarchaeometry. Scholars of different disciplines (mineralogists, petrographers, geochemists, physicists) have been trying for more than a century such an identification by means of a unique or multiple laboratory analysis without totally positive results. To-date the best probability of success are obtained by combining together at least two analytical methodologies and jointly processing all the data obtained. In particular, the detailed minero-petrographic examination of a thin section and the determination of the C & O stable isotopic ratios on the same sample is currently the most widely used combination. Such a combination takes advantage of the best existing databases for the main Mediterranean marbles very commonly used in Classical antiquity. On the basis of a detailed scrutiny of the recent literature data published from 2002 to 2012, we propose here an upgrade and a chronological reorganization on a geographic base of the petrographic and isotopic databank based on hundreds of analyses relative to the marbles from the major and some minor quarries active in Greek and Roman times. These new data, never considered before all together and implemented with unpublished results, let us both to increase the statistical significance of the whole database and draw new global reference isotopic diagrams related to the main petrographic features (i.e. maximum grain size - MGS, texture/fabric and grain boundary shapes) of the different lithotypes which are useful to better establish the provenance of a given archaeological objects.

Application of micro-Raman Spectroscopy for the characterization of rubies

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Keywords: Raman spectroscopy, gems, rubies.

The use of gems for manufacturing jewels and to adorn precious artefacts, such as royal insignia or liturgical objects, represents a well know practice since ancient times. Considering their value and the fact that they are often preserved in Museums, the use of non-destructive and non-invasive techniques for the characterization is required. Furthermore, the study of gems, and in particular the possibility to obtain information on their nature and provenance, represents a relevant procedure for archaeometric issues.

In this framework, Raman spectroscopy represents a useful tool being a quick, completely non-invasive and contactless technique which does not require any sample preparation.

Among the major commercial gems, ruby is considered one of the most precious gemstones, together with sapphire, emerald and diamond. Ruby is the red transparent gem variety of corundum; the colors are intense red to pink due to traces of Cr^{3+} ions.

In this context, this work is focused on the spectroscopic characterization of different kinds of rubies, by using micro-Raman instrumentations equipped with different laser excitation sources in order to furnish gemological identification and to acquire information about the provenance of the gems. In detail, Raman spectra have been collected on seventeen samples of red loose gems by means a confocal JobinYvon Horiba Labram, with 473.1 nm excitation line from a diode pumped Nd:YAG laser and a micro-Raman Jasco NRS-3100 apparatus, equipped with laser excitation source at 785 nm.

The obtained results allow not only to discriminate rubies from simulant and fakes but also achieve useful information on inclusions and treatments.

Therefore, the main aim of this work is to test the potentiality of micro-Raman spectroscopy in rubies identification, establishing the basis for the characterization of rubies with portable Raman spectrometers directly in museums, on gems mounted in precious and unmovable artworks. In this perspective, this should be considered as a first step of a campaign of portable Raman measurements we are carrying out on ancient jewelery collections preserved in Sicilian Museum.

The stones of the Egyptian Museum of Turin: geological, mineralogical and petrographic characterization

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Keywords: Applied Petrography, Cultural Heritage, Archaeometry, Egypt.

The Egyptian stones are of primary importance among all the natural stones used in various historical epochs, both for the wide use of the Ancient Egyptians and for the following use in Roman times. Rocks with different geological history and different chemico-mineralogical compositions represent, therefore, an unique artistic and cultural heritage.

A collaboration between the Egyptian Museum and the University of Turin started from 2005 with the aim to study the stones of Egyptian finds by a geological and minero-petrographical viewpoint in order to enhance the value of this artistic heritage and to set the base for its best conservation.

Magmatic, sedimentary and metamorphic rocks were recognised in decreasing order of abundance. The magmatic rocks of intrusive origin are the most represented and include the following varieties: - The "Red and Pink Assuan Granite": sieno-granite with porphyritic texture with pink to red K-feldspars. Macroscopically the rock is holocrystalline with a large grain size (millimetric to centimetric). The minerals are represented by pink-to-red K-feldspar, white plagioclase, glassy quartz and dark femic minerals.

- The "Black granite": granodiorite, quarzodiorite and tonalite varieties belong to this type of rock whose colour ranges from grey to almost black. The grain size is from medium to large. Peculiar is the presence of large white or pink feldspar porphyrocrystals, sometimes in aggregates, as well as the presence of lighter aplitic veins and darker mafic xenolites. .

These magmatic rocks belong to the Arabo-Nubian shield outcropping in the southeastern sector along and parallel to the Red Sea coastline as well as in the southern sector of Sinai peninsula. The historical quarries are located near Assuan.

The sedimentary rocks are represented by Tertiary white limestones and the Nubian sandstone. The sandstone is dark yellow, has a medium grain size and locally shows alteration spots in darker colour. Pink sandstone finds were also recognised.

The limestone finds show a granular, porous and not very solid aspect with the exception of Tut Ankh Amon statue which is made up by a solid and micritic white limestone characterised by the presence of stilolitic joints and veins of sparry calcite.

Among the metamorphic rocks it is worth noting the occurrence of the so-called Becken Stone, which was used to carve three sarcophagi of the Late Period. The Bekhen Stone (Lithos Basanites for Greeks and Lapis Basanites for Romans) is the name attributed to a green-black meta-greywacke belonging to the Hammamat series of late-Precambrian age and outcropping in the North and Central sector of the Eastern Desert.

Another objective of the project is to characterize a selection of amulets made of lapis lazuli, in order to verify the presence / absence of the archaeometric parameters so far identified to discriminate the different backgrounds and provide indications about the origin of the raw material.

The available set of samples will allow to increase the number of scanned objects belonging to the Egyptian culture and, consequently, the results of the investigations will enable to confirm or not the existence, starting from the II-I millennium BC, of trades between the Egyptian civilization and the near East, where there are major deposits of lapis lazuli exploited in Antiquity. The survey will be expanded to other Egyptian collections.

A new methodological approach for study pietra ollare artifacts

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Keywords: pietra ollare, ophiolites, petrograpic study.

The Italian term 'pietra ollare' indicates soft rocks, mostly basic and ultrabasic metamorphic rocks, that have been used, since the early times, for the production of pots, vessels and food containers. These rocks are characterized by good workability, fire resistant and refractory properties.

Quarries attested by historical sources as pietra ollare production centers are widespread in the Western and Central Alps and one of the goals of archaeometric studies is to find the extraction sites of the materials used to produce such artifacts.

In the last decades petrochemical studies of archeological findings of pietra ollare were carried out but these data do not allow to univocally associate shards to quarries, considering the diffusion of lithologies corresponding to pietra ollare throughout the Alps. These studies have also shown that the geochemical bulk analyses are not sufficient to discriminate artifacts of different geographical origin. We suggest a new archaeometric approach to characterize pietra ollare archeological findings, correlating archeological data, hand sample analysis and petrochemical analyses. This method hasn't the claim to establish the quarry from which the artifacts come but it can define a macro-area of provenance, with examples from the Alps.

The innovative methodology of this work concerns the petrographic study of the archaeological sample not only as an instrument for the identification of the mineralogical phases but also as the principal tool to reconstruct the blastesis-deformation history. Once the relative chronology of successive parageneses recorded by the rock is reconstructed, it is possible, for example, to distinguish among crystals of the same mineralogical phase that grew in different times of the rock history.

According to the petrographic study, geochemical analyses can be carried out on specific microstructural sites and the results can be compared to those obtained with the same approach on artifacts and samples extracted from quarries assumed to be the extraction sites. The strength of this approach is that the geochemical comparison must be made among crystals of the same mineralogical phase that presumably grew in the same time of the history of the rock, thus reducing the dimension of the provenance area, if the metamorphic evolution of different areas is known in detail.

Earthen mortars in historical buildings of Cremona: a multianalytical approach

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Keywords: earthen mortars, archaeometry, multianalytical approach.

The use of earthen mortars is widespread all over the Po plain and it is possible to attribute these materials to a long time span, ranging from the Roman Age to the Nineteenth Century. Considering the availability of good quality lime from the neighboring Piacenza area, the use of earthen mortars in the town of Cremona still needs to find a plausible explanation.

An accurate study of ancient architectural treatises was performed to better define the productive technologies of these materials and understand why they were used instead of the traditional lime-based ones. According to Sonsis (1807), a very good quality mortar could be obtained by mixing a red soil outcropping at Cava Tigozzi (a small town near Cremona) with a small amount of lime. To better understand the ancient productive technologies and define the raw materials utilized for the production of earthen mortars , a multidisciplinary mineralogical, geochemical and petrographical study was performed.

Samples of both earthen plasters and mortars with a structural function were collected in historical buildings of the XV-XVIII centuries. Fragments of mortars mounted in epoxy resin and thin sections were investigated with optical and electronic microscopy (SEM) to provide a textural and minero-chemical characterization of the materials. XRD and FT-IR studies better defined the mineralogical composition of the mixtures.

Furthermore, samples of soils were collected at Cava Tigozzi. XRD and FT-IR analyses were done in order to characterize these raw materials and compare them with the mixtures recognized in mortars.

From Roman to Romanesque, a mix of architectural styles and geomaterials in San Saturnino Basilica (Cagliari, Italy): petrophysical characterization, static-structural analysis and 3D laser-scan relief

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Keywords: Petrophysical, Static-structural analysis, Ancient marbles.

The Basilica of St. Saturnino rises over a sacred site since the origins of the town of Cagliari. The Roman Empire recognized the importance of such place implementing the original sepulchral function consolidating the function of the area. The *martyrium* of St. Saturnino (beginning of the IV Century A.D.) signed its passage from pagan to Christian cemetery. In this period the original chapel was built starting a long evolution of the building across half a millennium, until its Romanesque evolution and its later abandon and partial destruction at the beginning of the XIV Century. Its further story continued across time, bringing to our age a rich and interesting monument, articulated around its original structure mixing parts from the Imperial Roman, Byzantine and Romanesque phases together with clumsy attempt of modern restorations. The Byzantine phase has left us a large cubic structure, with robust arches and vaults testifying the evolution of construction techniques in Medieval Sardinia. The formal technical reading of the elevations is complicated by the frequent reuse of Roman artifacts, often of exquisite workmanship. The presence of diachronic source materials, together the technical problems of attribution, often make it difficult to study the building. The analysis of materials has led to a thorough investigation of the macroscopic number of lithologies, some of which are in an advanced state of alteration. To start a clear reading of this complex system a multidisciplinary approach was chosen, combining historical reading, analysis of the stones and digital survey solutions. The most significant materials in the church were sampled, taking precise reference to the various construction phases of each historical context and interventions of structural changes occurring in the various centuries and numerous restorations mirror of philological different cultures. The whole building and its surrounding area were surveyed with the following methods: photography, 3D Laser Scanner for the whole interior and exterior parts, 3D photogrammetry of a selected set of stone surface samples.

Were sampled and geochemical and petrographic analyzed several architectural stone elements (shafts of columns, capitals, etc.) used as building materials, characteristic of the Roman period, made in various kinds of marbles, currently distributed between the inside and outside of the monumental structure. Were also analyzed carbonate rocks ("pietra cantone", "pietra forte" of the Cagliari formation), used to make the most of the perimeter walls. To a lesser extent, there are ashlars of Oligo-Miocenic volcanics of Sardinia, and the occasional presence of other stone materials coming not from the island. A complex system of traces in need of contemporary and well organized digital and scientific approach in order to enhance the knowledge about this monument. The contribution proposed here will present the progress state of this research and its results.

Medieval Cu-Pb-(Zn)Ag smelting at Montieri and Cugnano, Colline Metallifere district (southern Tuscany)

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Keywords: Cu-Pb-Ag smelting, slag, Colline Metallifere, Medieval.

The Colline Metallifere district (southern Tuscany) hosts a number of Cu-Pb-Zn(Ag) vein deposits which fed a long-living mining and metallurgical industry, starting in the Chalcolitic period up to the 70s of past century. According to archaeological and historical documents, during the Medieval period (11th–14th cent. AD) metal production (copper and silver) in the district was mainly used for coinage. Recent archaeological excavations at the sites of Montieri (S. Niccolò Rectory) and Cugnano, uncovered several heaps of metallurgical wastes (mainly slag), whose detailed analysis revealed an extremely complex picture of metallurgical activities carried out in this area in the Middle Ages.

The considerable variability of slag's mineralogical/chemical composition partly reflects different metallurgical processes (and/or different steps of the same metallurgical process). In the lifetime of the S. Niccolò Rectory, at Montieri, the otherwise low amounts of metallurgical waste (slags) may be referred to preliminary steps of Pb (and Ag?) extraction from galena-rich ores, associated with Cu-Fe-Zn-Ag sulphides and sulfosalts. Slags contain variable amounts of (Cu-Fe-S) matte, As-Sb(Ag) speiss and metallic Pb. Interestingly, slags with low matte contents include abundant agglomerates of a phase (probable c-Al_2O_3), which could be the product of transformation at high temperatures of Al-rich phases (like alunite) either present in the ore gangue and/or in intentionally added fluxes and/or in the furnace walls. Also in the proximity to the S. Niccolò Rectory, within stratigraphic levels belonging to the 11th cent. AD, bell pits and high tin bronze fragments have been recently found which are a clear evidence of bell founding.

Neither at the Rectory nor in the partially excavated “Foundries” within the old Montieri village, clear evidence has been found of silver extraction (such as “cupels”, crucibles or other metal fragments), suggesting that the refinement processes were conducted elsewhere.

A much larger metallurgical waste deposit (around 450 tons of slag) has been found during excavations at the Cugnano castle. Slags are tapped and have relatively low viscosity; compositional features (prevalence of wüstite over magnetite; high content of S, As, Sb; presence of “speiss” with Pb+Ag; low diffusion of lead in the glassy matrix) suggest that they refer to the first steps of lead smelting from Cu-Pb-Ag sulphidic (galena, tetrahedrite) ores of local provenance, maybe preliminary to silver extraction.

Characterization of natural and artificial stone materials from S. Niccolò archaeological complex in Montieri (Tuscany, Italy)

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Keywords: Archaeometry, Mortars, Plasters, Bricks.

S. Niccolò archaeological site is situated on the north-east side of Montieri Hill (Southern Tuscany), in an ancient mining district. Ruins of the medieval ecclesiastical complex were discovered during recent excavations and consist of: a peculiar church, characterized by six apses; an annexe to the church; a productive area; a central place, interpreted as porticoed cloister; a great number of tombs.This archaeometric study is aimed to deepen the knowledge of the historical site through the characterization of natural and artificial building material rests (mortars, plasters and bricks). The petrographic analysis was performed on the thin sections by polarized light Optical Microscopy. Mineralogical and chemical composition was determined by XRPD and XRF, respectively. Textural and chemical micro-analysis were carried out by SEM-EDS. Preliminary petrographic study indicates that quartziferous-feldspathic-micaceous sandstone was utilized for the foundation walls of the complex, while the outer walls are mainly constituted by marly limestone and calcareous tufa ashlars. A petrographic, mineralogical and chemical study allowed us to distinguish various typologies of mortars, characterized by different aggregate and binder as well as by variable aggregate/binder ratios. The aggregate is constituted of minerals and lithic fragments. The most common minerals found were quartz, plagioclase, muscovite and calcite; sandstone, limestone, shale, quartzite, and phyllite were the most widespread lithic fragments. Shards of glasses, coal, metallurgic slags and crushed ceramic fragments (*cocciopesto*) were also identified. In the majority of the samples the binder is weakly hydraulic and it shows a moderate hydraulicity in the samples containing slags or *cocciopesto*. The archaeological and archaeometric data suggest a development of the site in different successive phases. The church was built during the most ancient one. The mortars sampled from all the six apses of the church belong to an unique typology, so that it can be ascribed to a single building phase. The fragments of metallurgic slags were observed in the mortar's aggregate of the annexe, of the productive area and in the complex's entrances, but they are lacking in the church. The use of slags as constituent of mortar's aggregate could be due to an evolution of building technology, with respect to the church, when probably the metallurgic activity have not yet started. These preliminary results represent the starting point for the future provenance study of the raw materials, in order to plan compatible products for restoration of the archaeological site.

Characterization of the ancient mortars and 3D laser scanner survey to define the construction phases of the *Heliocaminus* Baths in the Hadrian's Villa (Tivoli, Italy)

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Keywords: Mortar characterization, 3D Laser-Scanner, Roman Architecture.

Inside the Hadrian's Villa in Tivoli, it is possible to see the ruins of special and unique buildings, aimed at their time to create spectacular places, to give appropriate spaces to the court and to the people living in this architecture masterpiece. The reading of these structures sometimes is not easy, so the main idea in this project is to start from the small evidences in the single buildings, find rules and solutions to combine them into a global digital survey based on a 3D digital model and then start using this model for hypothesis formulation. This kind of approach should only be multidisciplinary combining the knowledge about petrographic, mineralogical and chemical characterization with the techniques of the digital survey (using 3D Laser Scanner based solutions) and the reading of the architectural aspects. The research presented here will propose this methodological approach as the tool to interpreter the different construction phases of the *Heliocaminus* baths (II Century A.D.): the first personal spa of Emperor Hadrian.

Using mineralogic-petrographic (by optical microscopy and XRD) and physical analysis a set of samples were investigated for their compositional aspects of the aggregate and of the pozzolanic binder of mortars, and their physical characteristics (real and apparent densities, open and closed porosity, water absorption kinetic, mechanical strength, etc.). These parameters, together with the analysis of the aggregate particle size and morphology, and a proper analysis of the relationships binder/aggregate, have shown a clear relationship between the physical-compositional characteristics of mortars and their function within the structure of the baths. Then, through the differential thermal analysis (TGA, DSC) it has been studied the hydraulic degree of mortars, which is also linked to the kind of aggregate and pozzolanic materials used.

All this has allowed us to detect some compositional discrepancies between the different mortars used in this building, even within the same room, highlighting how the *Heliocaminus* baths was carried out in several stages, with interruption of the construction works and with an evident change in the workers operating in its courtyard. All the gathered data, linked to the pointcloud 3D model of the *Heliocaminus* baths allowed an accurate location of all the meaningful traces of the story of this structure giving confirmations to the high architectural value of specific and innovative solution of that age. The contribution of the scientific analysis of the samples puts in evidence the importance of correct and innovative solutions in cultural heritage approach with proper technologies.

The stones used for building the apse of the Pisa's Cathedral (Italy)

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Keywords: stone, marble, building material.

A detailed knowledge of the building materials and of their main characteristics is a fundamental pre-requisite for a good stonework's restoration project. Nowadays Computer Aided Design (CAD) can be considered as an interesting tool for the achievement of stonework mapping and, more generally, to the management of a full restoration project.

This paper presents the mapping of the building stones used in the apse of the Pisa's Cathedral (XI century), with the scope of highlighting the potential of photogrammetry and CAD techniques in the field of restoration and conservation of stonework.

Once the survey of the apse masonry had been realized and the main geometry of each ashlar was detected, the building materials have been mostly identified by stone-to-stone visual inspection. For the recognition of the stones used for building the apse of the Pisa's Cathedral, the macroscopic characteristics widely described in several papers on the stones of medieval buildings in Pisa (Franzini & Lezzerini, 2003 and references therein) were exploited, while for marbles analysis traditional methods, such as textural features, accessory minerals and C-O stable isotope data (Moens et al., 1992; Gorgoni et al., 2002; Capedri et al., 2004) were applied.

Based on collected data, the Apse of Pisa'a Cathedral was mostly made up of Mt. Pisano and Apuan marbles and black limestones quarried at some kilometres northwest from Pisa in the Monti d'Oltre Serchio area. Re-used marbles from quarries located in Eastern Mediterranean area (Turkey and Egypt) characterise the first construction phase of this monument. The lithotypes identified in intarsia of the apse are serpentinites of unknown origin, used as decorative stones for their marble-like qualities, and small elements of red limestone probably belonging to the Scaglia Rossa Formation of the Tuscan sequence.

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A *crash test* for Michelangelo's David: results from small-scale centrifuge modeling

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Keywords: Michelangelo's David, crash test, analogue modeling.

It has been noted since the mid 1800s that the Michelangelo's David, the standing marble male nude representing a masterpiece of the Italian Renaissance, is affected by small cracks on both legs that threaten its stability. Understanding the characteristics and the conditions under which these lesions developed is thus critical for the preservation of this universal masterpiece.

In this study, we use an analogue modeling approach to test the conditions that led to the development of fractures in the David's legs and to get insights into its stability. The experiments were performed by using the centrifuge apparatus at the Tectonic Modeling Laboratory of the Institute of Geosciences and Earth Resources (CNR-IGG) settled at the Earth Sciences Department of the University of Florence. Small-scale (10 cm-high) gypsum replicas of the statue were deformed in a centrifuge, where the models were affected by a body force stronger than gravity but otherwise playing the same role. Analysis of the model results suggests that both the stability and the resulting deformation of the statue are highly sensitive to its attitude. A forward inclination promotes destabilization: the higher the angle of inclination (a), the more unstable the statue becomes under its own weight, confirming existing finite element modeling (FEM). In a vertical position, rupture of the statue typically occurs in the lower portions of the legs, while ruptures tend to develop progressively higher along the legs as forward inclination increases. Comparison of these results with the lesions detected on the actual David suggests that a long-lasting, small forward inclination (likely close to ∼ 5◦) of the statue may have represented a critical driving factor for the development of the observed damages.

These simple, preliminary models are characterised by many important simplifications, and can be thus improved in the near future. However, our results support the applicability of small-scale centrifuge modeling to problems of conservation of Cultural Heritage. At least in principle, through the analogue model approach, any feature of the original work of art, including anisotropies, aging, restoration etc., could be simulated by a suited model. Analogue modeling may thus represent a powerful technique to analyze the stability and deformation of other masterpieces, providing complementary information to the more classical FEM approach.

Non-destructive investigation on the pigments from the earliest painted ware in the Neolithic Age of Sicily

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Keywords: XRF; XRD; Neolithic Painted Pottery, Neolithic Sicily; Pigments; Manganese.

This paper examines the painted red and black painted pottery named in the archaeological literature as "Bichrome" and "Trichrome" ware, assigned to the late 5th millennium BC (calibrated date). The analyzed artifacts come from different sites of Central and East Sicily (district between the Mount Etna and Dittaino river, Enna), and the most important of them is the Neolithic settlement at Trefontane, Paternò, explored in the early 20th century by I. Cafici (1914).

X-Ray Fluorescence and X-Ray Diffraction analyses are presented, focusing on the red and black pigments used to decorate such two- and three-colors ceramics. We successfully obtained technological information about the employed raw materials and the surface decorations of these samples. The main results is to demonstrate the use of manganese in black pigments and indicate, for the first time, an occurrence of this element in the earliest painted pottery of the Neolithic Age of Sicily.

Micro-chemical and -structural study of pyro-metallurgical materials found in different archaeological sites of Sardinia (Italy)

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Keywords: smelting, slags, tuyeres, ancient metallurgy, refractory tools.

A large amount of pyro-metallurgical materials such as slags, tuyeres and refractory tools pertaining to metal extractive and smelting processes related to the Punic and Roman periods (IV-III BC) have been found in different sites of Sardinia (Italy).

Micro-chemical, micro-structural and mineralogical investigations have been carried out by means of the combined use of different analytical technique such as optical microscopy (OM), scanning electron microscopy (SEM) with energy dispersive X-ray microanalysis (EDS), X-ray diffraction (XRD) in order to identify pyrometallurgical processes and the technological parameters and to determine the technological level of competence reached by the ancient metallurgists.

The results reveal that the findings can be associated at Tharros (north-western Sardinia) with an iron ore smelting processes while in the Montevecchio mine basin with smelting and extractive processes carried out close to the metal ore deposit for the argentiferous lead production and for the silver recovery via cupellation process.

Microchemical study of the corrosion products on archaeological bronze artefacts by means of micro-Raman spectroscopy

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Keywords: corrosion; bronze; archaeological artefacts,patina, micro-Raman.

A large number of Roman and Punic bronze artefacts have been found during archaeological excavations carried out in different Italian sites characterised by different soil features and degrading agents thus giving rise to the formation of different corrosion products whose chemical nature has been investigated via micro-Raman spectroscopy.

The results reveal that the main corrosion agents is chlorine that is both present as copper oxy-chloride polymorphs (in the form of atacamite and clinoatacamite, $Cu_2Cl(OH)_3$) showing the occurrence of the most aggressive form of bronze corrosion called "bronze disease" and more rarely also as a stable and uncommon chlorine compound such as a lead chlorophosphate (pyromorphite $Pb_5(PO_4)_3Cl$). Furthermore, micro-Raman investigation reveals the presence of other corrosion products such as copper oxide, carbonates, silicates, phosphates, and copper-iron sulphide whose presence demonstrates the close relationship between the soil constituents (Cl, P, Si, S, Fe, Ca) and corrosion products. The results demonstrate the fruitful use of the non-destructive micro-Raman spectroscopy to study corrosion phenomena and to discriminate between different polymorphs with high spatial resolution thus extending the applicability of the surface analysis methods.

Mortars and plasters from the Forum of Pollentia (Mallorca, Balearic Islands, Spain): an archaeometric study

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Keywords: Pollentia, Balearic Islands, mortars, plasters, Roman production technology, constructive phases.

This work shows the result of the archaeometric study carried out on 27 samples of mortars and plasters coming from the *Forum* of *Pollentia*, an ancient Roman and Late Antique city located in the north-east coast of Mallorca (Balearic Islands, Spain).

The samples were taken from different buildings, in particular from some rooms of the so-called *Insula of tabernae*, the *Templete I*, the *Templete II*, the *East Building* (probably identified as a *Basilica*) and several other remains from the *East Sector,* where a *macellum* (market) could have been located (Orfila & Cau, 2004; Munar et al., 2009).

The petrographic, mineralogical and chemical characterization of the samples was carried out through the application of different analytical techniques: optical microscopy (OM), X-ray Powder Diffractometry (XRPD), X-ray Fluorescence (XRF), Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) and Image Analysis by the "JMicro Vision" software. The compositional data was also processed by the Aitchison's method regarding compositional data (Aitchison, 1982; 1983; 1986) and subsequently subjected to multivariate Cluster Analysis.

The results obtained from these analyses allowed to determine the raw materials used. As previously shown by the study of the mortars and plasters from *Sa Portella* (the residential area of *Pollentia*) (De Luca et al., 2013), also in the *Forum*, the samples show principally two different typologies of aggregate: one constituted almost entirely of bioclasts and fragments of sedimentary rocks and the other composed principally by quartz and rock fragments of different nature. These two typologies of aggregate constitute two clear different sources of raw materials, compatible with the geology of the area (De Luca et al., 2013).

The study of the samples had also provided useful information about the building techniques and the production technology of mortars and plasters.

Through this study it was also possible to identify three different groups of samples, that were attributed to three different constructive phases, in accord with those proposed by archaeologists. Two of these groups are composed of samples with the same raw materials (mainly bioclasts and sedimentary rocks): one of these concerns samples coming from the rooms of the *Insula of tabernae* and the remains from the *East Sector,* that are dated to the Republican period (1st century BC). The other group is formed of samples belonging to the *Templete I*, the *Templete II* and the *East Building,* that date back to the high imperial period (1st century AD). Instead, the third group includes samples composed of quartz and rock fragments of different nature. Some of these samples come from the *Templete I,* one sample comes from the *East Sector* and another one from the *Insula of tabernae*. Because of the presence of different raw materials, it is probable that these samples belong to a different constructive phase. However, we cannot exclude that they belong to a later restoration work.

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The provenance of volcanic millstones from archaeological sites of Messina

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Keywords: archaeometric analysis, volcanic rocks, millstones.

Archaeometric study of volcanic millstones from various archaeological sites of the Messina city and province was conducted. The archaeometric analysis included the petrochemical characterization of the lithologies used for their construction and the provenance attribution of the raw materials. The studied samples were divided into two groups characterized by different age. The former includes the Bronze Age samples and the latter the Roman age samples. They represent different building style, from rudimentary prehistoric grindstones to the most advanced rotary mills drawn by animals used in Roman Times. Most of these artefacts were obtained from scoriaceous volcanic rocks, selected for their peculiar textural and physical characteristics, such as high strength, hardness and good porosity. The two groups of grindstone samples were firstly characterized from the petrographic, micro-analytical and geochemical - geodynamic point of view. Afterwards, to define the probable provenance area, trace elements variation diagrams opportunely constructed and other diagrams used in literature to classify similar lithic objects, have been used. Finally all the data, in particular the geochemical ones were compared with literature data of rocks from the volcanic sites identified like before said, to verify the real comparability. The results of this work provide an important contribution to the establishment of trade routes in the Mediterranean area, confirming the presence of commercial and cultural relations already existing in the Bronze Age, as demonstrated the origin of samples studied for the prehistoric series. The presence of grindstones from many different volcanic sites in the prehistoric sites, such as Etna, Aeolian Islands and Santorini testify the resourcefulness of the primitive man that to survive and to improve their condition of life, even went ever further. In particular, the finding of the sample (pestle) that appears to come from the Aegean area, confirms that the exchanges between the Tyrrhenian and the Aegean populations in the prehistoric times, were already widespread. Furthermore, characterization of the Roman Times millstones, has instead allowed to increase the knowledge regarding the diffusion of mills in the Mediterranean area and to confirm the utilization of some volcanic sites such as Mount Etna, Linosa, Pantelleria and the Euganean Hills as quarries of raw material for the building of objects to grinding the cereals.

Archeometric characterization through geochemical data of Proto-Byzantine glassware from Roman Amphitheatre of Catania (Italy)

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Keywords: Proto-Byzantine ancient glass, glassware, Catania Roman Amphitheatre, chemical analyses, EMPA, SEM-E.

Twenty-five glass samples, including fragments of objects, glass drops and glass scoria coming from a Proto-Byzantine glassware of the Catania Roman Amphitheatre, were analysed for major, minor and trace elements. Two main groups of natron-based silica-lime glasses were identified. The majority of the samples (21) are High Iron, Manganese and Titanium (HIMT) glasses. Specifically, most of them (19) can be classified as HIMT1, while two as HIMT2 glasses, in agreement with the latest classification proposed in literature to classify this glass category. Three other samples belong to the Levantine I type.

Concerning the geochemical signatures of HIMT raw materials, the high abundance of HREE relative to LREE and of HFS elements (Zr, Nb, Ta, Ti, Hf, Th), suggests the use of impure sand, particularly enriched in heavy minerals and/or in mafic phases. Furthermore, the noticeable different contents of all the HFSE showed by the two main sample sub-groups - the enriched HIMT and the depleted Levantine I - allow us to propose these elements as discriminating factors between the two glass categories. This assumption is also confirmed by the analysis of literature data relative to coeval similar glass typologies, showing analogous HFSE distribution differences.

Hyperspectral monitoring of marble in buildings: a case study of the Santa Maria del Fiore (Firenze, Italy) facades

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Keywords: Hyperspectral technology, calcite alteration, spectral decomposition.

Hyperspectral instruments, discriminating materials on the basis of their different patterns of wavelength-specific absorption, might be employed in the characterization of the components in exposed stone surfaces, and therefore contribute to understand their conservation state. A portable radiometer (ASD-FieldSpec Pro spectroradiometer), which continuously and rapidly acquires punctual reflectance spectra in the 350-2500 nm spectral range, has the potentialities to be used for monitoring the state of conservation of stone surfaces through the evaluation of the relative abundance of some components considered precursor symptoms of decay. Major advantages of this technique include its non-destructive and non invasive nature.

In this study, gypsum is considered as a damage symptom in ancient building facades realized in marble. A method to unravel qualitative and semiquantitative information about the degree of alteration of the calcite to gypsum is proposed. This method is based on the spectral decomposition in individual spectral components assigned to calcite and gypsum, during the analysis of spectra of synthetic mixtures of microcrystalline calcite and gypsum. Advantages, perspectives and limits of the method are discussed. Furthermore, a case study is considered. The analysis of 24 areas of the white Carrara marble stones, was carried out on the facades of the Santa Maria del Fiore church (Firenze, Italy), cathedral of Florence belonging to the UNESCO world heritage monuments. The preliminary analysis of the data are presented and discussed.

Volcanic activity and human settlements in the past 10 ka in the city of Naples (Italy)

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Keywords: Geoachaeology, Naples, Explosive eruptions.

The Naples area (Italy) is located near and within the active volcanoes of Vesuvius, Campi Flegrei and Ischia. The area, variably affected by deposition of products of eruption of these volcanoes, has been continuously inhabited from Neolithic to Present. Remains of different archaeological cultures are interbedded with pyroclastic deposits of explosive eruptions of variable intensity.

We present joint archaeological and volcanological studies of excavations conducted in the city of Naples, between the eastern border of the Campi Flegrei caldera and the western slopes of Vesuvius. The area has been investigated mainly thanks to the excavations works for the construction of Lines 1 and 6 of the Naples Underground. The excavations have yielded many traces of settlements and land use, intercalated with volcanic products dated between 10 ka and the Late Middle Age. Gently sloping hills and coastal plains characterized the investigated area, which is very close to the first Greek settlement in Naples.

At least 15 deposits of explosive eruptions of the Campi Flegrei, Ischia and Vesuvius volcanoes have been recognized in the defined time span. These deposits are intercalated with reworked deposits and paleosols containing traces of human activities, such as ancient agricultural practices. The volcanic deposits consist of pyroclastic layers with variable grain-size (ash-to-lapilli) that are correlatable on stratigraphic, lithological and petrological bases. Pyroclastic fallout and density current sediments deposited by known eruptions and partially reworked in continental and transitional environments have been recognized.

The exceptional alternation of archaeological and volcanological sequences makes it possible: i) to date exactly prehistoric and historical volcanic eruptions, ii) to determine the influence of volcanic activity on human life, iii) to study the effect of the deposition of volcanic products on the territory, and iv) to use the volcanic deposits as marker levels for dating and correlating unknown archeological sequences. Furthermore our reconstruction reveals the high-level hazard posed to Naples by Phlegraean and Vesuvian high-to-low intensity explosive eruptions.

The Quaternary succession of the Bulè Valley (Po Valley, Piedmont) as possible supply for prehistoric jade axes

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Keywords: Monviso, prehistoric jade axes, glacial deposits.

This contribution presents a detailed geological mapping and preliminary data on the Quaternary succession of the Bulè and low Alpetto tributary valleys (Po Valley, Piedmont). The investigated area, in the altitude range between 3016 and 1487 meters, is located in the Monviso Massif Ophiolitic Complex and in the adjacent carbonatic units of the Dora-Maira Massif.

The Quaternary sequence consists mainly of glacial and landslide deposits with local lacustrine, fluvial, debris and colluvial bodies. The detailed investigation of the petrographic composition of the glacial deposits allowed to recognize the occasional occurrence of jadeitite boulders, exploited during the Neolithic age for axe heads production. Four main jadeitite blocks have been found, with sizes up to 1 m^3, some of them already reported by previous geological literature (Compagnoni et al., 2007) and other found during the present fieldwork (Avondetto, 2014). In detail, a Neolithic site of jade polishing has been discovered and referred to the middle of V millennium B.C. (Allisio, 2012) in the high Bulè Valley at 2880 meters. The jadeitite blocks have been mainly found in the glacial deposits. The petrographic characterization of the new jadeitite samples is in progress, and might potentially shed light on the still controversial genesis of these peculiar rocks.

The distribution of moraines (between 2450 and 1250 meters) and glacial diffluence saddles have led to the reconstruction of the glacial expansion episodes, reported in four major glacial steps. An ancient step (1), probably related to the Last Glacial Maximum, implies a confluence between the Alpetto Glacier and a left lobe of the Bulè Glacier. The subsequent step (2), related to the start of the glacial withdrawal, defines three progressive phases of glacial diffluence of the Bulè Glacier left lobe in the Alpetto Valley. The further step (3) suggests a right lobe diffluence of the Alpetto Glacier in the Vallone Bulè. Finally, the last step (4) is due to the drastic retreat of glacier fronts towards the valleys head. At the end of the last glacial period, some rock falls and sliding gravitational phenomena occurred, partly covering the glacial record. Small deep-seated gravitational slope deformations also developed, resulting in a loose or disjointed substrate and some morphological features, as doubled ridges, minor scarps and trenches.

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Portoro, the black and gold Italian “marble”

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Keywords: Portoro, "marble", chromatic alteration.

The “Portoro”, called also “*Mischio giallo e nero*”, “*Portovenere marble*”, *Black and Gold*”, is one of the most famous and expansive “black marbles” for its characteristics yellow gold veins on a black background. It is a limestone of Rhaetian-Hettangian age belonging to the Tuscan Nappe.

It was used since Roman times, particularly in the city of Luni. Since the Middle Ages its use is widespread in Genoa, for the construction of monuments, cathedral, villas. At the end of the XIX century its use has spread abroad, especially in England, where it was used for fireplaces, coverings, plinths and panels for furniture. It was extracted in several quarries located near la Spezia, precisely on the promontory of Portovenere, in Palmaria Island and Tino Island but at present only one quarry is active. The low volume production of this “marble” is now challenged by similar commercial marbles, cheaper and with huge production, from abroad. This material, exposed to the weathering, tends to fade with time losing the look of his golden streaks and spots that determine all the aesthetic appeal. In the paper, this chromatic alteration will be investigated in order to define the guidelines for the most suitable use of this stone and for eventual restoration works of recent as well as historical monuments. Moreover the knowledge and awareness of the characteristics of this precious stone material may help in recognizing and maintaining the value of Italian Portoro.

Common Ware from the environs of Vesuvius (Pollena Trocchia, Naples): new insights into the production technology of late Roman pottery

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Keywords: Late Roman pottery, quantitative analyses, Campania region.

The social and economical setting of Campania region, and in particular of the Vesuvian area, during the Late Roman period is almost unknown and is matter of hard debating among the researchers.

Recent studies brought evidence of a re-occupation of the Vesuvian area after the Pompeian catastrophe of the 79 AD and of a dense settlement pattern until the AD 472 eruption.

The archaeological sites in the environs of Vesuvius covered by the volcanoclastic deposits of the AD 472 eruption provide a clear *terminus ante quem* for the chronology and a snapshot of goods' circulation for a very narrow timeframe.

The 5th century AD represents, indeed, a moment of important transformation in the patterns of production and trade in the Mediterranean basin because while the African productions still played a prominent role, new regional workshops arose. At first these regional workshops imitated the African shapes, then evolved into independent productions which kept the traditional Roman skills in manufacture, but were scattered in several workshops in the region.

This study examines the ceramic fragments from the most prominent site (Pollena Trocchia) in the environs of Vesuvius as part of a broader study, which aims at the characterization of main productive units in Campania during the Late Roman period.

Twenty-five samples were selected among thousand of fragments; quantitative mineralogical and petrographical analyses (OM, IA, XRF, Quantitative X-Ray Powder Diffraction Method by using Rietveld approach, Mossbaüer spectroscopy) were carried out in order to recognize the technological features of the pottery.

The tablewares, grouped in Slipped and Painted wares on the basis of the different coatings, are constituted by high-CaO samples (CaO=7.7-17.3wt%), with skeleton particles composed by quartz, feldspar, micas and traces of carbonates. A variable content of additive (from 5 to 13%) made of quartz, sanidine, plagioclase, clinopyroxene, scoriae, lithic fragments and rare garnet and chamotte, were mixed to the base clay. The occurrence of newly formed diopside (4-16%), gehlenite (1-4%) and hematite (1–3%), along with the high quantity of amorphous phases (32–57%) inferred high firing temperatures (850-950°C).

The cooking wares, showing a "sandwich structure" of the matrix, were made with low-CaO base clay (1.6-5.5wt%). In the coarser paste higher percentages of skeleton particles (3-15%) and volcanic and/or siliciclastic additive (8-21%) were found.

The amount of hematite suggests low firing temperature (800-850°C). The Mossbauer Spectroscopy also inferred a not-well controlled firing atmosphere showing relevant differences in the amount of Fe(II). Cores with a higher Fe(II)/Fe(total) ratio, accounts for the presence of a local non-oxidant environment during the firing, conversely, rims also show the presence of Fe(III) oxide.

Production and provenance of Apulian Red Figured Ceramic from Taranto

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Keywords: SEM-EDS, ICP-MS, Apulian red figured pottery, statistical treatment.

A consistent physical-chemical and morpho-mineralogical research –started some years ago and still in progress- has been performed on Apulian red figured items (Mangone et al., 2008; Mangone et al., 2009; Mangone et al. 2013), dating back to the 5th and 4th cent. BC and coming from sites among the most relevant in Apulia (Southern Italy). The motive that fosters our project is the almost complete lack of information on technological production of this class of pottery, as well as the awareness that a systematic study on samples coming from representative sites of the entire production area can be a resource not only local.

We introduced here the study about the site of Taranto. The samples analyzed were found during archaeological excavations carried out in the last century in the Military Arsenal area and are stored in the National Archaeological Museum of Taranto (MARTA).

We examined ceramic bodies, red decorated areas, black gloss coatings and decorations by Scanning Electron Microscopy, X-Ray Diffraction and Ion Coupled Plasma Mass Spectrometry. Lastly, the compositional data matrix were processed with multivariate statistical analysis to identify groups of items with similar composition.

Our first aim was to discriminate the Apulian production from the Attic one by specific features in manufacturing processes.

The analytical results distinguished at least two unlike production technologies of Apulian red figured vases in Taranto during the 4th century BC: one characterized by a fine texture of the ceramic body, red figures saved from the ceramic paste and black gloss painted directly on the ceramic body, as traditional Attic production; the other one by a ceramic body with a coarser texture and a layer of *ingobbio rosso* to obtain red decorations, with a black gloss painted on it.

The *ingobbio rosso* technology, already highlighted in others sites of Apulia and never pointed out in Attic pottery- seems to represent a distinctive characteristic of Late Apulian production.

Also, data from Taranto show some clues about the beginning of this production during the second half of IV cent. BC, while the comparison with two clay slabs -coming from a tarantine workshop of black gloss and *acroma* pottery dated back to V-IV cent BC- supported the local provenance of the samples grouped in clusters, where all pottery attributed to Truro painter's, considered one of the most representative ceramist of tarantine production, is located together.

Archaeometric study of the more ancient painted wall found in Sicily (Apaforte – Licata)

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Keywords: plasters, production, Licata.

In the present work, an analytical study of painted plaster samples coming from an ancient tomb, dated back to 4th – 3rd cent B.C. and located in Licata (Sicily, Southern Italy), has been carried out. This tomb situated in the street called "c.da Apaforte" is an interesting hypogeum composed of a single room made of stone blocks. The importance of this tomb is represented by the presence of the most ancient painted wall recovered in Sicilian hypogea structures.

In order to identify the pigmenting agents, the preparation layers and the deterioration processes we carried out non-destructive micro-Raman spectroscopy and micro-destructive analyses through SEM-EDS. Preliminary characterization of samples was done by optical microscopy (OM) with the aim at characterizing plaster features and degradation processes.

The micro-Raman measurements have been performed in order to investigate the molecular nature of the used materials and to obtain the characterization of the decorated surfaces. The quantitative analysis of the chemical composition of the different layers (pigments, preparation layers, deteriorated parts) has been obtained by SEM-EDS.

In order to establish the production technique used by the craftsmen, the results were compared with our recent data on Hellenistic plasters coming from an ancient buildings located in Licata and dated back 2ndcent B.C (Aquilia E. et al., 2012).

Aquilia E. et al., 2012. Caratterizzazione delle superfici decorate: il caso delle pitture ellenistiche in Sicilia. Atti del VI Congresso Nazionale di Archeometria. Scienza e Beni Culturali. Pavia 15-18 febbraio 2010. Bologna, 1-5.

Mortars, plasters and mosaic floors from Ancient Stabiae: the art of building in Roman times (89 B.C.-79 A.D.)

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Keywords: Stabiae, roman mortars, ancient technologies.

Ancient *Stabiae* (Castellammare di Stabia, Naples) is the archaeological site with the largest number of roman seaside villas of the Mediterranean area. Among them, Villa San Marco is one of the most important examples of roman *otium villae*. During the last years, *Stabiae* has been subject of a restoration and development program driven by RAS Foundation (*Restoring Ancient Stabiae*) and involving several international and national academic and public stakeholders. The present research focuses on the archaeometric analysis of 10 plasters, 8 mortars and 2 mosaic floors from Villa San Marco, with the final aim to recognise the technology used by the ancient skilled workers.

Several analytical techniques were used for the study of plasters, mortars and mosaics (Digital videomicroscopy, Colorimetry, OM, XRD, SEM/EDS, DIA). A multi-layer study of the plasters was adopted to differentiate and characterise these materials.

We found out that the *rinzaffo* layer (rendering mortar) was a hydraulic lime mortar made with pozzolanic lightweight aggregate (pumices) and cocciopesto (1:1arriccio layer (scratch coat), lime mortars with volcanic sand and minor pozzolana and/or cocciopesto (1:1rinzaffo. The *intonachino* layer (B/A=2:1) was the removable support of the frescos and provided a lighter colour for the preparation layer of the frescos. This last thin layer, composed of lime mortars made with a carbonatic aggregate (B/A=1:1), is characterised by a low porosity in order to hinder the pigment adsorption. Encaustic painting technique was used for the fresco.

The structural mortars of the building were made with hydraulic lime and lightweight aggregate (pozzolana) and cocciopesto (1:1opus reticulatum.

The preparation layers (*rudera* and *nuclei*) of the mosaics were built with volcanic sand and abundant cocciopesto mixed to the hydraulic lime (B/A=1:1), providing a more resistant surface for the application of the *tesserae*, which were fixed only with lime. The white and black colours of the mosaics were yielded by limestone and tephritic lava.

These findings demonstrate a high level of specialisation own by the workers and artists involved in the construction of Villa San Marco and the other maritime villas of *Stabiae*. Moreover, the collected data highlight the wide potentiality of material supplying of the peri-vesuvian area.

The present research contributes to the knowledge of the technical, artistic and architectural skills achieved during Roman times and represent a valuable reference for future restoration interventions in Villa San Marco and in the other Roman villas in which similar materials were used.

Majolica from Sassari: first evidence of a production center in Sardinia

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Keywords: Majolica, Sardinia, XVI-XVII century.

Archaeological excavations begun in the city center of Sassari (Sardinia, Italy) in 1999, for the renewal of roads and underground utilities, have brought to light a significant amount of ceramic findings. These are mainly waste materials including spacers, incomplete ceramic products and polychrome majolica, whose abundances suggest the presence of a production center in the area. The possible local pottery was stratigraphically associated with monochrome and polychrome Ligurian, Tuscan (Montelupo), Latium and Spanish pottery, dating from the sixteenth and seventeenth century (Biccone et al., 2009).

The aim of this work is the preliminary textural, mineralogical and chemical characterization of the ceramic body and glaze of the unknown majolica, to provide information about the provenance of the raw materials and to get some data on the manufacture.

Twenty-one samples, containing 7 spacers, 11 painted open shapes (5 of uncertain production, 1 from Montelupo and 1 from Liguria) and 3 uncoated open form, have been selected for the analyses. Observations on thin sections through optical microscopy (OM) have been carried out in order to characterize the microstructure and the morphology of the pastes and the glazes, while chemical composition of the glazes were determined with a scanning electron microscopy equipped with an energy dispersion spectrometer (SEM-EDS). The crystalline phases of the paste have also been analyzed by means of X-ray diffraction (XRD).

The fragments of uncertain production show small variations in composition and texture. They are characterized by a very fine and isotropic marly groundmass with coarse inclusions of quartz, feldspars, oxides and fossils, mainly globigerinae.

Coatings consist of an opaque glaze layer on recto and on both recto and verso surfaces, characterized by lead and tin oxides, whose average thickness is ~300 μm.

Despite the paucity of clues for a pottery work, which are limited to good number of spacers, the archaeometric data point to a local production of majolica in Sardinia. Particularly, the provenance of the clay is referable to the local marls of Langhian age widely cropping around the town, which contain a sandy component coming from the dismantling of the Variscan metamorphic basement.

The study attest for the first time a production center for majolica in Sardinia.

Biccone L., Mameli P., Rovina D., Sanna L. 2009. La produzione di maioliche a Sassari tra XVI e XVII secolo: primi dati archeologicic e archeometrici. Atti XLII Convegno Internazionale della Ceramica Albisola, 297-310.

Archaeometric study of ceramic materials from archaeological excavations at the Roman iron-working site of San Giovanni (Portoferraio, Elba Island)

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Keywords: San Giovanni (Elba Island), Roman ironworking centre, ceramics.

In the framework of the AITHALE project , which promotes systematic research on Elba island through a cooperation among various Institutions (Soprintendenza ai Beni Archeologici della Toscana, Universities of Firenze and Siena, Scuola Normale di Pisa, IGG-CNR, Musei Archeologici elbani), archaeological excavations were carried out in 2012-13 at San Giovanni, in the eastern end of the Portoferraio Bay. The site, known as one of the main ironworking centres during the Roman period (3rd -1st cent. BC.), but possibly even earlier, occurs at the foot of the promontory on which the Roman "Villa delle Grotte" was built in the 1st cent. BC.

Abundant waste heaps of metallurgical production occur on the site, mainly including slag, pieces of ore charge and fragments of furnaces. Previous (2009-11) geophysical prospecting on the site revealed subsurface structures, which after recent excavations appeared to be walls and other remains of a Roman farm devoted to wine production, possibly the *pars rustica* of the neighboring Villa delle Grotte. Samples of different kinds of "ceramics" (bricks, *dolia*, metallurgical furnaces) were taken both from the farm and a trench dug through the earlier (underlying) metallurgical debris.

Archaeometric analysis provided us with interesting information on production technologies and the origin of the raw materials used at San Giovanni in Roman (and pre-Roman?) times.

Broken pieces of refractory ceramics, partly slagged and vitrified, commonly occur in the metallurgical heaps. They are constituted by clay tempered with abundant quartz and lithic fragments in order to augment its refractoriness; rare fragments of tuyeres and channels for slag tapping have been found as well. Apparently, iron smelting furnaces at San Giovanni, unlike those found in the Etruscan site of Baratti-Populonia in the mainland, were not (or only partly) armored with refractory stones.

Mud clay bricks from the Roman farm, in accordance with recipes reported by Latin authors (Vitruvius, Pliny the Elder), are made with clay, sand, and organic materials (straw, etc.). The composition of temper used for roof tiles shows significant variations, indicating either imports from different production centres or re-use of old roof tiles. Finally, we analyzed fragments of *dolia*, the large ceramic containers used for the storage and fermentation of wine. The employment of lithic fragments of basaltic to trachytic composition as *dolia*'s temper may point to a production area in the medium Tiber Valley, which hosted - in the 1st cent. B.C. - at least one famous *figlina* (pottery workshop) specialized in the production of *opus doliare*.

Development of an ultra-miniaturised XRD/XRF instrument for the in situ mineralogical and chemical analysis of planetary soils and rocks and implication for Archeometry

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Keywords: XRD, XRF, portable instrument.

The knowledge of the surface composition is crucial for the identification of potential resources and for the understanding of the surface/crustal evolution. An ultra-miniaturised (mass 1.5 kg; volume ~22x6x12 cm^3) combined XRD/XRF instrument has been developed for the mineralogical and chemical characterization of Martian soils/rocks and was included in the ExoMars-Pasteur payload (Marinangeli et al. 2007, 2011). The simultaneous acquisition of in-situ chemical and mineralogical information would give significant improvement to any robotic missions and may unravel many doubtful points regarding the mantle composition, crustal evolution and resource potential. The instrument is based on an innovative and advanced concept which gathers the experience achieved in Europe for the design miniaturisation in the space industries.

The instrument prototype built with ESA funding in 2006, consists of a radioisotope (55Fe) as source of X-rays, a collimator and a CCD-based detection system. The instrument follows a fixed reflection geometry to fulfill the diffraction principle. The instrument takes advantage of the use of a radioactive source to reduce the power consumption compared to an X-ray tube, a critical parameter for in situ power resources. However, given the status of the art for cold-cathode X-ray carbon nanotube, this option may be also investigated in the future.

A complete measurement cycle consists in the acquisition and integration of data for several hours. XRF and XRD data are acquired simultaneously and the separation of the two types of information is achieved via software. The instrument is able to analyze samples as fine powders or pristine surface with a clean and smooth cut. The latter option is applicable to analyze paintings or ceramics without sample preparation.

A number of measurements have been acquired on soils/rocks and compared with measurements acquired using commercial instruments in order to define the instrument detection limits and accuracy. Further tests on pottery as well as a field demo are planned in the next future.

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Traceability of iron from Elba Island: new data from experimental Archaeometallurgy

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Keywords: Ancient iron, Elba Island, traceability.

Iron deposits from Elba Island (Tuscan Archipelago) were extensively exploited since the 1st millennium BC: both raw iron ore and smelted blooms were extensively traded throughout the Mediterranean region. However, archaeological evidence of Roman and pre-Roman (Etruscan) ore exploitation and extractive metallurgy on Elba Island is extremely scarce mostly due to the past century's slag recovery for re-use in modern blast furnaces. Recent studies of hematite-rich ores from Elba showed a prominent and apparently unique (at an European scale) co-enrichment in W and Sn that may represent a provenance marker not only for the ore itself (remains of which are commonly found at many ancient smelting/smithing sites) but, possibly, also for iron blooms and metallurgical slag. Within the frame of the multidisciplinary research Project "AITHALE" (from the Greek name of Elba Island), we have performed a series of archaeometallurgical experiments primarily to investigate the extent of Sn and W partitioning during the various steps of the chaîne opératoire of bloomery iron production. On March 2013 at the Bacino stope, Rio Marina mine (Elba Island) a furnace was prepared entirely made of local clay; forced draught was provided by an air compressor connected through a clay tuyere with the furnace. After 1h preheating, about 45 kg of pre-roasted hematite-rich ore (taken from the nearby Bacino stope) and charcoal were regularly added to the top of the furnace in roughly a 1:1 ratio. A total of some 30 kg of fayalite-rich slag were tapped from the furnace in five separate steps. At the end of the experiment about 5 kg of iron bloom were obtained. The hematite-rich ores, analyzed by ICP-MS, have bulk contents of Sn and W of, respectively, 75 and 656 ppm; EMPA analyses showed that W is present both in solid solution in hematite and as micrometric crystals of scheelite ($CaWO_4$). The W/Sn ratio of the slag's silicate melt (≈20) is much higher than that of the bloom (≈3), indicating that under the operating conditions of this experimental process W preferentially partitions into the slag. Smelting experiments of Sn/W-rich hematite from Terranera mine (Elba Island, to the south of Rio Marina district) were also carried out in a Deltech DT-31VT-OS2 vertical quench furnace (at the Petrology Laboratory of the Dip.to Scienze della Terra, Firenze) under controlled redox and temperature conditions and variable ore:charcoal:(siliceous) flux ratios. In one experiment, we obtained metallic iron with appreciable amounts of dissolved Sn (0.2-0.3 wt%, EPMA analysis), but with W still below the instrumental detection limit (0.05 wt%). This confirms the preferential partitioning of W into the silicate slag. In both types of experiments the slags resemble in their mineralogical and textural features to analogue materials found at ancient ironworking sites, as for instance Baratti-Populonia, the most important site in ancient Italy for iron production during the Etruscan and Roman periods.

Archaeometric analysis of vitreous material ornaments from the Villa di Villa Sanctuary (TV, Italy)

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Keywords: Protohistoric glasses, archaeometric analysis, Northern Italy.

In the site of Villa di Villa (Treviso, north-eastern Italy) is located a Sanctuary that has been excavated since 1976. The vitreous material ornaments unearthed during the excavations are particularly interesting because have different typologies: two anular beads, one globular bead, one melon bead, three bracelet fragments and one semicircular rod fragment. The age of the finds cover a wide chronological range, from the Final Bronze to the Late Roman Age. Therefore the study of composition, texture and morphological characteristics of the ornaments enables to shed light on the different types of raw materials used and to relate the evolution of the glass production techniques within the period of the Sanctuary activity. Eleven micro-samples from the bodies and the decorations of eight vitreous material objects were sampled and analyzed by Scanning Electron Microscopy combined with EDS and Electron Probe Microanalysis (EPMA), whereas non – invasive X-Ray Diffraction was performed on the ornaments. Only one blue anular bead is an LMHK glass produced with mixed alkali plant ashes as flux, suggesting that the sample may be dated to the Final Bronze Age. The other vitreous materials are LMG glasses obtained using natron as flux, although some samples have a particular intermediate composition. A few specimens show relatively low content of Na_2O (12,15-14,23 wt%) but they are characterized by the presence of high amounts of Pb (about 10 wt%) or Sb (about 8 wt%) in the glass matrix. All the glasses have an elevated contents of Al_2O_3 (1,78-3,29 wt%) that testify the use of an impure sand as source of silica. The percentage of all the other elements are mainly linked to the colour and the opacity of the glasses. The dark blue arm rings and beads are Co coloured, while only the pale blue melon bead *faiänce* is coloured by Cu. The identified trace elements related to Co are not the same in all the samples suggesting the use of Co-colurant with different origins. White and yellow glasses are opicified respectively by $Ca_2Sb_2O_7$-$CaSb_2O_6$ (CaO in the glass phase about 8 wt%) and $Pb_2Sb_2O_7$ (PbO in the glass phase=10,71wt%); moreover they present a significant level of Sb_2O_3 in the glass matrix up to 8 wt%. All but one of the Villa di Villa samples have traces of Mn (0,32-0,79 wt%). In the site both glasses and *faiänce* are present. The chemical composition and the morphology observed reflect the variability of the materials in colour and age. Even if opacifiers are not present in some glasses, the heterogeneous texture observed is related to the presence of metal inclusions, unreacted raw materials and/or newly formed crystals. The results of the archaeometric study of the Villa di Villa ornaments allow the identification of the raw materials used and permit also to estimate the age of the finds. The relationship between the Villa di Villa ornaments and coeval European and Mediterranean vitreous materials will be discussed according to the specific object typologies.

The monumental submerged punic harbor of Malfatano and associated Piscinnì quarries, Archaeometric and Geoarchaeological approach

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Keywords: Archaemetry, Punic harbor, Sea level change.

The Ria of Malfatano is the site of the most important maritime structures from the Punic-Roman times in the Mediterranean, whereby the bay's two opposing monumental structures have been preserved between - 7 and - 2 meters due to the rising sea levels. Piscinnì quarries have recently been recognized together with other archaeological finds belonging to the Punic and Late Antiquity ages (Orrù et al., 2014), these were built with littoral sandstones of the Last Interglacial (MIS 5,5) (Lecca and Carboni 2007). Piscinnì's quarries because of the proximity of coastline to the basement didn't have access from land, thus it is likely that the placement of the material was done by means of floats, as for the loading of materials from the quarry. However, we may assign the date of the structure to the Carthaginian age (Mastino et al., 2005). Considering the military strategy adopted by Carthage from their second treatise with Rome in the middle of IV century B.C., it is eminently possible to envisage a military function of this port basin (V-III century B.C.; 2400±100 ky BP). Piscinnì quarries provided an extremely selective quality of construction material, sandstones and microconglomerates with strong carbonatic cementation, a lithotype that can easily and quickly be worked and which has good geomechanical characteristics both in terms of breaking loads and resistance to alteration. Using a high resolution terrain model has been possible to estimate the total extracted volume of about 120,000 m^3, for coastal quarries and about 30.000 m^3 for submerged quarries area; only a small proportion, estimated at 25,000 m^3 was used for the realization of the crowning work of the breakwater at the entrance of Capo Malfatano bay. There is also an extensive use of sandstone in the Bithia settlement, where, from the Phoenician tombs in the necropolis to the buildings found in the acropolis area in Torre di Chia to the Punic sanctuary of Bes,(Bassoli et al., 2013). Rocks analysis and high detail measures have involved both submerged reefs, harbor and quarries using a HR side scan sonar (800 kHz), while for the quarries coastal areas aerophotogrammetric surveys were performed using a automatic navigation drone.

Micropaleontological contribution to the archaeometric study of ceramics from Caltagirone (Sicily)

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Keywords: ceramic of caltagirone, microfossils, heating temperature.

This research deal with the role of microfossils for the ceramic paste characterization. This approach, so far rarely investigated in archaeometry, allowed to confirm the biostratigraphic position of the Monte San Giorgio clay, which was widely used in the past for the production of the Caltagirone (CT) ceramics. The micro and nanomorphological modifications and the geochemical changes of foraminifera tests engulfed in ceramics enabled to assess the firing temperatures. The research was developed in two phases. A systematic and biostratigraphic study on the planktonic foraminifera and nannofossils has been performed in the first phase, which permitted to recognize the age of the clayey sediment used as raw material. The second phase was focused on micromorphological and geochemical analyses performed on the experimental ceramic made with the clay of Monte San Giorgio. Different known firing conditions, according to the ancient techniques, were adopted to made the experimental samples. They were compared with the ceramic fragments, furnished by the Ceramics Regional Museum "Antonino Ragona" of Caltagirone, in order to validate our approach on unknown archaeological material. The micropaleontological study for archaeometric analyses seems to be useful in the evaluation of firing processes and sometimes decisive in distinguishing the typical features of the clay used in a given production.

Mortars from the Roman villa of the Vetti (Tuscany): preliminary data

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Keywords: plaster, pigment, building material.

Since the end of the III century A.D. the Roman Empire lived a period of relative stability and the following decades knew a sort of villas renaissance, especially in the peripheral areas.

The Roman villa of the Vetti (middle IV century), built in the town of Limite sull'Arno (Florence), is one of the most interesting late ancient aristocratic mansion discovered in the present Tuscany, comparable to other examples like those of San Vincenzino (Livorno) and Torraccia di Chiusi (Siena). The archaeological excavations have revealed a portion of the *pars urbana* and in particular an apsidal room and its mosaic floor in which a hunting scene is pictured (Alderighi *et al*., 2011). This work is focused on plasters and mortars found in this sector of the building during the campaigns of 2010 and 2011.

From the macroscopic point of view (number of layers, aggregate/binder ratio, colour of binder) four different types of plaster mortars have been identified; a fifth group comprehends the mortars from joints between masonry units and from the mosaic pavement. Mineralogical and petrographic data obtained by optical observation and XRPD, TG/DSC analyses as suggested by Riccardi *et al.* (2007) indicate the presence into mortars of hydraulic binders and river sand as aggregate fraction.

Some plaster fragments are characterized by the presence of decorative painting; petrographic features, XRPD and SEM data suggest the use of lime milk (white), ochers (red, yellow, brown and orange), carbons (black) and the typical egyptian blue pigment.

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Analysis of building stone materials used in Flavian Amphitheatre in Pozzuoli (Italy): types and provenance

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Keywords: Flavian Amphiteater, Campi Flegrei lavas, mineralogical-petrographical analysis, archeological site.

This work is the result of the interaction between archeological and geological investigations on the Flavian Amphitheatre, one of the most important archeological sites in Campania region, situated in an area of great geological and archeological interest: the Campi Flegrei.

The first aim of this research was to analyze stone material whenever employed for structural use, focusing on the type of materials and their provenance.

After several surveys and photographic campaigns, considering the overall complexity of the monument and the presence of different geomaterials, our work has been focused on subterranuem corbels and on pillars of external arches that show an severe state of decay. Thanks to the permission allowed by Special Superintendence of Archeological Heritage of Naples and Pompeii it has been possibile to take out small non-invasive, but representative, samples of geomaterials in order to reach our characterization scopes and to provide useful information on probable future restoration activities.

Mineralogical-petrographic characterization of samples taken by corbels and pillars have been performed mainly by X-ray powder diffraction (XRPD) and polarizing microscope analysis on thin sections (OM, optical microscopy).

The macroscopic analysis suggested, as regards materials used for the abovementioned structures, an interleaving of *Piperno* (eutaxitic texture characterized by long dark grey lenses – *fiamme* – and alveolization, a peculiar alteration style of this specific rock) and lavas from the Campi Flegrei district (porphyritic texture, along with spalling and fracturing as weathering pathologies). This alternation was also confirmed by historical literature data (Maiuri A., 1955). On the contrary, detailed OM investigation on thin sections revealed mineralogical and textural characteristics typical just of Phlegrean lavas.

From a comparison with available geo-petrographycal literature data (Melluso et al., 2012), samples taken from pillars revealed a similarity with lavas from the Monte Olibano dome, due to the precence of plagioclase and olivine xenocrysts, glomeroporphyritic clusters of clinopyroxene-plagiocase, or plagioclase and sanidine.

On the other hand, the weakly porphyritic texture, and the presence of sodalite and sanidine phenocrysts in the samples from corbels suggested their provenence from one of the other rare lava outcrop in the Campi Flegrei: the Punta Marmolite dome.

These findings (mineralogical and petrographic analysis vs. archeological descriptions) are clearly an example of what could be the results of a complementary study performed by different expertise, that could lead to more correct inputs in the framework of future restoration intervention, whenever any of these expertise provide their essential contribution in the field of diagnostics and conservation.

Maiuri A. 1955. Studi e ricerche sull'anfiteatro Flavio puteolano, Memorie dell'accademia archeologia, lettere e belle arti- serie 3, Napoli.

Melluso L., de Gennaro R., Fedele L, Franciosi L. Morra V. 2012. Evidence of crystallization in residual, Cl-F-rich, agpaitic trachyphonolitic magmas and primitive Mg-rich basalt-trachyphonolite interaction in the lava domes of the Phlegrean Fields (Italy); Geo. Mag 149, 532-550.

Petrochemical characterization of Bronze Age pottery from the settlement of Mt. San Paolillo (Catania, Italy)

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Keywords: Middle-Late Bronze Age, ceramics, Mount San Paolillo (Catania).

The excavations carried out in 1997 by the Superintendence of Cultural Heritage of Catania at the Mount San Paolillo, in the northern suburb of the city, bought to the discovery of a Prehistoric settlement that still represents the most important evidence for the Middle and Late Bronze Age in this area. During the explorations, a hut, a storage jars deposit and a pottery workshop have been located, all providing a high quantity of heterogeneous ceramics with apparent typological parallels in other cultural districts, such as the territories of Siracusa, Augusta and Messina. Due to the lack of data about Etnean Middle and Late Bronze Age pottery production, it has been decided to sample a large quantity of specimens, in order to include all the 15 fabrics visually identified and all the main typological classes, comprising tableware, cooking vessels, coarse ware, storage jars but also baking plates, kiln spacer and clay renders. 32 statistically representative samples have been studied though a palimpsest of petrographic and chemical analyses.

The archaeometric results show that the considered pottery is strongly heterogeneous and permit the identification of 5 petrographic fabrics. Those ceramics better studied are characterised by abundant temper consisting by volcanic rock fragments and rarely by grog. Only few samples present a fine grain and common quartz. The groundmass ranges from non micaceous to very micaceous, in some cases is also evident a mixing of clays.

The chemistry of ceramics has revealed the existence of two groups with low and high CaO contents. The chemical and petrographic differences suggest the use of different raw materials. Another distinctive geochemical character is the high Fe_2O_3 abundance (more than 8.7 wt.%) which is imputed to the use as temper of altered pyroclastic rocks cropping out nearby the archaeological site.

In addition, further data confirming a local provenance result from the analysis of the mineral phases carried out through SEM+ EDX.

The data provided by the archaeometric analyses gave a very significant contribute for the study of the Middle and Late Bronze Age pottery of the Catania territory, clarifying methods, productive strategies and technical levels of the prehistoric artisans. In particular, the most striking data has been represented by the operation of mixing clays with different composition in order to obtain a fabric with peculiar features. Furthermore, this work demonstrates some typological features are not connected with “imported products” but just simple local copy of other native ceramics of different cultural districts.

Strategies for the building stone and damage mapping applied to the historical center of Catania

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Keywords: degradation, stone material, conservation.

The problem of conservation and restoration of the historical centers request a knowledge of the effective state of deterioration with the definition of, not only the typology of damage, but also the intensity of degradation and its development. The degradation's maps are the first step for identifying macroscopic pathological manifestations. These are classified on the basis of Italian *UNI 11182* of 2006 but does not give sufficient information since it is purely qualitative and descriptive.

In the last decade of XX sec. the scientific group of Fitzener (Fitzener et al., 2002) developed a method for the complete definition of the degradation on monuments that was rarely used in Italian context. Moreover, the analysis of the interactions between micro-climate, material, shape, construction techniques and technological system are needed to understand the phenomena that, during time, have generated the degradation.

So, in this work we resume a sophisticated instrumental analysis implementing it with geometric, technical-constructive and modern digital survey.

With the aim to highlight the potentiality of the proposed method we report the study of the Villa Cerami portal, in which the degradation forms are mapped at decimetric scale and another example of baroque architecture belonging to the Catania post-earthquake reconstruction at large (architectonic) scale of observations to evidence the different damage in the façade. In both cases the method permitted to give a complete picture of the damage and to esteem the different degradation index. This preliminary report is encouraging and may be extended to the main monuments of historical centers with the aim to plan the correct restoration projects, and give the priority of interventions.

Fitzner B., Heinrichs K. & La Bouchardiere D. 2002. Damage index for stone monuments. In: Galan, E. &Zezza, F. (ed.): Protection and Conservation of the Cultural Heritage of the Mediterranean Cities, Proceedings of the 5th International Symposium on the Conservation of Monuments in the Mediterranean Basin, Sevilla, Spain. 315-326, Swets&Zeitlinger, Lisse, The Netherlands.

LA-ICP-MS analyses on clinopyroxenes for the provenance determination of the Pompeii cooking ware

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Keywords: LA-ICP-MS, ceramics, provenance, clinopyroxenes.

The cooking ware, is the most attested ceramic production found at Pompeii during the I.E. (= Impianto Elettrico) excavations in 1980-1981. The great variability of ceramic shapes and fabrics, have suggested a wide diffusion in Roman town, of products, not only of local provenance.

The analysed wares are dated from 1st century BC to 1st century AD and belong to different typologies of pottery: the pots with "*orlo a tesa*" and jar with "*orlo a mandorla*". The pots with "*orlo a tesa*" were distributed widely from the 1st century BC around the western Mediterranean basin, along the coasts of *Hispania Terraconensis*, Gaul, Tuscany and Carthage.

The jars with *"orlo a mandorla"*, were produced between the 2nd century BC and the Augustan age in the western Mediterranean and exported principally from the Tyrrhenian coast.

The following archaeometric study, aimed to identify the production area of some ceramic samples and to verify the archeological assumptions.

Petrographic and mineralogical analysis distinguished two groups characterized by a volcanic temper. Plagioclase, sanidine, clinopyroxene, amphibole, biotite crystals and a great amount of volcanic rock fragments were observed in both sets of ceramics. The differences are related to higher content of sialic minerals - i.e. plagioclase, sanidine and quartz- in a group and on the contrary of mafic minerals (in particular of clinopyroxenes) in the other one.

This mineralogical assemblage is common to several scoriaceous pyroclastic-flow and pyroclastic-fall deposits of the Campanian volcanoes, Vesuvius, Campi Flegrei and Roccamonfina as well as Roman province including the Vulsini, Vico and Monti Sabatini volcanic districts (Peccerillo & Turco, 2004; Marra & D'Ambrosio, 2013). It excludes the Alban Hills, whose products lack plagioclase and K-feldspar phenocrysts (Gaeta *et al*., 2006).

In order to characterize in a quantitative way the mineralogical assemblage, LA-ICP-MS coupled with SEM/EDS analysis were performed on clinopyroxene crystals, occurring in the volcanic rock fragments of the ceramics and in the juvenile products of Latium and Campania volcanic districts.

The statistical approach distinguished the two investigate magmatic Provinces, corroborating the Vesuvian production for a group and the Latium provenance for the other one.

Gaeta M., Freda C., Christensen J. N., Dallai L., Marra F., Karner D. B. & Scarlato P. 2006. Time-dependent geochemistry of clinopyroxene from the Alban Hills (central Italy): clues to the source and evolution of ultrapotassic magmas. Lithos, 86, 330-46.

Marra F. & D'Ambrosio E. 2013. Trace Element Classification Diagrams of Pyroclastic Rocks from the Volcanic Districts of Central Italy: the Case Study of the Ancient Roman Ships of Pisa. Archaeometry, 55, 993-1019.

Peccerillo A. & Turco E. 2004. Petrological and geochemical variations of Plio-Quaternary volcanism in the Tyrrhenian Sea area: regional distribution of magma types, petrogenesis and geodynamic implications. Periodico di mineralogia, 73, 231-251.

Implemented, *in situ*, water absorption test by contact sponge

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Keywords: Ornamental stones, contact sponge method, non-invasive *in situ* analysis.

Water absorption in heritage materials is a key parameter for which the UNI Normal normative deserved a specific protocol. In fact, difficulties arise in operating on test samples or on materials with porosity varied for decay, compared with fresh or reference rock or mortar.

The UNI Normal procedure requires to use a sponge with known density, soaked in water, weighed, placed on the material for 1 minute (UNI 11432, 2011; Pardini & Tiano, 2004), then weighed again.

While carrying on this test we noticed that fluctuation in the values of the environmental parameters during the single test were negligible, but not the pressure applied to the surface, that induced the release of different water amounts towards the material.

For this reason we designed a metal piece of the same diameter of the plate carrying the sponge to be screwed at the tip of a pocket penetrometer. With this instrument the sponge was put in contact with the surface for 1 minute applying two different loads, at first pushed with 0.3 kg/cm^2 in order to press the sponge, but not its holder, against the surface. A second load (1.1 kg/cm^2) was chosen to apply a relevant pressure, still avoiding deviating the load to the sponge holder.

We applied both the current and the implemented method to determine the water absorption by contact sponge on 5 fresh rock types (Fine - and Coarse grained Pietra di Vicenza, Rosso Verona, Breccia Aurora, Arenaria Macigno).

The results show that the current methodology imply manual skill and experience to produce a coherent set of data; the variable involved are in fact not only the imposed pressure but also the compression mechanics. The adoption of pressure parameterization allowed reproducible measurements. Moreover the use of a thicker sponge enables to apply the method even on rougher surfaces, as the device holding the sponge avoids the contact with the tested object.

Finally, the implemented measurements gave the possibility of a direct comparison with the capillary water absorption method.

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UNI 11432. 2011. Beni culturali Materiali lapidei naturali ed artificiali - Misura della capacita di assorbimento di acqua mediante spugna di contatto. Pagg 6.

New insights on production technologies of Late-Antique glass mosaic tesserae with calcium phosphate as opacifier

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Keywords: Glass mosaic, opacifier, calcium phosphate.

Glass mosaics are heterogeneous materials, composed of glassy matrix and crystalline phases, and produced by complex pyrotechnological processes from selected raw materials (generally minerals) with various functions (formers, fluxes, stabilisers, colourants, decolourants and opacifiers). In particular, this study focuses on opacifiers composed of calcium phosphate and identified into some Late-Antique glass tesserae, green or blue in colour, from Padova (Italy) (Silvestri et al., 2012) and Tyana (Turkey) (Serra et al., 2009). It is generally accepted that calcium phosphate is a primary opacifier, probably obtained by the intentional addition of bone powder to a transparent glass (Verità, 2000), but no specific crystallographic-mineralogical studies have been carried out on this opacifier until now. In tesserae from both sites, analyses, performed by scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD), show that calcium phosphate grains, probably hydroxyapatite, have a reaction rim, enriched in sodium, which comes from the surrounding glass and replaces the calcium of the opacifier. The above replacement process between opacifier and glassy matrix is also confirmed by the presence of newly formed crystals composed of calcium silicate (wollastonite), found in the proximity of calcium phosphate grains (Silvestri et al., 2012). The same micro-texture was found in all the tesserae, suggesting similar production technologies in both sites and that production technologies may be highly standardised. Investigations on the calcium phosphate, on its reaction rim and on interactions with surrounding soda-lime-silica glass are in progress by means of X-ray diffraction (XRD), electron backscattered diffraction (EBSD), electron microprobe (EMPA), and micro-Raman spectroscopy in order to clarify the nature of these inclusions and to make inferences on the production technologies of such kind of glass tesserae.

Serra C.L., Silvestri A. & Molin G. 2009. Archaeometric characterization, Appendix of Lachin M.T. “Vitreous Mosaic from Tyana (Cappadocia)”. In: Lafli E. Ed., Late Antique/Early Byzantine Glass in the Eastern Mediterranean, Colloquia Anatolica Et Aegaea –Acta Congressus Communis Omnium Gentium Smyrnae II, Izmir, Turkey, 175-183.
Silvestri A., Tonietto S., Molin G. & Guerriero P. 2012. The palaeo-Christian glass mosaic of St. Prosdocimus (Padova, Italy): archaeometric characterisation of tesserae with antimony- or phosphorous-based opacifiers. J. Archaeol. Sci., 39, 2177-2190.
Verità M. 2000. Tecniche di fabbricazione dei materiali musivi vitrei: indagini chimiche e mineralogiche. In: Borsook, E., Gioffredi-Superbi, F., Pagliarulo, G. Eds., Medieval mosaics: light, color, materials, 47-64, Silvana Editoriale, Milano.

Characterization of pigments and microclimate monitoring for the preservation of a rare medieval parchment

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Keywords: parchment, spectrophotometry, pigments.

A rare medieval parchment called Exultet I preserved in the Diocesan museum of Metropolitan Capitolo of Bari has been studied. The Exultet was sung after a procession with the Paschal Candle before the beginning of the Liturgy of the Word in the XI century and it is certainly one of the highest literary and artistic expressions that Bari produced. Eight sheets with text, music lines and numerous beautiful miniatures painted upside-down respect to the liturgical text compose the parchment roll. The opening of the theca that preserves the unwrapped roll gave us the opportunity to perform diagnostic measurement on the pigments of the illuminated areas and to locate a wireless weather station for monitoring the microclimate. For these analyses a mobile laboratory has been set up in the museum. The techniques used for a non-invasive and in situ analysis of miniature paintings has been microscopic observation with digital microscope, UV-VIS-NiR spectrophotometry in reflectance mode with optic fibres (FORS), X-Ray fluorescence spectrometry (XRF) and finally µ-Rman spectroscopy. The use of several techniques is able to give us all information without causing any stress to the parchment especially if the measures are fast, as in our case (Aceto et al., 2012). The pigments have been identified mainly with FORS with comparison with standards and they are: red ochre and red lead used as red, lapis lazuli and azurite as blue, green earth and copper resinate as green, yellow ochre and orpiment as yellow. In the most important miniatures in some areas of the background, several traces of a residual gold leaf have been identified by XRF. The presence of rare and precious pigments as gold leaf and lapis lazuli underline the importance of the parchment. The preparation of the figures made by using a lead stylus has been also identified. The presence on all the roll of humpbacks formed in the last years well fit with the data collected that shows a continuity of condition between the showcase and the museum room. These means that the presence of visitors leads to changes in temperature, humidity and CO_2, resulting much higher than those suggested for parchments. Finally the hypothesis of a repainting, formulated on the basis of the conservation status of the colours of the illuminated areas and from the comparison of similar hues, has been confirmed by the characterization of the colour palette. In some points the analysis returned the blue pigment as azurite and the red ones as minium, these results are in contrast with those of blue and red, respectively used, in all other illustrations of the roll were lapis lazuli and red ochre are plentiful.

Aceto M., Agostino A., Fenoglio G., Gulmini M., Bianco V., Pellizzi E. 2012. Non invasive analysis of miniature paintings: Proposal for an analytical protocol. Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc., 91, 352-359.

Ancient extractive metallurgy of copper in the Aosta Valley (Western Alps, Italy): new evidence from pre-Roman slags from the Misérègne site

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Keywords: slag, ancient copper extractive metallurgy, Aosta Valley.

Many metallurgical sites are scattered across the Aosta Valley territory (e.g. Tumiati *et al.*, 2005). The age of some of them is unknown and often the slag heaps are the sole vestiges of metallurgical activities. Such is the case of Miséregne (Fénis), where the village is built on an enormous slag deposit.

We performed radiocarbon dating on charcoal fragments included in the slags and obtained ages comprised between the 4th and 1st century BC. So far, these are the most ancient ages for early mining activity in the Aosta Valley, probably carried out by the local population of the Salassi.

We studied the slags following a petrologic approach. The occurrence of matte inclusions in the slags indicates that the processed raw minerals were Cu-Fe sulfides. Relying on morphologic and micro-textural features, we classified the slags into three categories, i.e., coarse, massive and flat, as suggested by Addis (2013). In all the slag classes the most abundant phase is olivine. Other common phases are spinel group minerals and sulfides, mainly pyrrhotite and bornite solid solutions. The olivine crystal shapes allowed us to qualitatively estimate the degree of undercooling (ΔT) and the rate of cooling of the slags: the coarse slags show a high ΔT; the massive slags seem to record an initial, long-lasting low-ΔT stage, followed by an increase in the cooling rate; the flat slags underwent a brief low-ΔT stage, followed by a sudden marked increase in ΔT. Combining this information with the slag bulk chemistry, the sulfide compositions, the slag morphology and the presence of inclusions of charcoal, quartz and other slag fragments, we hypothesize that the massive and coarse slags come from the lower and, respectively, the upper portion of the same slag contained in the furnace, while the flat ones were tapped slags. Minimum furnace working temperatures estimated by means of olivine-spinel geothermometry are in the ranges 932-964°C, 968-1037°C, 1202-1239°C for the coarse, massive and flat slags, respectively. According to the above observations, the flat slags should record conditions that are the closest to the actual furnace working temperature.

Addis A. 2013. Late Bronze Age metallurgy in the Italian Eastern Alps: copper smelting slags and mine exploitation. Tesi di dottorato, Dipartimento di Geoscienze, Università degli Studi di Padova.

Tumiati S., Casartelli P., Mambretti A., Martin S. 2005. The ancient mine of Servette (Saint-Marcel, Val d'Aosta, Western Italian Alps): a mineralogical, metallurgical and charcoal analysis of furnace slags, Archaeometry*,* 47, 317-340.

Looking for the Garamantian emeralds. An archaeometric approach to reconstruct the trading of amazonite stone beads in the ancient Sahara

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Keywords: Amazonite stone beads, Microprobe, Garamantes.

We discuss the results of the archaeometric study carried out on green-coloured stone beads found during the excavation of an historical site at Fewet (SW Libya, central Sahara). Therein, a compound, dated between the 2nd century BC and the 1st century AD and occupied by the Garamantes of the Fezzan, was one of the villages located along one of the most important trans-Saharan caravan route (Mori, 2013). In the current literature, Saharan green stone beads dating to historical times are generally identified with the term *émeraude garamantique*. Previous investigations in the region have generally attributed the green stone beads and pendants found in Garamantian archaeological contexts to amazonite and have identified the mining site with the pegmatite dike at Eghei Zuma (northern Tibesti, southern Libya), accepting the hypothesis initially proposed by T. Monod (1974). To confirm this observation we submit several samples of green stone beads from Fewet and several comparison samples, including samples of raw material from Eghei Zuma, to microprobe analyses. Geochemical results highlight that our green-coloured stone beads consist of different lithotypes (serpentinite and amazonite) and the source of this amazonite could not be the pegmatite outcrop at Eghei Zuma. Finally, we try to identify a list of potential sources of amazonite in the Sahara and surrounding regions and discuss the archaeological implication of our results, which concerns the main direction of ancient trade routes for elite goods and the movement of amazonite beads in the Sahara in Garamantian times (Zerboni and Vignola, 2013).

Monod T. 1974. Le mythe de «l'Émeraude des Garamantes». Antiquités africaines, 8, 51-66.
Mori L. 2013. Life and death of a rural village in Garamantian Times. Archaeological investigations in the Fewet oasis (Libyan Sahara). Arid Zone Archaeology Monographs, 6, Edizioni all'Insegna del Giglio, Firenze.
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SESSIONE S12

Looking inside the planet Earth: Experimental and Computational Methods in Mineralogy and Geochemistry

CONVENORS

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A comparison between *Ab Initio* calculated and measured vibrational frequencies of the triclinic Albite

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Keywords: Ab initio calculation, Raman Spectroscopy, albite.

Feldspar-group minerals are among the most common rock-forming minerals of planetary crusts. On Earth, they occur in igneous, metamorphic and sedimentary rocks. On the Moon, plagioclase is the most abundant mineral and feldspars are one of the main minerals in Martian meteorites. Feldspars show subtle variations in crystal structure that allow petrologists to gain information about the chemical and physical conditions prevailing during rock formation. The whole spectrum of their possible structural states can be found in rocks with different cooling histories, providing an opportunity to study the way a structure responds to a slowly changing geological environment.

Albite, $NaAlSi_3O_8$, is the sodic end-member of high temperature plagioclase and alkali feldspar solid solutions. The analysis of its vibrational frequencies and their assignments to the fundamental normal modes are the aim of this study.

The Raman spectrum of albite has been calculated by using the CRYSTAL14 program (Dovesi et al., 2014). Calculations were made at the hybrid Hartree-Fock/Density Functional level (HF/DFT): the WC1LYP Hamiltonian, which provides excellent agreement between calculated and experimentally measured vibrational frequencies (see e.g. Prencipe et al., 2012), was employed.

The comparison between the frequencies measured by Raman spectroscopy on an ordered natural albite, var. Cleavelandite from Minas Gerais (Brasil), with those calculated by HF/DFT is discussed. All the expected 39 A_g modes have been identified in the Raman spectra and their frequencies well correspond to the calculated ones (the average absolute discrepancy ($<|\Delta|>$) is ~ 3 cm^{-1}; the maximum discrepancy ($|\Delta|max$) is ~ 10 cm^{-1}). The good quality of the WC1LYP results allowed for reliable assignments to specific patterns of atomic vibrational motion (normal modes).

Dovesi R., Saunders V. R., Roetti C., Orlando R., Zicovich-Wilson C. M., Pascale F., Civalleri B., Doll K., Harrison N. M., Bush I. J., D'Arco P., Llunell M., Causà M. & Noël Y. 2014. CRYSTAL14 User's Manual. University of Torino.

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Effect of Transition Metal Ions (*TMI*) on the compressibility of orthorhombic perovskites

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Keywords: Orthorhombic perovskite, high-pressure, transition metal ions.

Variations in the chemical nature of *A* and *B* cations, as well as changes in *P* and *T*, are accommodated in the framework structure of perovskite (general formula $^{[XII]}A^{[VI]}BO_3$) by octahedral tilting and more distorted polyhedra. The structural answer to these internal and external stresses is a decreasing of the symmetry (Mitchell, 2002). From the cubic archetype, perovskites often become orthorhombic. This class of perovskites received considerable attention in Earth Sciences since it was discovered that the major minerals of the upper mantle (i.e. olivine, pyroxene, and garnet) transform into the denser $(Mg,Fe)SiO_3$ perovskite-structured mineral, at *P-T* conditions of the upper/lower mantle interface (Navrotsky & Weidner, 1989). Considered as the dominant component of the lower mantle, this orthorhombic compound remarked on the importance to understand the relationship between external condition, structural properties, and chemistry of perovskite phases. For these reasons, perovskites are the subject of many studies devoted to establish their *HP* behaviour. Part of these studies (Andrault & Poirier, 1991; Thomas, 1998; Zhao et al., 2004) attempt to predict the evolution of these compounds under *HP* regime by means of semiempirical and theoretical models. As a common generalization, the structural evolution of orthorhombic perovskites with *P* can be rationalized in terms of relative compressibilities of the two polyhedra (AO_{12} and BO_6): when the AO_{12} site is more compressible than the BO_6 octahedron, the volume reduction will lead to an increasing of the octahedral tilting; conversely, when the AO_{12} site is less compressible than the BO_6 octahedron, the structure will evolve by decreasing the octahedral tilting raising its symmetry towards the cubic archetype. The model proposed by Zhao et al. (2004) predicts that the polyhedral compressibility ratio can be devised as the ratio of the estimated variation of bond valence in the *A* and *B* polyhedral sites due to the change of the average metal-oxygen bond distance. In this contribution the structural evolution of perovskites upon pressure will be modeled through a new polyhedral bond valence approach. The obtained results will be compared with those derived from previous models, and it will be shown as transition metal ions at the B site act as an incompressibility factor.

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Ultrafast growth of quasicrystals in shock-produced melts and its implications for the early solar nebula

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Keywords: solar system, Earths core, quasicrystals.

The first natural quasicrystal (Bindi et al., 2009, 2011, 2012), icosahedrite ($Al_{63}Cu_{24}Fe_{13}$), was discovered in the Khatyrka meteorite (Macpherson et al., 2013), a CV3 carbonaceous chondrite (CV3 CC) that formed 4.5 billion years ago. The initial reports, based on a museum sample, revealed icosahedrite in a complex assemblage of unusual metallic crystal phases [khatyrkite ($CuAl_2$), cupalite (CuAl), and β-phase (AlCuFe)], and conventional chondritic minerals [diopside, forsterite, spinel ($MgAl_2O_4$), nepheline]. Understanding how this mineral assemblage formed has been a deep mystery. An expedition to the Koryak Mountains in far eastern Russia in 2011 recovered more samples (Steinhardt and Bindi, 2012). Here we present results from those samples that distinguish Khatyrka from previous CV3 CCs and strongly indicate a resolution of the mystery. Two new minerals are identified ($Fe_{3-x}Si_xO_4$ spinelloid with x = 0.4, and an AlNiFe phase); these are associated with Al-Cu-bearing taenite, Al- and Cu-bearing iron sulfide and an eutectic texture of khatyrkite and nearly pure Al. The presence of ahrensite (Fe-rich ringwoodite), spinelloid and stishovite show that the meteorite underwent the strongest shock ever observed in a CV3 CC (local pressures 5-10 GPa). Ahrensite-silica lamellar eutectic textures, the metal eutectic pattern, and the range of oxidation states all point to shock melts locally produced at about 1200 °C, followed by very rapid cooling and solidification down to temperatures.

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The energy and crystal morphology of diamond inclusions to explain their genesis

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Keywords: diamond, surface, olivine.

Inclusions in diamond (Dis) are among the deepest materials originating from Earth's interior reaching the planet's surface. Diamonds are billions of years old and remain unaltered over time, preserving the pristine conditions of Earth. Therefore, their study plays a key role in understanding and interpreting the geodynamics, geophysics, petrology, geochemistry, and mineralogy of Earth's mantle from the lithosphere to the lowermost part.

Diamond inclusions (DIs) are divided into three groups: protogenetic, syngenetic, and epigenetic (Meyer, 1987). DIs are classified as protogenetic when they form before encapsulation by the host diamond, whereas they are considered syngenetic when the inclusion and its host diamond form at the same time and by the same genetic processes. Both groups play a key role in the study of diamond formation processes, contrary to epigenetic phases, which are secondary minerals, usually associated with crustal processes, and are atypical with respect to the primary minerals in mantle xenoliths.

Such a distinction is important, because, in the case of syngenesis, any geological information extracted from the inclusion (e.g., pressure and temperature of formation, geochemical environment, age) would also unequivocally apply to its host diamond. On the other hand, a protogenetic inclusion would record conditions that existed before its encapsulation.

Distinguishing between syngenesis and protogenesis is as crucial as it is extremely difficult and controversial. The most common observation used to deduce syngenesis is the imposition of the host diamond morphology on the DI (Harris, 1968). Another significant contribution to the syngenesis-versus-protogenesis debate derives from the observation that some Dis occur in a specific orientational relationship with respect to diamond, which can be considered as evidence in favor of epitaxial growth of the DI above the diamond or vice versa and, hence, of syngenesis (Meyer, 1987).

Here, we discuss the peculiar crystal morphology of olivine included in diamond (DI). First, we show that the observed cuboctahedral shape of olivine in diamond is actually a combination of an orthorhombic bipyramid (i.e., {495}) and pinacoids. This implies that the shape of olivine can be equivalent to that of diamond, even if the forms making up the two crystals are completely different. Second, we demonstrate that the morphology of the DI cannot be considered as evidence of syngenesis. In particular, if the crystal morphology is modified but the DI does not show a preferential orientation with respect to the diamond, the bulk of the DI is protogenetic, whereas its shape is syngenetic.

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Reconstruction of rocks petrophysical properties as input data for analitical and numerical modeling

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Keywords: Thermo-physical properties, closed deep wells, numerical modeling, porosity-permeability profiles.

The worldwide increasing energy demand has favored several studies devoted to evaluate the underground energy potential also in areas previously discharged or neglected. Nowadays technologies such as geological storage of gas (CO_2 and/or CH_4), renewable energies, geothermal energy (from low to high enthalpy) and nuclear waste are considered strategic in terms of low carbon energy development.

For a safe and worthwhile use of these technologies, an accurate characterization of the substratum in terms of geology, hydrogeology, geochemistry and geomechanics is a pre-requisite. This includes knowledge of essential parameters such as texture, porosity, permeability, mineralogy and thermo-physical properties of rocks necessary to characterize the reservoir and consequently to model heat and fluid transport.

These parameters are strictly related to the tectonic history and the evolution of a specific area and should be measured directly on rock samples. Unfortunately, during the pre-feasibility study stage, available direct measures of target reservoirs are limited, moreover the reopening of closed deep wells, often, may be very expensive.

This work propose a methodology for the reconstruction of thermo-physical properties of rock formations, combining well-log information, measured temperatures and petro-mineralogical analyses.

As case study we used a deep structure (about 1900 m b.s.l.), located in the medium Tyrrhenian sea (i.e. Northern Latium off-shore), already identified as potential target for geological storage of fluids (Procesi et al., 2013). Local stratigraphy is constrained by well-log data of a deep well (Matilde 1, more than 3000 m deep) drilled in the 1975 for hydrocarbon exploration and closed soon after because unproductive.

The presented approach assumes that thermal properties of rock minerals contribute to total capacity and conductivity of the rock proportionally to their abundance. On the basis of thermal properties of rocks, relationship among thermal capacity, conductivity, porosity and permeability were established so that porosity was the only independent variable. Finally, with a trial and error procedure the vertical profile of porosity and permeability was reconstructed by numerical modeling of heat transport using the measured temperatures and the Italian heat flow maps as boundary conditions.

This method can represent an useful tool for reservoir engineering and geochemical modelers to estimate, in a first step, thermo-physical input data for analytical and numerical modeling without the reopening of a well.

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High pressure behavior of natural fluorapatite and carbonate-fluorapatite

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Keywords: apatite, single-crystal XRD, bulk modulus.

Knowledge of the mineral-physics of apatite helps to assess the geological implications of its actual stability field, but also its mechanical properties - useful for its technological applications. Changes in its chemical and physical properties are observed when carbonate is incorporated into the apatite structure. The entry of CO_3 can occur by substitution of both channel anion (type A) and phosphate ion (type B); the first process causes an increase in *a* and a decrease in *c,* vice versa the second one a decrease in *a* and an increase in *c*.

Several *in situ* HP experiments have been already carried out on synthetic samples of fluor-, hydroxyl-, and chlor-apatite. A study of natural fluorapatite was performed by Matsukage et al. (2004), who found a K_T lower than previous works (BM2: K_T = 91.6(1.0) GPa *vs* 97.9(1.9) GPa in Brunet et al., 1999 and 97.8(1.0) GPa in Comodi et al., 2001). Recently Liu et al. (2011) have studied the effects of carbonate substitution on the compressibility of hydroxylapatite: the presence of carbonate (type-A and -B) lowers the value of K_T. However, it is difficult to assess if the softening is due to type-A or -B or both.

We have performed a X-ray study on natural single crystals of both fluorapatite [FOW; a=9.3549(9)Å, c=6.874(1)Å, V=521.0(1)Å^3] and type-B carbonate fluorapatite [FRA; a=9.330(1)Å, c=6.898(1)Å, V=520.0(2)Å^3] The two crystals were mounted concurrently in a ETH-type DAC, with a single crystal of quartz as internal P calibrant and a 16:3:1 mixture of methanol:ethanol:water as P-transmitting medium. We used SINGLE program (Angel & Finger, 2011) on a Siemens P4 four-circle diffractometer and EosFit7c (Angel et al., 2014) to collect and fit the data, respectively.

Our data [28 P points up to 7.05(4)GPa; V values fitted with a BM3-EoS] confirm that type-B CO_3-substitution decreases the bulk modulus from K_T=89.4(1.3)GPa [K_T'=5.1(4)] to K_T=86.3(1.2)GPa [K_T'=5.0(4)]. This preliminary result well agrees with those ones previously found for fluorapatite.

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Water effect on clinopyroxene compositions: insights from high pressure experiments on hawaiitic magmas

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Keywords: Phase equilibria, clinopyroxene, geohygrometer.

Water is a critical component to magma genesis and evolution: its content affects liquidus temperatures, crystal fractionation trends, melt rheology and, in turn, the dynamics of magma ascent and eruption. Hence, it is of broad interest to determine the initial concentration of water in magmas and its variation during magma ascent and differentiation. Analysis of melt inclusions and experimental studies allowed to define the qualitative effects of water on magmatic processes; however, approaches for the quantitative estimation of water content in magmas are still scarce. Clinopyroxene (Cpx) is among the earliest and most abundant phases in basaltic rocks, being potentially the most complete tracer of magmatic crystallization. In addition, since the Cpx abundances and compositions are controlled by magma water solubility, this phase has been used as empirical hygrometer for magmas of Mt. Etna (Armienti et al., 2011). Available experimental data on hydrous liquids representative of Mt. Etna volcanics, used to calibrate the empirical method, cover a wide range of pressure ($0.2 \leq P \leq 0.8$ GPa). However, very few runs were performed at high pressure ($P \geq 0.5$ GPa) up to now. Here we report new HP experimental data on Etnean hawaiites, relevant for the implementation of the Cpx hygrometer. Experiments were carried out in a piston-cylinder apparatus at a pressure of 0.8 GPa in the presence of 2-10 wt% of H_2O, in a range of temperature from 1050 °C to 1175 °C. As expected, the results indicate that the increase of water content (up to 6 wt%) decreases the liquidus temperature of about 100 °C. Cpx and plagioclase are the liquidus phases at all hydrate conditions, followed by oxide and olivine for water contents lower than 4 wt %. Higher H_2O concentrations strongly reduce the stability field of oxides, which disappear at $H_2O > 4$ wt%. In terms of Cpx end-members, it appears that, at a given temperature (e.g. 1125 °C), the main effect of an increasing water content is to increase the DiHd, EnFs and Jd components, coupled with a decrease of Ca-Ts end-member. These results confirm that Cpx composition is an effective tool to estimate H_2O contents in mafic magmas.

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Elastic Properties of Minerals from Ab initio Simulations: The case of Silicate Garnets

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Keywords: Elastic constants, ab initio simulations, silicate garnets.

Standard ab initio quantum-chemical methods based on the Density Functional Theory (DFT) represent a powerful tool for the accurate determination of a variety of properties of materials, such as structural, electronic, spectroscopic, optical, elastic, magnetic, etc. (Dronskowski, 2005). The increasing efficiency of the algorithms and the growing parallel computing resources are rapidly widening the range of applicability of such schemes that can now be routinely used for studying minerals of geophysical interest. We have recently developed and implemented in the CRYSTAL14 public program (Dovesi et al., 2014) a fully-automated, general-purpose, computationally-efficient algorithm for the calculation of the elastic tensor of crystals (Erba et al. 2014b). Related quantities such as bulk, shear and Young moduli, Poisson's ratio and directional seismic wave velocities can now be computed. The effect of pressure on elastic response properties can be computed as well (Erba et al. 2014a). A family of silicate garnets (namely, pyrope, almandine, spessartine, uvarovite, grossular and andradite) has been considered which are major rock-forming minerals of the Earth's mantle. They are cubic crystals of space group Ia-3d, with 80 atoms in the primitive cell; their size represents a challenge for the ab initio description of their elastic properties at geophysical conditions. Calculations performed with the popular hybrid B3LYP functional provide an excellent description of the elastic properties of such garnets at ambient conditions as well as at high pressure, up to 60 GPa (Erba et al. 2014a; Erba et al. 2014b). The evolution of the elastic anisotropy under increasing pressure has been evaluated. Recently developed techniques for the study of solid solutions have been applied to the investigation of compositional effects on the bulk modulus of the grandite (grossular-andradite) solid solution series: while heterogeneous experiments were suggesting a strong deviation from linearity, our simulations reveal an almost linear behavior thus contributing to define a clear picture according to which the bulk modulus-composition trend is linear for all silicate garnets solid solutions.

Dovesi R., Orlando R., Erba A., Zicovich-Wilson C.M., Civalleri B., Casassa S., Maschio L., Ferrabone M., De La Pierre M., D'Arco Ph., Noel Y., Causà M., Rérat M. & Kirtman B. 2014. CRYSTAL14: A program for the *ab initio* investigation of crystalline solids. Int. J. Quantum Chem. DOI: 10.1002/qua.24658.

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Modeling of Ca, Si and Al structural environments in glasses of the CAS system

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Keywords: CAS glasses, structure, XANES modeling.

Alkaline-earth aluminosilicate glasses are an important type of materials, both for the many technical application in materials science and also because glasses of this composition can be used as analogues of basaltic melts. The understanding of the structural behavior of the cations in the glasses can provide more detailed data on the relationship between chemistry, structure and physical properties. In Earth Sciences, these information are the key for the comprehension of igneous processes as well as for the modeling of physical properties for these industrially-relevant materials.

In this work, X-ray absorption near-edge structure spectroscopy (XANES) has been applied to determine the structure of Ca, Al and Si in glasses in the CAS system (Wu et al., 1999). Experimental XANES spectra have been collected for a series of samples of peralkaline composition along the joints SiO_2-$Ca_3Al_2O_6$ and SiO_2-$CaAl_2O_4$ with variable contents of SiO_2, CaO and Al_2O_3. First, the glass spectra have been compared with those obtained on minerals with well-known structure and chosen to represent a variety of coordination numbers and cation polyehedral geometries and distortions. The geometrical information obtained by this comparison have been used to build model structures surrounding each cation to approximate the glass structure. Using the clusters as starting tridimensional networks, theoretical XANES modelling has been carried out by means of the MXAN code which makes use of Full Multiple Scattering calculations and, by fitting the experimental spectra, allows to iteratively modifying the cluster structure (bond distances, coordination numbers, bond angles).

The results obtained are very promising to be used to:

a) unravel the geometrical environment around each cation, even with low atomic number,

b) interpret even subtle modifications of the spectra observed in the experimental spectra with the chemistry,

c) acquire structural information also beyond the first coordination shell.

Cancrinite-group minerals at non-ambient conditions: a model of the thermo-elastic and structure behavior

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Keywords: cancrinite, high pressure, comparative elastic behavior.

The cancrinite-group of minerals comprises more than ten species sharing the [CAN]-topology of the tetrahedral framework. Their microporous structure has wide 12-ring channels, bound by columns of cages (*can* units). Besides the aluminosilicate composition of the framework (with the only exception of tiptopite, having instead Be and P), the minerals of the cancrinite group show a remarkable chemical variability concerning the extraframework population. Two subgroups can be identified according to the content of the *can* units: the first with Na-H_2O (cancrinite and vishnevite) and the second with Ca-Cl chains (balliranoite and davyne). The channels are stuffed by cations, anions and molecules. In Nature, cancrinite-group minerals occur in the late/hydrothermal stages of alkaline (SiO_2)-undersaturated magmatism and in related effusive or contact rocks. On the technological front, cancrinite-group compounds have been proposed as stable storage form for alkaline waste solutions, of which are common precipitation products.

We aimed to model the thermo-elastic behavior and the mechanisms of (P,T)-induced structure evolution of cancrinite-group minerals, focusing to the role played by the extraframework population. The study was restricted to the following (CO_3)-rich and (SO_4)-rich end-members: cancrinite $\{[(Na,Ca)_6(CO_3)_{1.2-1.7}][Na_2(H_2O)_2][Al_6Si_6O_{24}]\}$, vishnevite $\{[(Na,Ca,K)_6(SO_4)][Na_2(H_2O)_2][Al_6Si_6O_{24}]\}$, balliranoite $\{[(Na,Ca)_6(CO_3)_{1.2-1.7}][Ca_2Cl_2][Al_6Si_6O_{24}]\}$ and davyne $\{[(Na,Ca,K)_6((SO_4),Cl)][Ca_2Cl_2][Al_6Si_6O_{24}]\}$. Their high-$P$ and low-T ($T < 293$ K) behavior was investigated by *in situ* single crystal X-ray diffraction, using diamond-anvil cells and (N_2)-cryo-devices, respectively.

Though sharing a similar volume compressibility [i.e., ~ 0.021 GPa^{-1}, K_{V0} ~ 47 GPa] and thermal expansivity [i.e., ~ $4.0\text{-}4.5\cdot10^{-5}$ K^{-1}], these minerals show a different anisotropic pattern, more pronounced in cancrinite and vishnevite. This behavior is governed by different deformation mechanisms, which reflect the different coordination environments of the cage population between the minerals of the two subgroups. In vishnevite, a P-induced re-organization of the channel population took place at P >= 3.5 GPa, suggesting that also the channel-constituents (and not only the cage one) can play an active role on the structure response at non-ambient conditions.

In addition, the high-T behavior of cancrinite was studied up to 823 K, by *in situ* single-crystal X-ray diffraction. At 748 K, a slow dehydration process takes place towards a (quasi)-anhydrous structure.

These are the first experimental findings aimed to provide a comparative thermo-elastic analysis of the CAN-group compounds, expanding the knowledge about the P/T-behavior of isotypic materials with open-framework structures.

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Ab-initio investigation of the thermodynamic stability of the magnesio-wüstite solid solution under Earth's lower mantle conditions

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Keywords: solid solution, Mg-wustite, quantum mechanical.

Mg-wüstite, (Mg,Fe)O, is the second most abundant phase in the Earth's lower mantle. A profound understanding of the thermodynamic stability of this phase under deep mantle conditions is thus crucial for developing accurate models of the Earth's interior and the importance of drawing a complete picture of the stability fields of the Mg-wustite solid solution, especially at high pressure/temperature regimes, is straightforward.

In the light of the above considerations, the present work has been undertaken where the thermo-chemical properties of the (Mg,Fe)O solid solution, over a wide PT range, have been modelled using mixing Helmholtz energy, $\Delta F(T,x)\ mixing$. Calculations have been performed by means of cluster expansion, quantum mechanical and semi-empirical techniques.

Both high-spin (HS) and low-spin (LS) configurations of iron have been explored as a function of composition (x: molar fraction of FeO) over the MgO-FeO binary. Only the HS-model provides physically sound results at room pressure, yielding a correct trend of cell edge versus composition, whereas LS's issues are at variance with observations. Mixing Helmholtz energy has been parametrized by the following relationship $\Delta F(T,x)\ mixing = x\times y\times[(U(T)_0 + U(T)_1 \times (x-y) + U(T)_2 \pm (x-y)^2$, where $y = 1-x$ and $U_j(T)$ are polynomials in T of the third order. $\Delta F(T,x)\ mixing$ exhibits a quasi-symmetric behaviour and allows one to build the T-X phase relations diagram over the MgO-FeO join. On the basis of the HS-model including vibrational contribution to Helmholtz energy, a solid solution's critical temperature of some 950 K has been predicted, remarkably lower than olivine's and Mg-Fe-garnet's. All this points to a more difficult Mg-Fe mixing in periclase-like structure than olivine and garnet, which, in turn, provide more degrees of freedom for atomic relaxation. From $\Delta F(T,x)\ mixing$, the values of $\Delta H(T,x)\ mixing$ and $\Delta S(T,x)\ mixing$ have been derived, both exhibiting so modest a dependence on T as to be negligible. $\Delta H(T,x)\ mixing$ and $\Delta S(T,x)\ mixing$ exhibit quasi-regularity; either has been parametrized as $W\times x\times(1-x)$, obtaining $W_{H,Mg-Fe}$ and $W_{S,Mg-Fe}$ of 17.7 kJ/mol and 26.8 J/mol/K, respectively. $\Delta S(T,x)\ excess$ has been estimated to be smaller than 0.5 J/mol/K in absolute Moreover, it has been observed that the HS-configuration is stable and promote Mg-Fe solid solution up to ≫15 GPa better than LS does. At higher pressures, the LS-model becomes favourite and increasingly stabilizes (Mg,Fe)O upon rising P, whereas HS predicts ex-solving into the end members above ≫40 GPa.

New iron-carbonates and iron-oxides at core/mantle boundary conditions

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Keywords: crystal structure, lowermost mantle, carbonate.

The recent improvements at synchrotron beamlines, currently allow single crystal diffraction experiments at extreme pressures and temperatures (Merlini et al., 2013; Dubrovinsky et al., 2010) on very small single crystal domains. We successfully applied such technique to determine the crystal structure adopted by carbonates at lower mantle pressures. The knowledge of carbon-bearing phases is in fact fundamental for any quantitative modelling of global carbon cycle. The major technical difficulty arises after first order transitions or decomposition reactions, since original crystal (apx. 10x10x5 μm3) is transformed in much smaller crystalline domains often with random orientation. The use of 3D reciprocal space visualization software and the improved resolution of new generation flat panel detectors, however, allow both identification and integration of each single crystal domain, with suitable accuracy for ab-initio structure solution, performed with direct and charge-flipping methods and successive structure refinements. At higher pressure, towards Mbar (lowermost mantle and D'' region) in agreement with theoretical calculations (Arapan et al, 1997; Oganov et al., 2008) and other experimental results (Boulard et al., 2011), carbon coordination transform into 4-fold CO4 units, with different polymerization in the structure depending on carbonate composition. The second important crystal chemistry feature detected is related to Fe2+ in Fe-bearing magnesite, which spontaneously oxidizes at HP/HT, forming Fe3+ carbonates, Fe3+ oxides and reduced carbon (diamonds). Single crystal diffraction approach allowed full structure determination of these phases, yielding to the discovery of few unpredicted structures, such as Mg2Fe2C4O13 and Fe13O19, which can be well reproduced in different experiments. Mg2Fe2C4O13 carbonate present truncated chain C4O13 groups, and Fe13O19 oxide, whose stoichiometry is intermediate between magnetite and hematite, is a one-layer structure, with features encountered in magnetic materials. The results fully support the ideas of unexpected complexities in the mineralogy of the lowermost mantle, and single crystal technique, once properly optimized in ad-hoc synchrotron beamlines, is fundamental for extracting accurate structural information, otherwise rarely accessible with other experimental techniques.

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Diamond-garnet geobarometry using isomekes: the role of garnet compressibility and thermal expansion

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Keywords: garnet, diamond, isomekes.

Some of the diamonds formed in the sub-cratonic lithospheric mantle contain mineral, fluid and melt inclusions which have been trapped during diamond formation. These inclusions represent therefore a direct window on the Earth's upper mantle which is otherwise inaccessible to direct observations. Study of inclusions in diamonds, therefore, is important for better constraining the chemical and physical conditions which determine the processes of diamond formation.

The pressure and temperature at which the diamond-inclusion pairs grown are usually calculated applying classical geothermobarometric methods based on the chemical exchange between minerals. However, these geothermobarometers can be applied only when the appropriate set of mineral assemblages is present in the same inclusion. Recently, a method based on the pressure exerted by the diamond on the mineral inclusions and on the stresses in the surrounding diamond has been applied to obtain the pressure of the diamond source for olivine inclusions. The method can be applied to any single mineral inclusion. However, it requires accurate knowledge of the thermoelastic parameters (e.g. bulk modulus, thermal expansion) for both diamond and inclusion. While the thermoelastic parameters of the diamond have been already determined to a precision that yields insignificant uncertainties in calculated entrapment pressures (P_e), this is not true for what concern the so far published data for garnets, that show a wide scatter. The uncertainties that arise from the comparison of these published data may indeed propagate in considerable uncertainties to the pressure calculated by the method described above.

In order to avoid inconsistency issues arising from the use of different datasets, we have measured the *P*-*V* equations of state (EoS) and *T*-*V* equations of state for different garnet compositions (i.e. pyrope, $Py_{60}Al_{40,}$ almandine, uvarovite, grossular) by single-crystal X-ray diffraction using one single experimental setting (i.e. instrument, method, etc.). The set of elastic coefficients obtained are therefore intrinsically-internally consistent one to another and can provide a fundamental reference to estimate the compositional effect on the elastic properties. These data can be used to calculate the compositional effect on the positions of garnet-diamond isomekes and thus the entrapment pressures for garnet inclusions found trapped in diamonds.

The Moving CMAS: Thermodynamics of Silicate Melts at High Pressure and Temperature

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Keywords: CMAS liquid, Polymer chemistry, Thermodynamics.

The CMAS system (CaO-MgO-Al_2O_3-SiO_2) is a reasonable proxy to the complex chemistry of natural melts. Though this compositional reduction may appear excessive at first glance, it is justified by the heterogeneity of the system and the complexity of the thermodynamic interactions which determine the aggregation state in a wide P-T regime. In fact, though the energy transfer involved in the crystal-liquid and liquid-glass state transitions of prototypical glass-forming oxides (SiO_2, Al_2O_3) may be precisely assessed through quantum mechanical computations of the translational (Q_{tra}), rotational (Q_{rot}) and vibrational (Q_{vib}) components of the partition function, the complex interplay between the $Q_{rot} + Q_{tra}$ and Q_{vib} components controls the amount of heat internally released through partial solidification of the crystal mush that partly counterbalances the loss of heat toward the exterior along a P-T trajectory. The chemical interaction among components at the liquid state may be resolved by quantifying electrostatically the interaction between Network Formers (NF) and Network Modifiers (NM) in terms of delta of donor-pressure. A polymer chemistry application, widely known as "Toop-Samis" approach, is able to "count" the contacts among structural units in the liquid and, coupled with a Toop's asymmetric deconvolution that reduces all binary interactions basically to two sub-lattice (NF-NM) interaction terms (i.e. the HPA model and its developments), allows us to quantify the Gibbs free energy of mixing of the liquid independently of its chemical complexity. The mathematical handling of the hyper-surfaces representing the equipotential loci which delimit the stability fields at liquidus may be carried out through segmented Delaunay triangulations and efficient convex hull techniques. For a simplex of rank 3 (i.e. a four-component system like the CMAS) we may only "see" the primary phase volumes in a distorted tetrahedral representation. However, to depict the lines of descent (i.e. the chemical path of the liquid in the tetrahedron, induced by loss of heat), we must precisely know the primary phase volumes at all P conditions and the composition of the precipitating solids. This task is computationally very demanding. Adopting for instance a 5×10^{-2} compositional step and a 5 K T-discretization, each isobaric outcome in the 3000-1000 K T-range implies the generation of 8×108 Gibbs free energy points, which, when coupled with the corresponding values computed for all the crystalline, gaseous and glassy phases nucleating in the system and constrained to obey the principle of minimization of Gibbs free energy at equilibrium, must be handled by the convex-hull routine to generate the equipotential loci hyper-surface.

A Bader's topological approach for the investigation of the high pressure stability field of the Mg-perovskite phase

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Keywords: Bader, electron density, phase transiton.

The stability field of the Mg-perovskite phase, has been investigated by characterizing the evolution of the electron arrangement in the crystal.

The interest in the structural stability of this phase comes from the consideration that the Mg-perovskite is assumed to be the dominant component of the Earth's lower mantle (Oganov and Price, 2005) and the transition to the so-called post-perovskite phase can explain the discontinuity in seismic velocities observed above the core–mantle boundary (the D'' discontinuity).

Although quite a large amount of data on the perovskite so far exists, its behavior at the extreme conditions of the Earth mantle is still lacking information. This is mainly due to the technical difficulties related to the experimental setup. At extreme conditions, where the experiments lose accuracy, computational approach can be very helpful in complementing these studies.

In the present work, *ab initio* calculations of the perovskite structures in the range 0-180 Gpa have been performed at the HF/DFT exchange–correlation terms level, using Hamiltonians based on a WC1LYP hybrid scheme. The electron densities, calculated throughout the ab initio wave functions, have been analyzed by means of the Bader's theory, coupled with Thom's catastrophe theory.

The topological results show the occurrence of two topological anomalies. The first, i.e. the appearance of a cage critical point coalescent with a ring critical point, occurs at ~20 GPa and is a clear indication of the stabilization of the perovskite phase. The inverse process, observed at ~110 GPa, i.e. the vanishing of a cage-ring crititical points couple, indicates the destabilization of this phase, and can be interpreted in the light of the perovskite to post-perovskite phase transition, which seems to be responsible of the discontinuity in seismic velocities observed above the core–mantle boundary (the D'' discontinuity).

It is worth to underline the important geophysical implication of these results. The stability field of perovskite explains several observed puzzling properties of the D'' layer: its seismic anisotropy, the strongly undulating shear-wave discontinuity at its top and possibly the anticorrelation betweens hear and bulk sound velocities.

The proposed approach is addressed to depict a phase transition from a novel viewpoint, particularly useful in predicting the stability of a compound at extreme conditions, at which laboratory experiments are extremely difficult.

Thermal expansion behavior of orthopyroxenes: the role of the Fe-Mn substitution

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Keywords: Orthopyroxene, high temperature, thermal expansion, single-crystal X-ray diffraction.

Two Pbca orthopyroxene samples, donpeacorite and bronzite with chemical formula $Mn_{0.54}Ca_{0.03}Mg_{1.43}Si_2O_6$ (X_{Mn}=0.27) and $Fe_{0.54}Ca_{0.03}Mg_{1.43}Si_2O_6$ (X_{Fe}=0.27) respectively were investigated by single crystal X-ray diffraction (SC-XRD) at high-temperature conditions (see Pandolfo, 2014 for further details). The nearly identical X_{Fe} and X_{Mn} make the two samples the perfect candidates to investigate the effect of the compositional change at the M2 site (i.e. Fe-Mn substitution) on the thermal expansion behavior of orthopyroxenes.

The unit cell parameters thermal expansion behaviour of both samples have been investigated at 17 different temperatures between room-*T* and 1073 K. In the entire temperature range no evidences for phase transitions have been found. In order to avoid any effect of the ordering-disordering process during the high-temperature in situ experiment both samples have been previously disordered with an ex situ annealing at about 1273K (following the protocol given in Alvaro et al., 2011).

The unit-cell parameters and volume thermal expansion, collected on the disordered samples have been fit to a Fei-type and Berman-type Equation of State (EoS) using EoSFit7c program (Angel, 2014). As a consequence of the compositional change while the thermal expansion along *b*-direction is nearly identical for both samples, slight differences have been found along *a* and *c* lattice. However, the differences in thermal expansion along *a* lattice are counterbalanced by the differences along *c* lattice. Therefore, as results of the different behavior along *a* and *c*, the unit cell volume thermal expansion for both samples is identical within standard deviations.

At room temperature the relative magnitudes of unit-cell thermal expansion coefficient for our sample are in clear agreement with the literature available data for Fe-Mg orthopyroxene, while at high-temperature thermal expansion coefficients show different behavior for the two sample mainly because of the changes of the expansion mechanism. Therefore it seems that the Fe-Mn substitution controls the unit-cell volume–expansion with temperature only by affecting V_0 unit cell volume at room-T.

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Effect of alkali on the structure and viscosity of iron-bearing silicate glasse

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Keywords: silicate glasses, structure, viscosity, alkali.

In the frame of a larger work aimed at studying the Fe-S interaction in silicate magmas and its effect on S solubility, the purpose of this project is to synthetise and study a series of rhyolitic glasses, with 5 wt% of FeO and different Na/Na+K ratios, equilibrated in air under controlled oxygen fugacity conditions. Together with composition, temperature and pressure, oxygen fugacity (fO_2) plays an important role on physical and chemical properties in glasses and melts. Due to different fO_2, in fact, transitions elements such as iron can exist in glasses in different oxidation states (Fe^0, Fe^{2+} and Fe^{3+}), which also influence the glass properties.

Alkali content is known to affect strongly the Fe oxidation state in silicate glasses (Moretti and Ottonello, 2003) but it is still controversial to which extent alkali can modify Fe structural role in glasses/melts. In this work the iron speciation ratio of each sample was determined by colorimetric wet chemistry and by XAS to study how Fe^{2+}/Fe_{tot} vary as a function of oxygen fugacity. X-Ray Absorption Spectroscopy (XAS) has been also employed to unravel Fe local geometry in the glasses: Fe^{3+} is in 4-fold coordination (tetrahedral) whereas Fe^{2+} coordination number is intermediate between 4 and 5.

Viscosity of the glasses has been measured by micropenetration method: the rate at which a 2 mm diameter single crystal sphere of Al_2O_3 is forced into the melt is measured, and viscosity (in Pa s) is calculated by knowing the applied force (F), the time (t), the radius of the sphere (R) and the indentation depth (L) (Pocklengton, 1940). Preliminary results show that viscosity of Fe-bearing melts strongly increase with decreasing Na/Na+K ratio in the oxidized samples.

These results have important implications for the effect of alkali ratio on the Fe speciation and on the solubility of sulphide in pantelleritic magmas, and will be essential for the improvement of comprehensive thermodynamic models able to predict S solubility variations in a wide range of silicate compositions.

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Understanding pyroxene vibrational properties: ab initio calculated and experimental Raman spectra of spodumene ($LiAlSi_2O_6$)

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Keywords: Ab initio method, Raman Spectroscopy, Pyroxenes.

Mantle dynamics and its mineral properties are an active research field. Minerals of pyroxene group are one of the most abundant rock-forming minerals on Earth's crust and mantle (Deer et al., 1966). Studying the vibrational properties of pyroxenes under different environmental conditions would lead to understand the propagation of seismic waves in the mantle and consequently its constitution and dynamics. Depth, mantle temperature and pressure conditions preclude the application of a fully experimental scientific approach and force to create theoretical models mostly based on simulation.

Currently *ab initio* methods are used in simulations and predictions of properties of minerals with excellent agreement with experimental data. In addition, Raman scattering methods probe the lattice vibrations of a material. The applications of these techniques to the study of rock-forming minerals and therefore to the Earth's interior, enable us to describe their crystal lattice dynamics and to calculate thermodynamic parameters (Huang et al., 2000). The aim of this study is to improve the interpretation of Raman experimental spectra of spodumene, a Li and Al monoclinic chain silicate belonging to *C*2/*c* space group at ambient condition, by exploiting the accuracy of the quantum mechanical calculations.

An *ab initio* HF/DFT study of Raman spectra of spodumene has been performed with the program CRYSTAL14 (Dovesi et al., 2013) which employs localized, gaussian-type basis sets. The chosen Hamiltonian WC1LYP is based on the Wu-Cohen exchange functional (Wu & Cohen 2006), corrected by a fraction (16%) of *non-local exact* Hartree-Fock exchange, and Lee-Young-Parr correlation functional (Lee et al.,1988) .

The simulated data have been compared with experimental data on a natural sample of spodumene, that was already characterized by single crystal X-Ray diffraction (Tribaudino et al., 2003). All the 30 expected Raman active vibrational modes (14 A_g and 16 B_g) have been recognized by the polarized spectra. The calculation provides an excellent agreement with the experimental results: the average absolute difference between calculated and experimental Raman frequencies is about 4.8 cm^{-1}. The predicted Raman intensities are also in good agreement with the experimental data.

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Ab Initio calculated and experimental Raman spectra of Ca-Mg germanate ($CaMgGe_2O_6$): studying phase transitions of the Earth mantle

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Keywords: Ab initio methods, Raman Spectroscopy, Germanates.

Pyroxenes are chain silicate minerals, widespread constituents of the Earth crust and of the upper mantle, as well as of rocky planets and meteorites. Crystal chemical relationships between germanates and silicates have acquired a lot of interest since the beginning of speculations on phase transitions and constitution of the mantle, because germanates behave as high-pressure models for high pressure transformations of the corresponding silicates (Ringwood et al., 1963; Ringwood, 1968).

In this study we highlight the importance to create theoretical models based on simulation to predict mineral properties. We have performed an *ab initio* HF/DFT calculation of the Raman spectrum of $CaMgGe_2O_6$ at ambient conditions to study the vibrational properties of Ge-pyroxenes. $CaMgGe_2O_6$ is a monoclinic pyroxene belonging to $C2/c$ space group. The simulation has been performed with the CRYSTAL14 (Dovesi et al., 2013) software which employs localized, gaussian-type basis sets. The chosen Hamiltonian WC1LYP is based on the Wu-Cohen exchange functional (Wu & Cohen, 2006), corrected by a fraction (16%) of non-local exact Hartree-Fock exchange, and Lee-Young-Parr correlation functional (Lee et al., 1998).

The simulated data have been compared with experimental micro-Raman spectroscopy measurements on a synthetic sample of $CaMgGe_2O_6$, obtained from a ceramic solid-state sintering route at T = 1573 K of a mixture of $CaCO_3$, GeO_2 and MgO in the desired stoichiometry. The cell parameters for $CaMgGe_2O_6$ are: a = 10.0987(9) Å, b = 8.9777(8) Å and c = 5.4214(5) Å with β = 105.3729(9)° and V = 473.93(7) Å^3. The satisfactory agreement between calculated and measured Raman spectra (frequencies and relative intensities) enables the attribution of specific vibrational normal modes to the observed features.

Dovesi R., Saunders V. R., Roetti C., Orlando R., Zicovich-Wilson C. M., Pascale F., Civalleri B., Doll K., Harrison N. M., Bush I. J., D'Arco P., Llunell M., Causà M. & Noël Y. 2014. CRYSTAL14 User's Manual. University of Torino.

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Dolomite behaviour at high-pressure and phase transition to Dolomite-II. A couple of theory and experiment

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Keywords: dolomite, synchrotron X-ray diffraction, ab-initio calculations.

Carbonates are found to be stable up to lower mantle conditions. Thus, they are considered as possible carbon carrier minerals into the deep upper mantle by subduction processes. This work is aimed to study dolomite compressibility as a function of disordering and temperature. Moreover, time was devoted to analyse how ordered and disordered dolomite crystal structures behave as the phase transition to dolomite-II (Merlini et al. 2012) is approached. Both experimental and theoretical approaches were used. The high pressure–high temperature (H*P*-H*T*) experiments were carried out at ID09A beamline at the European Synchrotron Radiation Facility ESRF, Grenoble, France. Data were collected up to 20 GPa. *Ab-initio* calculations were carried out by means of CRYSTAL09 program (Dovesi et al. 2005). Ordered and disordered geometries (Zucchini et al. 2012) were optimised at different pressures up to approximately 26 GPa. Dolomite *P*-*V* data were fitted by a third order Birch-Murnaghan Equation-of-State. Results of both theory and experiments show that ordered and disordered dolomites have approximately the same bulk compressibility; whereas *T* has a significant effect in increasing dolomite compressibility. Ambient temperature experimental data were also used for crystal structure refinements. Results show that octahedra in the ordered sample are almost equally compressible; whereas CaO_6 in the disordered sample is less compressible than MgO_6. That is, the partial replacement of Ca by Mg increases CaO_6 and decrease MgO_6 bonds strength, thus making stiffer CaO_6 and more relaxed MgO_6. Moreover, structural refinements and calculated geometries show that octahedra are distorted. A decrease of distortion with *P* is observed as both O-Ca-O and O-Mg-O angles approach 90° as *P* increases, approaching regularity. Cation polyhedra in the ordered dolomite became almost regular at approximately 14–15 GPa. Both experiments and calculations allow to conclude that dolomite-I/II transformation is approached at ~14–15 GPa in the ordered dolomite and at ~17GPa in the ordered dolomite at H*T*. As regards the disordered crystal structure, there are no strong evidences of the phase transition. Two main hypothesis arises: either (i) disordered dolomite is stable at higher pressure than the ordered one, that is, disordering stabilizes dolomite-I or (ii) disordered dolomite does not undergo phase transition to dolomite-II.

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SESSIONE S13

New Minerals: The role played by the Italian Community - A tribute to Carlo Maria Gramaccioli

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New fumarolic minerals from Mt. Hekla volcano, Iceland: $FeF_3(H_2O)_3$

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Keywords: Hekla sublimates, iron fluoride, new minerals.

Mt. Hekla is located west of Iceland SE volcanic rift-zone and represents the Iceland's most famous and historically most active volcano. A systematic sublimates and incrustations collection and analyses has been performed subsequently to the 1991 eruption and it conducted to the discovery of a number of new mineral phases: eldfellite (Balić-Žunić et al., 2009), heklaite (Garavelli et al., 2010), jakobssonite (Balić-Žunić et al., 2012), leonardsenite (Mitolo et al., 2013), oskarssonite (Jacobsen et al., 2014). Natural Fe-fluoride hydrate, with ideal formula $FeF_3 \cdot 3H_2O$, was found in the Hekla fumaroles both in the tetragonal and rhombohedral forms. The rhombohedral polymorph is still under investigation. Natural, tetragonal $FeF_3 \cdot 3H_2O$ is the new phase here described and corresponds to the synthetic β-$FeF_3(H_2O)_3$ (Teufer, 1964). It occurs as micrometer-sized quadratic crystals, or aggregates inside up to 3 mm thick yellow to brown crust on altered scoria together with hematite, opal, malladrite, heklaite and ralstonite. X-ray powder diffraction data indicate tetragonal symmetry, space group *P4/n*, with unit-cell parameters *a* 7.8383(4), *c* 3.8718(2) Å, *V* 237.88(3) Å^3 and $Z = 2$. The average chemical composition is (wt.%) : Fe 38.52, F 38.23, Cl 1.03, O 21.10, total 98.88. The empirical formula (based on Fe = 1) is $Fe(F_{2.94}Cl_{0.04})_{\Sigma 2.98}(H_2O)_{1.94}$ corresponding to the ideal formula $FeF_3(H_2O)_3$. Fe-fluoride hydrate is isostructural with rosenbergite, $AlF_3(H_2O)_3$ (Olmi et al., 1993). The crystal structure consists of infinite straight chains of $[FeF_3(H_2O)_3]$ octahedra extending along [001] (Teufer, 1964). The adjacent octahedra share apical F atoms, whereas the four unshared, equatorially coordinated atoms, are represented by disordered arrangement of two F and two O atoms (from water molecules). The additional water molecules occupy the spaces between chains and are tetrahedrally coordinated by four (F, H_2O) from four different chains. The new mineral will be submitted for approval to the IMA-CNMNC.

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Teufer, G. (1964. The crystal structure of β-iron(III) trifluoride trihydrate, β-$FeF_3.3H_2O$. Acta Cryst., 17, 1480.

Mambertiite (IMA 2013-098), a new bismuth-molybdenum oxide from Su Seinargiu, Sardinia

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Keywords: mambertiite, new mineral, bismuth, molybdenum, Su Seinargiu, Sardinia.

The Mo-Bi mineralization of Su Seinargiu, Sarroch, Cagliari, Sardinia, Italy, is hosted in granitic rocks of Hercynian age (Caboi et al., 1978; Ghezzo et al., 1981). The alteration of the primary Mo and Bi minerals has originated a series of secondary minerals, among which six new minerals: sardignaite, gelosaite, tancaite-(Ce) (Orlandi et al., 2013), and the recently approved phases ichnusaite, nuragheite, and mambertiite.

Mambertiite has been identified in small vugs of quartz veins, as pale yellow {100} tabular crystals, up to 1 mm in length and few microns thick, with adamantine luster. The mineral is brittle, with a conchoidal fracture.

Electron microprobe analysis gave (wt% - mean of 12 spot analyses): Mo_2O_5 59.59, Bi_2O_3 36.96, WO_3 2.03, H_2O 1.44, sum 100.02. On the basis of 9 O atoms per formula unit, the empirical formula is $Bi_{0.99}(Mo^{5+}_{2.74}W_{0.05})_{\Sigma 2.79}O_8(OH)$.

The crystal structure of mambertiite is composed by eight-fold coordinated Bi-centered polyhedra and five independent Mo-centered octahedra. Among the latter, two of them are completely filled by molybdenum, whereas the remaining three have a partial occupancy. Two kinds of (1-10) layers occur in mambertiite, alternating along [1-10]*: one is composed by Bi-centered polyhedra and the two partially occupied Mo4 and Mo5 sites, the other is composed by the zigzag chains, running along **c**, formed by the fully-occupied Mo1 and Mo2 sites, and the partially occupied Mo3 site.

Mambertiite, whose name honors the mineral collector Marzio Mamberti (b. 1959) for his contribution to the knowledge of the Sardinian mineralogy, is the fourth mineral species having Bi and Mo as essential components, the other three being koechlinite, Bi_2MoO_6, sardignaite, $BiMo_2O_7(OH)\cdot 2H_2O$, and gelosaite, $BiMo^{6+}_{(2-5x)}Mo^{5+}_{6x}O_7(OH)\cdot H_2O$ ($0 \leq x \leq 0.4$). Mambertiite is structurally related to gelosaite. With respect to gelosaite, mambertiite has a greater Mo content (interpreted as Mo^{5+}) and this probably is responsible for the lowering of the space group symmetry from $P2_1/n$ in gelosaite (Orlandi et al., 2011) to P-1 in mambertiite. Hence, mambertiite and gelosaite could be two members of a series of compounds having different Mo^{6+}:Mo^{5+} atomic ratios.

The mineral and its name have been approved by the IMA-CNMNC (IMA 2013-098).

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Apuan Alps: a reference ore district for the study of sulfosalt crystal-chemistry

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Keywords: lead, antimony, arsenic, thallium, mercury, sulfosalts.

Since the description of meneghinite from the Bottino mine by Bechi (1852), the Apuan Alps have become a reference ore district for the sampling and the study of sulfosalts. Up to now, 55 different sulfosalt species have been identified; among them, 17 have their type-locality in this area. This richness is related to the occurrence of small polymetallic hydrothermal ore bodies whose present mineralogy and parageneses are related to the Tertiary Alpine tectono-metamorphic events.

The majority of the new sulfosalt species have been described in the last twenty years. In particular, the most prolific kind of ore deposit is represented by the baryte ± pyrite ± iron oxides ores exploited at the Buca della Vena, Monte Arsiccio, and Pollone mines up to the end of 1980s. A common feature of these occurrences is the presence of oxysulfosalts, i.e. sulfosalts in which oxygen plays a structural role. Scainiite, pillaite, pellouxite, and rouxelite have Buca della Vena as their type locality. Recently rouxelite was identified also from the Monte Arsiccio mine, associated with chovanite, another oxysulfosalts first found in Slovakia (Topa *et al.*, 2012). A new occurrence of this latter mineral from the Pollone mine allowed the solution of its real 8 Å structure. Pollone mine is type locality for meerschautite, an Ag-Pb/Sb-As oxysulfosalt characterized by the lowest O:S atomic ratio described so far. In addition to meerschautite, other complex Ag-Pb/Sb-As sulfosalts like sterryite and the new minerals parasterryite and carducciite have been found at this locality.

Recently, Tl-Hg-Pb-As-Sb-(Ag,Cu) sulfosalt assemblages have been identified at the Monte Arsiccio mine (e.g., Biagioni *et al.*, 2014), with the description of three new minerals, i.e. boscardinite, protochabournéite, and arsiccioite. These phases are associated with other very rare compounds (aktashite, laffittite, routhierite, and a Cu-Hg derivative of quatrandorite).

Finally, particular physicochemical conditions promoting the crystallization of persulfides, i.e. compounds characterized by S–S bonds, were present in the cavities of the Liassic marbles, as testified by the crystallization of two new mineral species, moëloite and disulfodasonite.

Consequently, the hydrothermal veins of the Apuan Alps represent an extraordinary natural laboratory for the study of the crystal-chemistry of sulfosalts in metamorphic settings.

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Topa D., Sejkora J., Makovicky E., Pršek J., Ozdín D., Putz H., Dittrich H. & Karup-Møller S. 2012. Chovanite, $Pb_{15-2x}Sb_{14+2x}S_{36}O_x$ ($x \sim 0.2$), a new sulphosalt species from the Low Tatra Mountains, Western Carpathians, Slovakia. Eur. J. Mineral., 24, 727–740.

Two As-bearing new mineral species from Valletta mine: grandaite and braccoite

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Keywords: Valletta mine, grandaite, braccoite.

The Valletta Mine (Canosio, Maira Valley, Piedmont, Italy) is a small iron deposit with subordinate manganese. A systematic study of the mineral phases in the quartzites with quartz veins revealed that those contain a large variety of mineral phases rich in arsenic, vanadium, barium and strontium. Among those, two mineral species have been found and approve by IMA-CNMMC: braccoite, ideally $NaMn^{2+}_5[Si_5AsO_{17}(OH)](OH)$, and grandaite, ideally $Sr_2Al(AsO_4)_2(OH)$.

Braccoite (IMA 2013-093) occurs as subhedral crystals in brown-red colour thin masses, with pale yellow streak and vitreous to resinous luster, and is associated with tiragalloite, gamagarite, hematite, manganberzeliite, palenzonaite, quartz, saneroite, tokyoite, unidentified Mn oxides, organic compounds, and Mn arsenates and silicates under study. Its crystal structure have been solved and refined. Braccoite is triclinic, space group P1 with *a* 9.7354(4), *b* 9.9572(3), *c* 9.0657(3) Å, α 92.691(2)°, β 117.057(4)°, γ 105.323(3)°, *V* 740.37(4) Å^3 and *Z* 2. Chemical analyses by WDS electron microprobe gave the empirical formula calculated on the basis of Σ cations-(Na,K) = 11 p.f.u. $Na_{1.06}(Mn^{2+}_{4.46}Mn^{3+}_{0.32}Mg_{0.19}V^{3+}_{0.01}Al_{0.01}Ca_{0.01})[Si_5(As_{0.48}Si_{0.37}V^{5+}_{0.15})O_{17}(OH)](OH_{0.98}F_{0.02})$. Braccoite Is isostructural with sanneroite, but has dominance of As over V. Braccoite is named in honour of Roberto Bracco, a systematic collector with a special interest in manganese minerals.

Grandaite (IMA 2013-059) occurs in quartz veins as thin masses of bright orange to salmon to brown colour, or infrequently as fan-like aggregates of small (< 1 mm) crystals, with reddish brown streak and waxy to vitreous lustre. Grandaite is associated with aegirine, baryte, braunite, hematite, tilasite, quartz, unidentified Mn-oxides, and Mn-silicates under study. Its crystal structure has been solved and refined. Grandaite is monoclinic, space group $P2_1/m$, with *a* 7.5764(5), *b* 5.9507(4), *c* 8.8050(6) Å, β 112.551(2)°, *V* 366.62(4) Å^3.

Chemical analyses by electron microprobe gave the empirical formula calculated on the basis of 9 O a.p.f.u., $(Sr_{1.41}Ca_{0.64}Ba_{0.05}Pb_{0.01})_{S=2.11}(Al_{0.68}Fe^{3+}_{0.14}Mn^{3+}_{0.12}Mg_{0.13})_{S=1.07}[(As_{0.96}V_{0.01})_{S=0.97}O_4]_2(OH)$. Grandaite is isostructural with brackebuschite and is named after the informal appellation of the province in which the type locality is located.

The Italian contribution to the tourmaline systematics

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Keywords: Tourmaline, new mineral, systematic.

The contribution of the Italian Community to discovery of new minerals and their classification is certainly important as shown by the tourmaline case.

Tourmalines are complex borosilicates described by the general formula: $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, where $^{[9]}X = Na^+$, K^+, Ca^{2+}, (=vacancy); $^{[6]}Y = Al^{3+}$, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Li^+; $^{[6]}Z = Al^{3+}$, Fe^{3+}, Cr^{3+}, V^{3+}, Mg^{2+}, Fe^{2+}; $^{[4]}T = Si^{4+}$, Al^{3+}, B^{3+}; $^{[3]}B = B^{3+}$; $^{[3]}V = OH^{1-}$, O^{2-}; $^{[3]}W = OH^{1-}$, F^{1-}, O^{2-}. The dominance of these ions at one or more sites of the structure gives rise to a range of distinct mineral species. Tourmaline is a supergroup currently consisting in twenty-eight species approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association.

Fourteen tourmaline species were approved after the publication of the recent tourmaline classification (Henry et al., 2011), and nine of them were found by Italian mineralogists (e.g. Bosi et al., 2012; 2013). Of these nine, six define a new compositional field characterized by $(Cr,Al,V)^{3+}$ over the Y and Z sites and O^{2-} at the W position of the general formula. Furthermore, two of these nine (tsilaisite and fluor-tsilaisite) come from Italy (Elba Island) and were found in the same zoned crystal.

The impact of these new minerals on the systematic and crystal chemistry of tourmaline is relevant. For example, the ternary diagram in terms of Al-V-Cr at Y and Z shows a full solid solution among oxy-dravite – oxy-chromium-dravite – oxy-vanadium-dravite along with the following site preferences: $V^{3+} > Cr^{3+} > Al^{3+}$ for the Y site and $Al^{3+} > Cr^{3+} > V^{3+}$ for the Z site. Such site preferences determine the existence of three end-members between the apices of the triangular compositional diagram: Al and Cr (chromo-alumino-povondraite), Cr and V (vanadio-oxy-chromium-dravite), V and Al (vanadio-oxy-dravite). With regards to the tourmalines from Elba Island, fluor-tsilaisite shows a solid solution with the tsilaisite (by F ↔ OH) as well as with the fluor-elbaite (by $2Mn^{2+} \leftrightarrow Al + Li$). Although fluor-tsilaisite may ideally be linked to the elbaite through the substitution $2Mn^{2+} + F \leftrightarrow (Al + Li) + (OH)$, the occurrence of such a substitution is unlikely because of the observed inverse correlation between F and Mn^{2+}. In the above mentioned zoned crystal, tsilaisite and fluor-elbaite are linked through fluor-tsilaisite, which appears to be a stepwise intermediate composition from the tsilaisitic core to the fluor-elbaitic rim.

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Bosi F., Andreozzi G.B., Skogby H., Lussier A.J., Abdu Y., Hawthorne F.C. 2013. Fluor-elbaite, $Na(Li_{1.5}Al_{1.5})Al_6(Si_6O_{18})(BO_3)_3(OH)_3F$, a new mineral species of the tourmaline supergroup. Am. Mineral., 98, 297-303.

Henry D.J., Novák M., Hawthorne F.C., Ertl A., Dutrow B., Uher P. & Pezzotta F. 2011. Nomenclature of the tourmaline supergroup minerals. Am. Mineral., 96, 895-913.

A new natural ammonium decaborate from La Fossa crater, Vulcano Island, Italy

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Keywords: diammonium tetrahydroxydecaborate monohydrate, La Fossa crater, Vulcano Island, Italy.

Boron is a widespread element in the fumaroles of La Fossa crater at Vulcano Island and forms a number of different minerals such as the particularly abundant boric acid sassolite, H_3BO_3, metaborite, HBO_2, clinometaborite, HBO_2, some borates such as santite, $K[B_5O_6(OH)_4]\cdot 2H_2O$ and larderellite, $NH_4[B_5O_7(OH)_2]\cdot H_2O$ and a number of fluoroborates such as barberiite, NH_4BF_4, knasibfite, $K_3Na_4[SiF_6]_3[BF_4]$ and avogadrite, KBF_4 (Campostrini et al., 2011). Ammonium is also particulary abundant in the intracrater fumarolic system and in the last few years, due to a decreasing of temperature and magmatic fluids flow, the mineral assemblage of the fumaroles has changed leading to the formation of ammonium bearing sulfates and sulphate-chlorides minerals.

In Spring 2013, a new ammonium borate mineral was found in the FA fumarole (temperature about 250° C) as white crystals up to 0.2 mm, together with sassolite, adranosite and alunite: it corresponds to the synthetic compound diammonium tetrahydroxydecaborate monohydrate, $(NH_4)_2[B_{10}O_{14}(OH)_4]\cdot H_2O$ (Li et al., 2003). The mineral crystallizes in the triclinic space group P-1 with a = 7.638(2), b = 9.253(2), c = 11.959(3) Å, alpha = 99.44(1), beta = 105.92(1), gamma = 91.51(1)°. Its structure contains infinite chains of composition $[B_{10}O_{14}(OH)_4]_n^{2n-}$ linked by hydrogen bonds to form borate sheets. Water molecules an ammonium ions are located between these sheets and connect adjacent sheets via hydrogen bonds. The basic structural unit contained is a double ring formed by one BO_4 tetrahedron and four BO_3 triangles, an unit already observed in santite as an isolated ion (Zachariasen, 1937; Merlino & Sartori, 1970) or linked to form infinite chains in larderellite (Merlino & Sartori, 1969).

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A new ammonium arsenite chloride from the Solfatara di Pozzuoli, Napoli, Italy

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Keywords: ammonium arsenite chloride hydrated, Solfatara di Pozzuoli.

The Solfatara di Pozzuoli is one of about 40 volcanoes in the Campi Flegrei area and is located three kilometers from the center of the town of Pozzuoli. Solfatara formed during the third Flegrean eruptive period and dates to about 3700-3900 years ago. Inside the Solfatara some active fumaroles are present, the most important of which is called "Bocca Grande" and has a temperature of about 160 °C.

During a research campaign carried out in 2011 we could collect at “Bocca Grande” fumarole some samples with small yellow or colorless hexagonal tabular crystals. The mineral is associated with realgar, dimorphite, alacranite, salammoniac, mascagnite and an amorphous arsenic sulfide. Its powder pattern corresponds to that of the synthetic compound $NH_4ClAs_2O_3(H_2O)_{0.5}$ (PDF2 entry 00-076-1366) and the hexagonal unit-cell parameters obtained using the unit-cell software (Holland & Redfern, 1997) are: a = 5.259(2); c = 12.590(5). Due to the small size of the crystals was not possible to obtain structural data from single-crystal diffraction.

The mineral has probably some structural relationships with lucabindiite, $(K,NH_4)As_4O_6(Cl,Br)$, a complex arsenite chloride found for the first time at La Fossa crater, Vulcano Island, Sicily and described by Garavelli et al. (2013).

The chemical analysis carried out in EDS mode using a JEOL JSM 5500LV scanning electron microscope equipped with a iXRF EDS microprobe gave a composition very close to that of lucabindiite, but with an ammonium content significantly greater than that of potassium and a lower bromine content.

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A monoclinic K-Li-Cu-Mg silicate from the Cerchiara mine: a dimorph of lavinskyite?

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Keywords: Lavinskyite, monoclinic dimorph, Cerchiara mine.

A possibly new K-Li-Cu-Mg silicate occurs at the Cerchiara mine (Liguria, Italy) as blue, micaceous aggregates embedded in calcite-filled microfractures and veinlets related to re-equilibration of the ophiolitic sequence during tectonometamorphic overprinting under prehnite-pumpellyite facies conditions (Lucchetti et al., 1988). The associated minerals include calcite, quartz, norrishite and "*schefferite*" (a Mn-bearing variety of diopside). Micro-Raman, and chemical analyses by SEM-EDS and LA-ICP-MS confirm the compositional analogy of this K-Li-Cu-Mg silicate with lavinskyite. The crystal structure has been solved using single-crystal X-ray diffractometer data (R_{int} = 5.2 %) from a tiny crystal fragment (0.015 x 0.05 x 0.10 mm) by direct methods and refined in space group $P2_1/c$ (no. 14) to R1 = 5.1 % and wR2$_{\mathrm{all}}$ = 13.2 % [1942 'observed' reflections with $F_o > 4\ s(F_o)$, 200 parameters]. Refined unit-cell parameters are: a = 10.224(2), b = 19.085(4), c = 5.252(1) Å, β = 92.23(3)°, V = 1024.0(4) Å^3 (Z = 2). The atomic arrangement is best described as a sheet structure consisting of corrugated brucite-like $(CuO_2)_n$ layers with amphibole-type $(SiO_3)_n$ chains joined to both their upper and lower surfaces. Adjacent complex sheets are linked by (Li,Cu,Na,Mg) atoms in square coordination (nearly planar) and interlayer K atoms. The K site is fully occupied by K, whereas the Li site [M(4) site] is occupied by major Li and more or less minor Cu, Na and Mg. This silicate has basically the same topology as orthorhombic lavinskyite [$K(LiCu)Cu_6(Si_4O_{11})_2(OH)_4$, Pcnb (Yang et al., 2014)], which is isostructural with plancheite (Evans & Mrose, 1977). The monoclinic silicate and lavinskyite also have nearly the same empirical formula: $(K_{1.08})_{\Sigma 1.08}(Li_{0.89}Mg_{0.36}Cu_{0.33}Na_{0.22}Mn^{2+}_{0.04})_{\Sigma 1.85}Cu_{6.00}Si_{8.08}O_{22}(OH)_{4.02}$ and $(K_{0.99}Ba_{0.01})_{\Sigma 1.00}(Li_{1.04}Cu_{0.93}Na_{0.10})_{\Sigma 2.07}(Cu_{5.57}Mg_{0.43}Mn_{0.01})_{\Sigma 6.01}(Si_{4.00}O_{11})_2(OH)_4$, respectively. The most important difference between the two apparent dimorphs is the fact that the M(4) site in lavinskyite is distinctly split, unlike the corresponding site in the silicate. The occupancy of the split site is M(4a) = 0.5Cu, M(4b) = 0.5Li (Yang et al., 2014), whereas the non-split M(4) site in the silicate shows a mixed occupancy by Li and Cu (and possibly minor Na and Mg), based on the chemical analysis and the structure refinement. In conclusion, it appears that a complex and delicate interplay between the Li:Cu and Cu:Mg ratios, along with an additional influence of impurity cations such as Na, results in a slightly distorted atomic arrangement for the silicate from Cerchiara and a different space group ($P2_1/c$, a subgroup of lavinskyite's Pcnb) and unit cell.

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"Mesitine" and its relationship with other carbonates from Traversella Mine

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Keywords: Traversella, carbonate, mesitine.

Mesitine, sometimes also written *mesitite,* is an old name, not I.M.A. approved, used for the identification of iron-rich magnesite with different iron percentage (Dana, 1911; Bayliss, 2011). Between the most famous samples collected in the mineralogical museum of Europe, *mesitine* of Traversella are amongst the most representative and beautiful, but sometimes the identification of the mineral specie was inferred mainly through provenience of the specimen, visual appearance and minerals association rather than with analytical determination.

During a survey of some samples of the Regional Museum of Science in Turin, in a frame of valorization of the mineralogical collection coming from the localities of Brosso and Traversella (Torino, Piemonte, North West Italy) some old samples of this second locality (collected around 1850-70) were analyzed together with some freshly obtained samples (2010-2012) from the still open galleries existing in the Traversella mining complex, kindly provided by the Gruppo Mineralogico Traversella. Analysis were performed by mean of SEM-EDS and ICP-OES facilities in the Department of Earth Science at the Turin University.

Results shows that only part of the samples previously identified as *mesitine* are really iron-rich magnesite, whereas a substantial amount of samples was actually dolomite; these carbonates coexist in the Traversella complex with calcite, siderite and sporadic ankerite.

In the paper the authors will examine the presence of these carbonates in the mineralogical samples from Traversella, the role of the term *mesitine* in the mineralogical community and the complexity to achieve a secure identification on some carbonate samples coming from site with high geochemical complexity and mineralogical variability.

The research was conducted within the project "PROactive Management of GEOlogical Heritage in the PIEMONTE Region" (www.progeopiemonte.it/en) co-founded by the University of Turin – Compagnia di San Paolo Bank Foundation "JCAPC - Progetti di Ateneo 2011" grant on line B1 "Experimental Sciences and Technology" (Project Id: ORTO11Y7HR, P.I. Prof. Marco Giardino).

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Chemical, Mössbauer and structural data on a potentially new mineral from Harrow Peaks (Antarctica) in the oxo-amphibole group (amphibole supergroup)

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Keywords: amphibole supergroup, oxo-amphibole group, new mineral, Antarctica.

Among the 89 minerals currently recognized as valid species within the amphibole supergroup, only six belong to the oxo-amphibole group: ferri-obertiite, ferro-ferri-obertiite, kaersutite, mangani-dellaventuraite, mangano-mangani-ungarettiite, and oxo-magnesio-hastingsite. According to the newly approved report of the amphibole subcommittee (Hawthorne et al., 2012), minerals of the oxo-amphibole group must have $^{W}O^{2-} > (OH+F+Cl)^{-}$.

We collected chemical (electron and ion microprobe), micromössbauer and single-crystal X-ray diffraction data on a potentially new mineral in the oxo-amphibole group. Its end-member formula is $NaCa_2(Mg_3Fe^{3+}Ti)(Si_6Al_2)O_{22}O_2$, and it would represent the Fe^{3+}-dominant analogue of kaersutite. The mineral occurs in mantle spinel-bearing lherzolite from Harrow Peaks, Victoria Land, Antarctica.

The chemical composition was determined by ion microprobe (hydrogen, fluorine and chlorine) and electron microprobe (all other major elements) analyses. The Fe^{3+}/Fe_{tot} ratio was collected at room temperature by micromössbauer technique. The result shows a Fe^{3+}: Fe^{2+} atomic ratio of 59:41. Analytical data (wt%) gave: SiO_2 41.69, TiO_2 5.30, Al_2O_3 13.65, Cr_2O_3 0.09, Fe_2O_3 4.52, MgO 15.54, CaO 11.03, MnO 0.11, FeO 2.83, Na_2O 2.88, K_2O 0.96, H_2O 0.70, F 0.24, Cl 0.08, O=(F,Cl) -0.12, sum 99.50. The empirical formula, based on 24 total anions is: $^{A}(Na_{0.82}K_{0.18})$ $^{B}(Ca_{1.73}Fe^{2+}_{0.26}Mn_{0.01})$ $^{C}(Mg_{3.38}Fe^{2+}_{0.09}Fe^{3+}_{0.50}Al_{0.44}Cr_{0.01}Ti_{0.58})$ $^{T}(Si_{6.09}Al_{1.91})$ O_{22} $^{W}[O_{1.19}(OH)_{0.68}F_{0.11}Cl_{0.02}]$.

The mineral is monoclinic, space group $C2/m$, a 9.8378(8), b 18.0562(9), c 5.3027(6) Å, β 105.199(9)°. The crystal structure was refined to $R_1 = 0.040$ for 1783 observed $[F_o > 4\sigma(F_o)]$ reflections. The partition of cations among the various sites was carried out so as to match the chemical data and minimize the differences between theoretical and experimental site scatterings. The refined site scattering at M4 site showed no substantial Fe^{2+}, whereas the comparison of theoretical and experimental site scatterings from M1, M2, M3 and A sites shows a fairly good agreement. This suggests that the crystal used for the structural study has a slight Fe^{3+}/Fe_{tot} ratio higher than the crystal used for the Mössbauer analysis, and this would place it closer to the end-member composition.

A proposal for the approval of the new mineral and its name will be submitted soon to the IMA-CNMNC.

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First occurrence of octahedral V^{5+} in micas: the case of the new mineral balestraite, $KLi_2VSi_4O_{10}O_2$

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Keywords: balestraite, new mineral, Li-mica, V-mica, Cerchiara mine, pentavalent vanadium.

A mica-supergroup mineral characterized by a very high V content and completely free of Al was found at the boundary between carbonate secondary veins and hematite bands occurring in the manganesiferous ores associated to the metacherts of the ophiolitic sequences at the Cerchiara mine, Eastern Liguria (Italy). Chemical (EPMA and LA-ICP-MS), as well as structural (SX-XRD) characterization, supported by Raman data, led to the definition of a new mineral species belonging to the mica supergroup which was named balestraite after Corrado Balestra, a prominent Italian amateur mineralogist. Balestraite, ideally $KLi_2V^{5+}Si_4O_{10}O_2$, is a 1*M* trioctahedral mica crystallizing in the *C*2 space group, with a = 5.2024(5) Å, b = 8.9782(7) Å, c = 9.997(2) Å, β = 100.40(2)°, V = 459.3(1) $Å^3$, Z = 2. The reduction of symmetry from the “ideal” space group *C*2/*m* is due to the ordering of V at only one (M2) of the two pseudo-symmetric octahedral sites, while Li almost fully occupies the other two sites. This ordering scheme is made evident by both the site scattering (22.4 e^- in M2 vs. 3.0 and 3.2 e^- in M1 and M3, respectively) and the geometrical features of the three octahedra. The Raman spectrum shows no peaks in the region of the O-H stretching band (3300-3800 cm^{-1}) and therefore balestraite was considered as completely anhydrous. With this assumption, the charge balance of the formula requires all vanadium to be present at the pentavalent state. This requirement is fully confirmed by the geometrical features of the M2 octahedron exhibiting a [2+2+2] distribution characteristic of the valence state +5 (Schindler et al. 2000). The presence of octahedral V^{5+} is also supported by the occurrence of a high-wavenumber Raman band (973 cm^{-1}), in keeping with what reported by Frost et al. (2005) for symmetric vibrational modes from $V^{5+}O_6$ units in decavanadate minerals. The peculiar composition of the octahedral sheet together with the tetrasilicic character of the tetrahedral sheet and its anhydrous character lead to unusual geometrical features for this mica.

The occurrence of V^{5+} together with the virtually complete $O^{2-} \rightarrow OH^-$ substitution at the O4 site indicate strongly oxidizing conditions of crystallization which are supported by the occurrence of balestraite at the boundary of hematite bands.

The mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2013-080).

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"La Fossa" crater at Vulcano, Aeolian Islands (Italy): A treasure trove of minerals important for material science

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Keywords: Bi-oxysulfate, sublimate, Vulcano fumarols.

Bismuth oxide sulfates meet with interest in chemistry and material sciences as high ionic-conducting materials (Smirnov *et al.*, 2003; Crumpton & Greaves, 2004). The occurrence of these compounds in Nature is very rare, although more than 10 synthetic bismuth oxysulfates have been described in the literature (Aurivillius, 1987, 1988; Francesconi *et al.*, 1998; Smirnov *et al.*, 2003; Crumpton & Greaves, 2004). To date, only two hydrated phases, cannonite, $Bi_2(SO_4)O(OH)_2$ (Stanley *et al.*, 1992; Capitani *et al.*, 2013) and riomarinaite, $Bi(SO_4)(OH)\cdot H_2O$ (Rögner, 2005), and the two recently approved anhydrous oxysulfates, baliæžuniæite, $Bi_2O(SO_4)_2$ (Pinto *et al.* 2013) and leguernite, $Bi_{12.67}O_{14}(SO_4)_5$ (Garavelli *et al.* 2013), are known as minerals. Baliæžunicite and leguernite were found in a sublimate assemblage collected in 1990 from high temperature fumaroles of the La Fossa crater of Vulcano (Aeolian Islands, Italy). In the same sublimate assemblage, strictly associated to them, a third Bi-oxysulfate phase was found. It represents a potential new mineral corresponding to the synthetic phase $Bi_{28}O_{32}(SO_4)_{10}$ described by Aurivillius (1987). This new natural Bi-oxysulfate from Vulcano occurs as needle-like crystals up to 0.4 mm long and 0.01 mm across. Single-crystal X-ray diffraction data indicate monoclinic symmetry, space group $C2$, with unit-cell parameters a 21.659(4), b 5.6648(9), c 15.092(3) Å, β 119.43(1)°, V = 1612.7(5) Å^3 and Z = 4. The crystal structure is built up of blocks of Bi and O atoms extending in the b direction, but separated from each other in the a and c directions, and of pleated layers of SO_4^{2-} tetrahedral roughly parallel to (100). The Bi, O blocks of composition $[Bi_{14}O_{16}]^{10+}$ have a fluorite-like structure and contain 6 rows of (OBi_4) tetrahedral chains. The structure of this new phase shows strong similarities with that of leguernite, in which similar fluorite-like Bi-O blocks of composition $[Bi_{12}O_{14}]^{8+}$ extend along [010].

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Fumarolic minerals after the 1944 Vesuvius eruption

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Keywords: Vesuvius, 1944 eruption.

The 1944 eruption of Vesuvius was the last eruption of this volcano and marked the transition from an open conduit to a closed conduit state. The eruption took place during wartime so that nobody was interested to sample fumarolic minerals before and after the eruption. The only mineralogical studies were made by A. Parascandola (1951) who indicated the presence in the fumaroles of twelve mineral species. As a part of a joint project concerning the study of fumarolic minerals of the Italian volcanoes, a systematic investigation was undertaken by us.

A number of species never found before at this locality have been characterized: ammineite (Russo & Campostrini, 2011), artroeite (Campostrini & Gramaccioli, 2005), brochantite, caledonite, cerusssite, connellite, coulsellite, gearksutite, hydrocerussite, linarite, matlockite, mimetite, parascandolaite (Demartin et al, 2014), phoenicochroite and sellaite. Many of these species such as phoenicochroite, coulsellite and caledonite have never been found in fumarolic environment and their occurrence is particularly interesting.

Parascandolaite, $KMgF_3$ is a new perovskite-type fluoride and the presence of matlockite was confirmed after the doubtful report by Zambonini (1910).

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The structure of cyanotrichite: a combined analysis of Automated Electron Diffraction Tomography and Synchrotron Powder X-ray Diffraction

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Keywords: Electron crystallography, automatic diffraction tomography, powder X-ray diffraction.

The hydrated copper-aluminium sulphate cyanotrichite, ideally $Cu_4Al_2(SO_4)(OH)_{12}2H_2O$, often occurs in sky blue clumps or aggregates of sub-millimeter sized fibrous crystals. The problem of indistinguishable admixing of variable amounts of carbonate-cyanotrichite with cyanotrichite, the close association with other copper sulphates (chalcoalumite, brochantite) and the very small size of the acicular crystals hampered to date an *ab initio* structure determination from conventional X-ray diffraction. In light of these difficulties, we have taken advantage of the recent development of precessed automated electron diffraction tomography (ADT) combined with synchrotron powder X-ray diffraction to investigate the crystal structure of cyanotrichite. Through ADT investigation, two similar monoclinic cell were determined, corresponding to cyanotrichite (a = 10.16, b = 2.90, c = 12.64 Å and β = 92.4°) and carbonate-cyanotrichite (a = 10.16, b = 2.91, c = 12.42Å and β = 98.4°). A structure model was obtained *ab initio* by direct methods in space group *C*2 from electron diffraction data and tested with the Rietveld method against X-ray powder diffraction profiles. All reflections in the powder pattern were indexed with the two cyanotrichite-like phases, according to electron diffraction data. The Rietveld analysis, consistently with electron diffraction investigations, indicates that the refined structural model has based on $Al(OH)_6$ octahedra interconnected through common edges to build infinite columns running along **b**. Each Al-columns is coupled by sharing the remaining edges to two Cu-columns based on Cu distorted octahedra giving rise to ribbons along **b**. These ribbons are linked by SO_4 tetrahedra to form corrugated layers.

SESSIONE S14

Human activities and natural environment: News from Environmental Mineralogy and Geochemistry

CONVENORS

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Antimony removal from aqueous solutions by the use of Zn-Al sulphate layered double hydroxide (LDH)

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Keywords: Zn–Al sulphate layered double hydroxide, Sb(V) contamination, wastewater treatment.

Antimony represents an element of increasing environmental concern for its toxicity. It is listed as a priority pollutant by the World Health Organization, which established a guideline value of 20 µg/L for drinking water. Due to its various industrial uses, its global fluxes have increased at least ten-fold in the last decades, resulting in an increase of environmental Sb contamination. There are not many developed methods for the removal of Sb from contaminated waters. In oxic conditions $Sb(OH)_6^-$ is the dominant Sb(V) form over a wide pH range. This study focuses on the efficiency of a specific LDH in removing Sb(V) from aqueous solutions. LDHs are a group of compounds with a layered structure, hosting anions in the interlayer, which can exchange with anions present in solution, making LDHs potentially suitable for the removal of contaminants from aqueous solutions. Among the possible LDHs compositions, in this study we examined the removal of aqueous Sb(V) by Zn–Al sulphate LDH (Ardau et al 2013 and references therein). The removal of Sb(V) from solution was carried out in a batch system by using variable Sb(V) concentrations and LDH amounts. Dosages were chosen assuming that the main Sb(V) removal mechanism is an interlayer anion exchange, and that for maintaining the electroneutrality of the LDH, the entrance of 1 mole of $Sb(OH)_6^-$ should be compensated by the exit of 0.5 mole of SO_4^{2-} present in the interlayer. Effectively, the removing of Sb(V) from aqueous solution is accompanied by a concomitant release of sulphate from LDH to solution. Sulphate release increases vs time proportionally to the Sb(V) removal. The $Sb(V)_{removed}/S_{released}$ molar ratio results close to 2. XRD analyses showed a complex LDH structural rearrangement during the exchange processes. Such rearrangement possibly entails for an initially rapid Sb(V) removal, slowing down as the availability of "exchange sites" diminishes. The efficacy of Zn–Al sulphate LDH in removing Sb(V) from solution can rapidly reach ~100%, providing that in starting conditions $Sb(OH)_6^-{}_{solution}/SO_4^{2-}{}_{solid}$ 4^{2-} substitution cannot be obtained, and the final product will always contain a certain amount of residual SO_4^{2-}. All above granted, the study confirms the huge capacity of Zn-Al sulphate LDH to adapt the original structure in order to host different-sized/charged anions, supporting their potential key role in the water treatment. For Sb(V), the optimal operational conditions will be a compromise between the time wished for its removal and the cost of LDH dose.

Acknowledgements: This study was financially supported by the Consorzio AUSI (Consorzio per la Promozione delle Attività Universitarie del Sulcis-Iglesiente).

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New data on composition, leaching behaviour and citotoxicity of urban $PM_{2.5}$ from Rome city, in the year 2013

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Keywords: Urban PM2.5, leaching test, citotoxicity.

Previous investigations on $PM_{2.5}$ from the city of Rome provided information about the inorganic fraction, constituted by abundant sulphates, oxides and other mineral phases. Moreover, preliminary data from leaching tests of heavy metals, referred to 2011 and 2012 samples, were also reported in previous works (Mazziotti Tagliani et al., 2012; Armiento et al., 2013). Bulk chemical composition evidenced the presence of heavy metals, in particular As, Cd, Cu, Cr, Fe, Ni, Pb and Zn, and their potential mobility was evaluated by a batch kinetic leaching test, using a physiological solution (mimicking the pulmonary environment, pH 7.4, 37 °C). According to standard procedures (2008/50/CE), both PTFE and quartz filters were utilized.

In 2013, two new $PM_{2.5}$ seasonal samplings, in three different urban sites, were carried out, during winter and summer.

Interestingly, the total metal concentrations measured show, for some elements and in some urban stations, substantial differences between the winter and summer samples. Regarding the leaching behaviour, Cd resulted always as the most mobile heavy metal, whereas no Fe release was observed so far. In winter, only Cd and Pb were detected in leaching solutions, with lower mobility respect to the summer samples, which present higher elements leaching also for Cu, Ni, and Zn.

Different heavy metal concentrations originate from various and different sources, and are influenced by different climate conditions, e.g. during winter, cold and rain inhibit air particles dispersion, which is much more abundant in summer. Leaching tests seem to confirm this inference, suggesting that the elements are present in different mineralogical phases.

The toxicity of the leached material was evaluated in an array of *in-vitro* experiments by using two different, physiologically relevant cell models: a human alveolar epithelial cell line, A549, and human polymorphonuclear leucocytes freshly purified from periferal blood. Cell homeostasis and responsiveness to primary functional stimuli were significantly affected by the compounds leached from $PM_{2.5}$ without impairement of cell vitality, with the compounds leached from winter PM being generally more effective than those from summer PM. Further experiments are in progress to evaluate whether either soluble compounds or nanoparticles play a role in the effects observed.

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Removal of metals from mine-waste drainages (Iglesias, Italy) by Al-induced precipitation of LDH

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Keywords: mine drainages, metal contamination, waste-water treatment.

The removal of toxic metals from waste waters is one of the most important problems in mining environments. A number of technologies to reduce the release of toxic metals to the environment have been developed. Layered double hydroxides (LDH) are a series of lamellar compounds with the general formula $[M^{2+}{}_{1-x}\ M^{3+}{}_{x}\ (OH)_2]\ (A^{n-})_{x/n}\ .\ mH_2O$, widely studied for the removal of anionic pollutants from water thanks to their large specific surface area and their high anion exchange capacity. Starting point of our study was the finding of LDH (i.e., glaucocerinite and zincowoodwardite) spontaneously formed in mining environments and their efficacy in the attenuation of As content in drainage water (Ardau et al., 2011). Synthetic LDH of Zn-Al were prepared in laboratory and tested for sorption of As, Mo and Sb (Ardau et al., 2012; Ardau et al., 2013 and this issue). Our idea was to use mine-waste drainages of the Monteponi mine area (Iglesias, Italy) as a reagent for the precipitation of LDH and the consequent removal of metals. The mine-waste drainage used in the first experiments is characterised by neutral pH and high levels of SO_4 (~ 4000 mg/L), Mg (~ 600 mg/L), Zn (~ 200 mg/L) and other metals such as Pb, Mn and Cd, but very low concentration of Al. The experiment was carried out by adding to water an adequate amount of a salt of Al in order to induce the LDH precipitation. NaOH was added to solution before the beginning of the experiment to maintain a neutral pH. White precipitate was obtained and successively analysed by XRD and, prior acid digestion, by ICP-OES. Chemical analysis was also carried out on the water before the experiment and after filtration to separate the solid phase. First results showed that the mineralogical nature of the compound is a pure LDH, without the apparent co-precipitation of other phases, in which the chemical composition showed a molar $[Zn^{2+}]/[Al^{3+}]$ ratio equal to 2.4. Aluminium was not detected in the water at the end of the experiment, which indicates a complete precipitation of Al added to the mine-waste drainage. These preliminary results encourage further investigations on the removal of divalent metals (e.g. Zn, Mn, Cd, Ni, etc.) from M(III)-poor mine waters by inducing LDH precipitation.

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Chromium adsorption and desorption on naked Surface Active Maghemite Nanoparticles (SAMNs): possible environmental implications

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Keywords: water remediation, Cr(VI), magnetic nanoparticles.

The importance of the interface between geosphere and biosphere is known and represents one of the most fascinating frontiers of minerals science, especially if explored at nanoscale. Heavy metal release, transport and dispersion into the biosphere have a direct impact on the environment and on human health. Therefore, there has been an increasing development of applications for water and soils remediation, among which magnetic nanoparticles stand out. Environmental applications and risk assessment of manufactured nanoparticles greatly depend on the understanding of their interactions with water and soils. Novel superparamagnetic nanoparticles (SAMNs), constituted of stoichiometric maghemite, characterized by specific surface chemical behavior without any coating or superficial modification, are stable in water for months as colloidal suspensions, present a high average magnetic moment and can be easily derivatized to immobilize specific molecules. Various studies were recently carried out exploiting these peculiar properties (Magro et al., 2012a; Magro et al., 2012b). The applicability of SAMNs as adsorbent for chromium(VI) in water and soil remediation is under study. Chromate adsorption on the nanomaterial was attributed to the presence of under-coordinated iron(III) sites on nanoparticle surface, which allow the binding of Cr(VI) via dative bonds. The interaction of Cr(VI) with SAMN surface caused a red shift (140 nm) of SAMN@Cr(VI) spectrum compared to bare SAMNs. Chromate binding on SAMNs was studied according to the Langmuir isotherm model and Langmuir isotherm constants, K and Γ_{max} were found to be 2.5 L × g^{-1} and 44.0 mg × g^{-1}, respectively. This last value is higher than those reported for various compounds commonly used as adsorbents. Recovery of the SAMN-chromate composite can be accomplished using magnetic properties of the material and chromate can be desorbed by increasing solution pH. By this way, SAMNs can be utilized for subsequent cycles of remediation without reducing their efficiency. This is one of the very few studies that have, to date, examined chromium removal by naked maghemite nanoparticles. The maintenance of adsorption capacity coupled with the easy removal make these nanoparticles an attractive material for large scale water purification applications. Future experiments using this strategy with SAMNs are planned.

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A time- and cost-saving method for the quantitative determination of inorganic soil conditioners: a case of study on zeolitite in clay soils

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Keywords: zeolitite, polyphasic, clay-soil.

Zeolitites are natural rocks with peculiar physical chemical characteristics, which make them capable of controlled cations exchange mechanism when mixed to soils, with evident advantages for a sustainable development of agricultural practices. A new method is presented to quantitatively determine the amount of zeolitite added to soils during field tests conducted within the European LIFE +2010 project "ZeoLIFE - Water pollution reduction and water saving using a natural zeolitite cycle" (project code: LIFE +10 ENV/IT/000321), in order to assess the effectiveness of zeolitites as soil conditioners, partly replacing chemical fertilizers.

Standard samples were prepared by mixing known amounts of zeolitite and an "averaged soil sample" obtained by carefully quartering, grinding and mixing soil samples randomly taken from different points of the selected experimental field. In detail, 1, 2, 3, 4, 5, 7, and 10 wt% zeolitite coming from a selected quarry were added to the averaged soil; 10 wt% corundum NIST SRM 674a was also introduced in each standard sample in order to estimate intensity variations due to sample preparation and instrumental biases.

Soil sample taken from different parcels (5, 7 and 15 tons/ha zeolitite) in which the experimental field was divided were manually crushed and dried under the same ambient conditions used for the preparation of the standards. After quartering and grinding, each sample was added with 10 wt% NIST certified standard, and XRPD patterns were collected, at the same experimental conditions used for standards.

Measurements on soil samples demonstrate a good agreement between calculated and measured values, even if almost all replicas underestimate the calculated values. Slight variations with respect to calculated values can be attributed to inaccuracy during zeolitite spreading on the experimental plot, as well as to inhomogeneity due to imperfect plowing. In addition, assuming that spreading and plowing were homogeneous, and that the samples collected were representative, in our opinion underestimation can be attributed only to an overestimation of the apparent density of the soil.

Despite the fact that the discussed method is specifically suited for the ZeoLIFE project purposes, it could be conveniently generalized to all the applications that require the quantitative determination of mono or polyphasic crystalline materials within complex mixtures.

The wild rat as sentinel animal to detect potential risk for human environmental exposure to asbestos: seeking latent sources in Casale Monferrato (NW Italy)

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Keywords: Asbestos, Sentinel animals, SEM-EDS, Hidden sources.

Asbestos have been incorporated into many different products since its discovery, centuries ago. Countless applications of asbestos result from their many unique characteristics. It has long been recognized the link between their breathing and the pulmonary related diseases (asbestosis, malignant mesothelioma and lung cancer) in occupational exposed workers. For this reason asbestos have been banned in many countries, including Italy (L.257/92). Also a particular kind of exposure, specifically anthropogenic environmental exposure, shown his dangerousness, e.g. in the areas where asbestos industries were active.

At present, the dose-response relationship has no a threshold and the relationship between exposure to environmental sources of asbestos and health effects still represents an open issue. In Casale Monferrato city (Piemonte Region, NW Italy), the biggest Italian plant of Eternit® (a mixture of cement-asbestos) was active from 1907 to 1986 but sources of exposure may still exist in the environment and they can represent a potential of human exposure. The idea was to identify the possible presence of previously unrecognized asbestos sources, by measuring the asbestos fibre content in the lungs of wild rats (used as sentinel animals). Measurement of the lung fiber burden in wild rats has proved feasible. Previously we carried out a pilot study that demonstrated that it was possible not only to detect, but also to characterize asbestos fibers both qualitatively and quantitatively. Casale Monferrato district has been divided in a grid with 61 cells (200 x 200 m). Neighborhood with different degree of priority have been identified, based on technological processes and asbestos transports, historically reported within the city. We established to capture a minimum of 5 wild rats in each cell with a multi-capture device and for each pool constituted by 5 lungs, SEM–EDS investigation will be carried out. Until now, 18 wild rats have been captured in five different cells but only in one of them, the completed pool has been collected. The SEM-EDS investigation of this pool showed 40800 fibers per gram of dry weight (ff/gdw) of asbestos tremolite and 5100 ff/gdw of asbestos grunerite, i.e. a burden of asbestos both from natural and anthropic source. In April this project titled "Sentinel animals for asbestos", was introduced to the citizenry and authority of Casale Monferrato with the aim to make the inhabitants aware of our research, and to involve them to obtain directly indication about the sites where rats are present to increase their capture. A Facebook page for this aim has been opened and promoted.

Geosphere-biosphere interactions in soil-plant systems, Iglesiente mining district, Sardinia

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Keywords: heavy metals, soil, plant.

The Iglesiente area (southwestern Sardinia) is characterized by a geochemical anomaly of heavy metals such as Zn, Pb, and Hg, and is affected by environmental pollution associated with several centuries of mining activity.

In this study, we investigated the mobility of heavy metals in the interactive environmental system soil - soil pore water- plant, with specific reference to *Pistacia lentiscus* L., a spontaneous vegetal species that may be useful for phytostabilization of mine waste piles (Bacchetta et al., 2012).

The soil bulk contents of several heavy metals (Zn, Pb, As, Cd, and Hg) exceed Italian law limits (D.Lgs 152/2006) for 'industrial' soils. These high contents are partly the expression of a natural anomaly; however, in mining affected sites contents are higher than the local background, demonstrating the anthropic contribution. The mobility of metals was estimated through two different single extraction chemical methods: with DTPA solution, followed by analysis of the extracted metals by ICP-OES; and with sodium citrate/hydroxylamine hydrochloride/TEA followed by colorimetric titration with Dithizone (DZ) solution (Pinto et al., 2010). The two methods show a good correlation, although the DZ method gives higher estimates of 'mobile' metals.

An innovative aspect of this study was the sampling and analysis of soil pore waters as a direct measure of metal mobility and bioavailability (Tye et al., 2003; Di Bonito et al., 2008). Among trace metals, Zn is usually the most abundant (up to 8 mg/L), except for two sites where very high Ba contents (up to 73 mg/L) were measured. Geochemical modelisation shows in general an approach to equilibrium of the solutions with the minerals present in soils.

With respect to transfer to the biosphere, the metal concentrations (Zn, Pb and Hg) in *P. lentiscus* are much lower than, but roughly proportional to, contents in soil (BAC<<1), and decrease in the order roots>stems>leaves, with the partial exception of Hg, for which there is locally an enrichment in leaves. The P. lentiscus seems then to behave as a tolerant species with strategies of exclusion, and with character of 'indicator'.

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Colloidal precipitates related to AMD settings: a combined HT-XRD and bulk leaching test approach

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Keywords: Colloidal precipitates, Libiola mine, PTE.

The AMD (Acid Mine Drainage) alteration processes influence deeply the dispersion of chemical elements around abandoned mine sites. Previous works highlighted the fact that near abandoned Fe-Cu mine where AMD takes place low-crystallinity and/or amorphous precipitates play a major role in controlling the fate of pollutants in the surrounding environment. While it is well known that Fe-rich precipitates tend to transform to more stable crystalline phases little is known on the phase transition of Cu-Al rich amorphous phases. The colloidal precipitates object of this study were distinguished on the basis of their crystallinity. The aim of this work was to a) induce a possible phase transition through HT-XRD analyses and b) evaluate the capacity of the transformation product to release PTE (Potential Toxic Elements) using bulk leaching tests. The four samples are representative of 1) Fe-rich amorphous phases deposited by waters with pH= 7,62 and Eh=265 mV; 2) Al-amorphous phases originated by water with pH= 4,95 and Eh= 298,5 mV 3) Cu-Al low crystallinity precipitates composed by (hydro)woodwardite [$(Cu_{1-x}Al_x)(OH)_2(SO_4)_{x/2}\cdot nH_2O$], allophane [$Al_2O_3(SiO_2)_{1.3-2}\cdot 2.5\text{-}3H_2O$] (pH= 7,8 and Eh=230,5 mV) and 4) Fe-rich crystalline phases (pH= 6,8 and Eh= 179,6 mV) composed by goethite (FeOOH), jarosite [$KFe_3(SO_4)_2(OH)_6$] and an unidentified amorphous phase. Bulk chemical analyses were carried out to study the chemical composition of the samples, and showed sharp differences between the chemistry of Fe-rich precipitates and the others. The major element in these samples is by far Fe, followed by Cu, S, and Al with minor amounts of Ni and Zn. The major elements of Al rich and Cu-Al rich precipitates are Si, Al, Cu, Zn, S, Fe with minor amounts of Ni. In particular, in the Cu-Al rich samples were found high amounts of REE, which show an average concentration of 137 ppm, with a maximum of more than 600 ppm for Y. In order to monitor the possible transition to crystalline phases, in situ HT-XRD coupled with TG-DTA analyses were carried out. These experiments highlighted that the transition to more crystalline phases can occur in two different ways a) a direct transition to product with higher crystallinity b) an indirect transition with the occurrence of an intermediate amorphous phase precursor to the high crystallinity phases. To investigate the possibility that these low crystallinity or amorphous phases release into the environment PTE during their transformation into crystalline phases, bulk leaching tests were performed on the untreated samples and on the heated ones. The results testify that the elements show different behaviour due to their different affinity with the reaction product and to their chemical behaviour; in particular, the high amount of the PTE is not released during the phase transition process and is still retained by the solids.

Antimony removal from aqueous solution by Layered Double Hydroxides

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Keywords: Antimony, Layered Double Hydroxides, polluted water treatment.

Antimony (Sb) is a toxic trace element widely present in environmental compartments through both natural and anthropogenic sources. The World Health Organization and the Italian Legislation set safe drinking water levels for Sb at 20 µg L^{-1} and 5 µg L^{-1}, respectively (WHO, 2011; GURI, 2006). Typical concentrations of Sb in natural unpolluted waters are very low, less than 1 µg L^{-1}, but increase up to few tenths of mg L^{-1} as a consequence of anthropogenic activities, especially in areas near mining sites and smelter activities (Cidu et al., 2013). In oxygenated waters Sb(V) is the predominant species in solution as the oxyanion $Sb(OH)_6^-$.

Possible solutions for pollutants abatement from water comprise the use of sorption technologies. Layered Double Hydroxides (LDHs) are a group of natural and synthetic compounds, widely used in remediation studies. LDHs have general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}]^{x-} \cdot mH_2O$, with large compositional variability (e.g. M^{2+} = Mg, Zn, Ca; M^{3+} = Al, Fe; A^{n-} = Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}); their structure consists of brucite-like sheet, positively charged, stacked along the *c* axis with (oxy)anion and water molecules in the interlayer. LDHs have high anion exchange capacity and are able to remove environmental pollutants present in neutral and slightly alkaline waters as (oxy)anions. Also $M^{2+}M^{3+}$ oxides derived from LDHs calcination can be used to remove toxic (oxy)anions from water, because are able to reconstruct the layered structure trough rehydration and sorption of (oxy)anions (Goh et al., 2008). Batch sorption experiments were carried out to test the ability of LDHs in $Sb(OH)_6^-$ removal from aqueous solutions. Experiments were performed with synthetic NO_3-LDHs and calcined LDHs, with different cationic composition (Mg/Al,Fe-LDHs and Zn/Al-LDHs) in order to identify the most effective composition. First results show that both calcined and uncalcined LDHs have good potential use as $Sb(OH)_6^-$ removers. XRD and Attenuated Total Reflection (ATR) IR data suggest that $Sb(OH)_6^-$ can be efficiently removed from solutions through different processes in function of different cationic composition, and encourage further investigation.

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Chrysotile within calcite veins from Northern Apennines

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Keywords: Chrysotile, calcite veins, Northern Apennines.

In the Northern Apennines several olistoliths made up of serpentinites, calpionelle limestones and ophiolitic breccias have been recognized within the Porcellara Complex, Monte Cassio Unit. These olistoliths are frequently crossed by a dense network of centimeter to decimeter veins generally filled by carbonate minerals (e.g. La Costa, Berceto, PR). Morphological and compositional data (SEM-EDS and XRPD) have revealed that these carbonate minerals consist mainly of well-formed, white to milky calcite crystals, strictly associated with chrysotile. This mineral is found as white thin fibers (< 1 micron), grew up in intimate association with calcite crystals. These fibers may be very rare and randomly scattered within the crystals of calcite, or can be grouped into bundles of millimeter to centimeter size. At times, the chrysotile can get to completely fill the vein. Chrysotile fibers are well-formed and euhedral at all scales from hand specimen to electron microscope images. In some cases, individual fibers of chrysotile are not visible in hand specimen or under the petrographic microscope; however, SEM images show the characteristic elongate crystal morphology. The fibers are also characteristically curved at the millimeter scale.
It is important to note that the fibers of chrysotile appear, frequently, as a physical extension of calcite crystals, without any evident morphological discontinuity in the transition from a massive (calcite) to a fibrous (chrysotile) appearence. The results of detailed SEM-EDS elemental analyses carried out in various segments of the contact areas between calcite and chrysotile crystals seem to show a gradual transition in chemical composition from pure calcite to pure chrysotile phases, passing through various intermediate arrangements.

Employment of zeolitites in open field experiments: characterization and monitoring of the cation exchange mechanisms in relation to the crop cycle progress

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Keywords: zeolitite, ammonium, CEC.

The project "ZEOLIFE - Water pollution reduction and water saving using a natural zeolitite cycle" (LIFE+10 ENV/IT/000321) has been conceived to test an innovative integrated zeolitite application having the aim to experience the employment of natural and ammonium exchanged zeolitite (NH_4-zeolitite hereafter) in a two-years open field test (www.zeolife.it for more details).

This summary describes some of the results relating to the characterization of zeolitite samples collected in the experimental field during different stages of the crop cycle (i.e., after the application of synthetic fertilizers but before the development of the plants, and at end of cultivation cycle after harvest). In fact, during the first crop year, the experimental field was subdivided in six plots of about one hectare each: one plot was amended with 7Kg/m^2 of NH_4-zeolitite prepared by the prototype, two plots with 5 and 15 Kg/m^2 of natural zeolitite, and three plots were not amended and used as control. The NH_4-zeolitite plot was amended with 50% chemical fertilizers comparing to the quantity used in the control plot, while 5 and 15Kg/m^2 natural zeolitite plots with 70% chemical fertilizer. All plots were sown with grain sorghum.

Fertilization was done with urea and diammonium phosphate using 5.561 Kmoli/ha and 0.1945 Kmoli/ha (relative to the control plot), respectively, according to the production disciplinary. Since the conversion of urea to ammonium occurs according to the following reactions:

$$(NH_2)_2CO+H_2O \rightarrow NH_3(gas)+H_2NCOOH$$
$$2NH_3(gas)+H_2O \rightarrow 2NH_4(+)+2OH(-)$$

it follows that for each mole of urea can be formed, as a maximum, two moles of NH_4 (diammonium phosphate has the same conversion ratio). Therefore, in the control plots may be formed, as a maximum, 11.557 Kmoli/ha of NH_4 (5.578, 8.090 Kmoli/ha in the plots in which the reduction of synthetic fertilizers compared to control were 50 and 30%, respectively).

The laboratory tests indicated that the maximum operational C.E.C. of the selected zeolitite for ammonium is 0.389 moles/Kg; it is likely to assume an "in-situ (on field) C.E.C." not higher 50% of the operational C.E.C. It follows that in the two plots amended with natural zeolitite, all the ammonium that may be formed from synthetic fertilizers can potentially be absorbed by zeolitite itself. On the other hand, this should not occur in the plot amended with NH_4-zeolitite that should be completely ammonium saturated.

Experimental measurements (chemical analysis of major elements, exchangeable ammonium and total nitrogen) on soil-zeolitite samples collected in the experimental field, show that there is a net change in the chemistry of zeolitite after the cultivation cycle. In particular, at the end of the first one:

1) in NH4-zeolitite there is almost no residue of exchangeable ammonium (0.248mmol/Kg, equivalent to 17.3 moles/ha referred to the parcel amended with 7Kg/m^2);

2) in the natural zeolitite (i.e., parcels amended with 5 and 15Kg/m^2 of natural zeolitite) remains a modest amount of exchangeable ammonium (0.638 and 0.428 mmol/kg, equal to 31.9 and 64.1 moles/ha);

3) in the zeolitites of all plots the content of Ca and Mg increases, whereas Na and K decreases, both with respect to NH_4- and natural zeolitite at the beginning of the experiment.

Morphological and compositional data of erionite from Lessini Mounts, NE Italy

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Keywords: Lessini, zeolites, erionite.

In the Lessini Mounts a volcanic activity developed from the late Paleocene to the late Oligocene (De Vecchi & Sedea, 1995) with the emplacement of submarine and subaereal lava flows and tuffs. These rocks (basanites, alkali-basalts, transitional basalts to tholeiites) are often deeply weathered, with vesicles and fractures filled by secondary minerals . These are mainly represented by zeolites such as phillipsite, harmotome, chabazite, analcime, gmelinite, natrolite, offretite and erionite. Recently, erionite has been carefully investigated because of its link to malignant mesothelioma (Dogan et al., 2006); Bertino et al., 2007). As a consequence, erionite has been classified as a Group I Human-Carcinogen by the International Agency for Research on Cancer and this makes it the most carcinogenic naturally occurring fibrous mineral known. In this work, we present morphological and compositional data on erionite crystals recently discovered in the Lessini Mts. (Mattioli et al., 2008).

From a morphological point of view the studied samples show two different types of erionite. (1) Prismatic to acicular crystals ended by short hexagonal prisms of about 15 µm in diameter, whereas the main body of the crystals is extremely thin (diameter is 5 µm), is characterized by an excellent, prismatic cleavage and devoid of any geometry. (2) Fibrous crystals with diameter <1 µm and a length up to about 50 µm; these fibers are flexible and tend to intimately aggregate in parallel bundles of up to 10 µm in diameter. Erionite of both types show a great tendency to break down into fibers, which are potentially extremely pathogenic upon inhalation. In the type (1) the majority of the measured fibers is in the range 2-30 µm in length and 0.1-0.4 µm in diameter, whereas in the type (2) almost all of the measured fibres are 50 to 60 µm in length and <0.1 µm in diameter. The EDS spectra acquired on the bundles of fibers revealed the occurrence of Ca, Mg, Na, and K as extra-framework cations. In addition, a small amount of Fe was detected. Preliminary semi-quantitative analyses in the type (1) fibers pointed out that chemical composition differs depending on the analytical point, indicating a significant inhomogeneity of the sample.

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Si, Al and Zn biomineralization processes in plant roots of *Euphorbia pithyusa*

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Keywords: biomineralization, soil minerals, phytoremediation.

In the abandoned mine of Ingurtosu (SW Sardinia, Italy) a field experimental trial was carried out in the frame of the UMBRELLA project (7FP EU). The idea of this project was to couple microorganisms with plants to favour metals accumulation in plants and reduce the effects of metal pollution in soils of heavy metals contaminated sites. *Euphorbia pithyusa* was selected as an endemic pioneer plant. About two years after the beginning of the experiment, exploration of the processes occurring at the soil-root interface was carried out by combing X-ray fluorescence mapping (S-XRF) and X-ray absorption spectrometry (XAS) to X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). We observed that Si and Al are mainly concentrated in the epidermis of the roots forming a rim that represent a physico-chemical barrier against organic and inorganic stresses. In addition, Si is able to bind Zn by forming an amorphous Zn-silicate in the epidermis zone. This process leads to the decrease of Zn concentration from the epidermis to the internal part of the root, where Zn is bonded to other Zn atoms. In the case of Fe, the Si-Al rim seems to be more efficient and, as observed in LEXRF maps, Fe is mainly concentrated in the external zone of the roots. EXAFS analysis reveals that the coordination environment of Fe is comparable to that of hematite. The exact cause of Fe precipitation around roots or in the epidermis zone is unknown, but the oxidizing activity of roots, together with the action of microorganisms, is thought to be involved. Si and Al particles of the rim can act as a nucleus for hematite precipitation (Batty et al., 2000) that, in turn, could act as a barrier against metals penetration.

Although Si and Al are not regarded as essential nutrients and the later is an important growth-limiting factor (Rout et al., 2001), obtained results suggest that these elements are fundamental for controlling metal migration through the roots, and their beneficial function for plant need to be reassessed. The addition of microorganisms to the soil at the Ingurtosu mine seems to have no effect on biominerals features, and on Zn and Fe speciation. Our results can be useful for environmental science because biomineralization in plants can lead to development of specific phytostabilization techniques, reducing the mobility of the contaminants and prevents their migration to the groundwater or air, thus decreasing bioavailability for entry into the food chain.

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X-ray absorption spectroscopy study of the structural environment of iron in mineral fibers

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Keywords: Mineral fibers, structural environment of iron, X-ray absorption spectroscopy.

The oxidation state and chemical environment of iron in mineral fibers are crucial factors to assess the bio-chemical activity induced by surface iron activity, which is known to be a primary cause of toxicity as it produces free radical release, mobilization by chelators and iron-catalyzed reactions (Hardy & Aust, 1995). It was observed that antioxidant enzymes and strong iron chelators decrease the toxicity of mineral fibers in cell cultures and experimental animals, strongly suggesting that a crucial role might be played by iron-generated active oxygen species (Fubini & Mollo, 1995). In this context, in order to understand the relationship between structural environment of iron and fibers' pathogenicity, XAFS spectra at the iron K-edge of eight mineral fibers of social and economic importance (chrysotiles, amphiboles and erionite, systematically investigated for the first time) were collected at the BM08 GILDA-CRG beamline (ESRF, Grenoble, France). Both the XANES and EXAFS region were investigated; for all experiments, energy calibration was achieved using iron foil as reference and the position of the first inflection point was taken at 7112 eV. The results show that there is no predominant oxidation state of the iron while the octahedral coordination seems to be prevalent chemical environment, in agreement with literature data (Morgan et al., 1971; Roque-Malherbe et al., 1990; Hardy & Aust, 1995). The present work is within the context of a systematic study of main mineral fibers, in order to get a better understanding of the processes that are the basis of cyto- and geno-toxicity of these compounds, with the final aim to get a conclusive comparison of the toxicity of chrysotile and amphibole asbestos and refute the "amphibole hypothesis" (only amphibole asbestos is hazardous to human health); by ruling out this "hypothesis" there is basically no scientific support to the use of chrysotile asbestos. Within this scenario, the results of this project should be of help to make aware the scientific communities worldwide of the actual toxicological potential of these minerals fibers, and especially that of chrysotile, in order to supply objective tools to the World Organizations to test the "amphibole hypothesis" and decide on the ban of asbestos worldwide.

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The quality of sediments in the Mt. Amiata Hg district (southern Tuscany)

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Keywords: Mercury, Mt. Amiata, multivariate analysis, sediment quality.

The establishment of adequate Sediment Quality Guidelines (SQGs) is a crucial point of the recent debate among the EU member states. In most jurisdictions, there is an increase awareness that proper SQGs for contaminants should be site-specific, and should rely on background concentrations. Accordingly, a detailed characterization of background conditions is fundamental in mineralized areas, where background levels of contaminants may exceed the SQGs proposed for other (non-mineralized) locations.

The Mt. Amiata Hg district (southeastern Tuscany, Italy) hosts the fourth largest Hg producing region worldwide, which was active up to 1970s. In this region, anthropogenic contamination overlaps on the natural Hg (and associated As) anomaly. In the present work, sediments of different age (pre-mining, syn-mining and post-mining) were sampled in order to: (i) reconstruct the history of Hg(As) diffusion in this region; (ii) identify a geochemical marker for sediment quality; (iii) establish the Hg(As) background. The chemical dataset (major elements and Hg and As concentrations) was explored by multivariate analysis by taking into account the properties of compositional data. This analysis showed that pre- and post-mining sediments can be distinguished on the base of the Al_2O_3/CaO ratio. Accordingly, a progressive enrichment in CaO was shown as sediments become younger in age (up to $Al_2O_3/CaO \approx 1$ for syn- and post-mining sediments). Furthermore, Hg in the Mt. Amiata sediment is not randomly distributed, but it is inversely correlated to CaO ($R^2 = 0.87$ after that the terms of the subcomposition Hg-Al_2O_3-CaO were transformed in two coordinates of the real space), increasing up to two orders of magnitude between pre- and syn-mining sediments. Common to most of Hg mines worldwide, final roasted wastes (calcines) at Mt. Amiata are enriched in: (i) CaO, due to the calcination process (lime addition), and (ii) Hg, due to the inefficiency of the Hg extraction process. Then, natural weathering of discarded materials caused CaO and Hg enrichment of post- and syn-mining sediments at Mt. Amiata. According to these results, CaO may act as a proxy for Hg in this area, representing a geochemical marker of calcine weathering and an easy way to evaluate sediment quality.

On the base of Hg contents in pre-mining sediments, a preliminary Hg regional background of 2-6 μg/g is suggested, which largely exceeds the Hg established contamination level for soils in Italy (1 μg/g).

Background levels of potentially toxic elements in ultramafic soils from the Voltri Unit: a mineralogical and geochemical approach

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Keywords: background values, ultramaphic soils, ecotoxic metals.

Ultramafic soils are characterized by the presence of several potentially toxic elements (PTE's; such as Cr, Co, and Ni) that commonly exceed residential and industrial concentration limits according to Italian laws (D.M. 471/1999; D.Lgs 152/2006). Therefore, the determination of the background levels and baseline values of PTE's within serpentinitic and peridotitic soils is of paramount importance in order to evaluate the potential risk of contamination for ecosystems as well as to distinguish between lithogenic and anthropogenic inputs. With this work we investigated the mineralogy, the mineral chemistry, and the bulk chemistry of undisturbed soils and associated parent rocks from four selected sites occurring in the "Bric del Dente Serpentinite" and "Monte Tobbio Peridotite" Formations (Voltri Unit, Ligurian Alps). Selected metal and semimetal concentrations (V, Cr, Co, Ni, Cu, Zn, As, Cd, Sb, Pb) were assessed by ICP-OES at the ARPA-Liguria laboratories according to the EPA-3050B and EPA-6010 methods. The mineralogy and the mineral chemistry of soils and rocks have been determined by means of optical microscopy (transmitted- and reflected light) and electron microprobe analyses (WDS). The bulk chemistry analyses evidenced very high concentrations of Cr (up to 3020 ppm in rocks and 1269 ppm in soils), Ni (up to 1855 ppm in rocks and 1041 ppm in soils), Co (up to 85 ppm in rocks and 64 ppm in soils), and V (up to 199 ppm in rocks and 39 ppm in soils). The mineralogical results showed that most of the Cr is contained within primary Fe-oxides and spinels (mainly magnetite and chromite). Olivine and serpentine group minerals are the main Ni-bearing minerals though non-trascurable Ni concentration have been also detected in Fe-oxides and Ni-sulphides. Among the other identified primary minerals only chlorites are characterized by significant, though very variable, amounts of Co, V, Ni. In general, most of the detected metal-bearing mineral species resulted completely unaltered either in rocks and soils evidencing their resistance to weathering and their tendency to remain as stable residual minerals within soils. Secondary authigenic minerals in soils are mainly represented by Fe-oxides and -oxyhydroxides and clay minerals. In general they contain relative small amounts of PTE's if compared to primary minerals and cannot be considered as the main source for the bulk metal content of soils. These preliminary results evidenced that all the studied rocks and soils have a baseline values of Cr, Ni, Co, and V well above (up to one order of magnitude) concentration limits of the Italian laws for industrial and residential sites. These baseline values should be considered as the natural background levels of the studied soils since most of the metals are related to the residual mineral species derived from the parent rocks. Further studies are in progress, through leaching experiments, to determine the relative mobility and bioavailability of the studied metals.

Asbestos fate in ACM and lungs: a comparative characterization

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Keywords: Transmission electron microscopy, asbestos, mineral fibers.

In 2006 it has been proposed to introduce the term of "nanosafety". Nowadays, developments in nanotechnology grow increasingly, with the intention of new useful discoveries and the concern of possible health consequences, some of them have been already experienced by mankind since more than 100 hundred years.

Among these health risks, asbestos cement was invented by Hatschek and patented under the name "Eternit" in 1900. Until now, this technologically exceptional material is used in many countries, however accepting the fatal health consequences created by the disease asbestos. It is evident that many protocols applied to the asbestos problem can be easily exploited to monitor these emerging technologies and new harmful mineral nanoparticle and fiber.

From this perspective, we will analyze the fibers contained in two different matrices: the first type artificial and the second type organic. We have purposely avoided to gather information on the source material, not to influence our judgment or to address the analytical process, as if it were performed on an unknown material. In order to characterize the target materials, we combined different analytical techniques: XRPD, SEM and TEM. Handling the three, depending on what samples gradually reveals.

A sample from an unknown fiber cement sheet roof was characterized, combining X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The same was performed on a lung of a eternit factory worker died of mesothelioma, using only TEM because of the sample nature (received already embedded in paraffin).

To the naked eye the ACM sample present two principal component: the cement matrix and the fibrous component. A first investigation through XRPD reveals the possible presence of typical cement phases in the matrix. No fibrous phases has been identified at this point. Having a thought on the production process, we could imagine that the fibers presence in an XRD support is really low in relation to other components. Historically, in asbestos sheet, was recognized a percentage of fibers variable from 10 to 16, randomly distributed in the whole matrix.

Moreover, the sample is heterogeneous powder, multiphase and randomly oriented, all factors that tend to hide the possibility to detect the fibrous component. SEM observation brings in evidence the presence of many fibers bundles distributed in the whole sample and in intimate contact with the matrix components. Going beyond with the TEM, it's possible to identify the fibrous phase combining high resolution (HRTEM) techniques, bright field (BF) imaging and selected area electron diffraction (SAED).

In a preliminary TEM investigation the specimen contained in the lung present partially and totally amorphized fibers, mainly of chrysotile and rare amphibole fibers. These fibers are more sensitive to the beam than the natural ones and seems to be covered by an amorphous shell that shows that the amorphization process starts from the surface and proceed through the core of the fiber.

Isomorphic substitution in mica: implications on the weathering process

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Keywords: flogopite, alteration, surface.

Aim of the work. With this research we have studied the morphological changes, induced by the exposure to acid vapors at controlled temperature, on the surface of selected mica crystals. Specific consideration has been paid to the role of isomorphous substitutions in tetrahedral and/or octahedral sites by bi-and trivalent iron, being this element particularly susceptible to redox reactions.

Materials and methods. To model the surface alteration processes it is necessary to start from minerals that, in addition to being well characterized from the crystal chemical point of view, present a large surface and that, at the same time, have a structure comparable to that of other smaller minerals. For this reason, were selected crystals of phlogopite, a trioctahedral mica, with formula $KMg_3(AlSi_3)O_{10}(OH)_2$, that forms a solid solution with the member annite. In particular were selected crystals that present: i) Fe^{3+} replacing the aluminum in tetrahedral coordination (label FLO); ii) Fe^{3+} and Fe^{2+} only in octahedral coordination (label CZA2d). Natural and acid vapor exposed crystals were characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS); it should be pointed out that the measurements were performed on the same face before and after treatment.

Exposure to oxidising vapors. The treatment in an oxidising atmosphere was done by exposure to sulfuric acid vapors. In particular the samples, glued on coverslips, were placed inside a desiccator containing 20mL of sulfuric acid, and then was left in a oven at 75°C for one week. At his temperature value, H_2SO_4 partially vaporizes generating also SO_3 and SO_2, rendering the atmosphere strongly oxidizing. It is expected that the oxidation interaction takes place for the most part with hydroxyl groups by tearing them a proton. Secondly, it is possible that occurs a redox between Fe^{2+} and the anion $(SO_4)^{2-}$. The divalent iron may oxidize to Fe^{3+} donating electrons to the sulfur that could be reduced to sulfide.

AFM results.

1) Sample FLO. Natural sample presents on the surface patterns, with almost constant profile, that are no longer recognizable in the sample exposed to acid vapors, where also occurs the appearance of well-defined alteration structures of polyhedral shape.

2) Sample CZA2d. Natural sample presents an irregular surface with a larger number of flaking and cleavage structures compared to the sample FLO. The surface exposed to the acid vapors shows alteration structures, with pseudo-parallel trend, that suggest the presence of cavities that are formed along preferential directions; the depth of these cavities is approximately 1nm and is therefore compatible with the removal of an entire coordination polyhedron (tetrahedron-octahedron-tetrahedron).

The profiles obtained from AFM measurements on sample CZA2d, show that polyhedra formed by the union of rings of six tetrahedra are no longer recognizable on the surface of the exposed sample, unlike what happened in sample FLO subjected to the same oxidizing treatment. This evidence suggests that the process of alteration, locally, may have acted more in depth, thus being more incisive in this type of structure or, conversely, that substitutions in octahedra favor surface alteration processes.

SESSIONE S15

Gemstones: from Nature to marketing

CONVENORS

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Val Malenco, Central Alps, Italy: a source of gem materials

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Keywords: Val Malenco, green andradite, nephrite jade, rhodonite, serpentine, clinozoisite.

A distinguish feature of Val Malenco, Central Alps, Italy, is the remarkable number of recovered minerals (more than 250 species), which have attracted the interest of mineralogists since the end of 18th century, making the valley renowned at international level. Among the various minerals, some have a significant gemological interest and are used in jewelry as gems or ornamental carvings.

The most notable and one of the best Italian gem material is the green andradite garnet ($Ca_3Fe_2Si_3O_{12}$), known with the varietal name "demantoid" (Adamo et al., 2009). Attractive gemstones have been produced from crystal recovered in asbestos mines hosted by serpentinites and located in a small area, where the most famous localities are: Cengiàsc (including the Sferlùn quarry), Dossi di Franscia, Coston d'Acquanegra, Valbrutta, and Al Ross (Bedogné et al., 1993). These asbestos deposits, now closed for safety reasons, are sited at ~1800–2200 m above sea level. The gemological properties, including the characteristic "horse-tail" inclusions (fibrous chrysotile), and the chemical composition (Adr ≥98 mol%) are typical of serpentinites-related demantoid. Trace of chromium, together with major iron, are responsible for the green color of this gem.

Another interesting gem material is the nephrite jade, discovered at Alpe Mastabia and hosted in a talc-tremolitic orebody, associated with dolomitic marbles (Adamo & Bocchio, 2013). The jade, occurring as intergrowth of fine fibers, is mainly composed of pure tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$, and contains a low concentration of iron, which causes its typical pale green color. The occurrence of other constituents, including calcite, molybdenite and galena, influences the color of the jade.

Gem-quality rhodonite ($Mn_5Si_5O_{15}$) from Val Malenco occurs in the Mn-mineralization at Monte del Forno. Rhodonite has typically a massive aspect, with an attractive pink color (due to Mn). It is always associated with tephroite, spessartine, pyroxmangite, biotite, magnetite, calcite, quartz, and Mn-oxides and hydroxides.

"Noble" serpentine, green and yellowish green in color, composed mainly of lizardite and antigorite (with various amount of calcite, dolomite, brucite, and chlorite) was found at Pizzo Tremogge included in forsterite-bearing marbles. In the same area, precious Mn-rich clinozoisite (clinothulite variety) has also mined for its fine pink color.

Other interesting gem materials from Val Malenco include diopside (green or, more rarely, blue) and Cr-bearing green grossular.

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"Noble" serpentine: a case study from Val Malenco, Central Alps, Italy

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Keywords: serpentine, lizardite, antigorite, Val Malenco.

Serpentine-group minerals (chrysotile, lizardite and antigorite) are common rock-forming hydrous magnesium phyllosilicates, with ideal chemical formula $Mg_3Si_2O_5(OH)_4$. They form under a wide range of temperatures, including Earth surface conditions and hot hydrothermal temperatures (Evans et al., 2013). When characterized by a compact microstructure and fine and uniform colors (generally green), they are used in gemology for ornamental carvings and gems, often referred as "noble" or "precious" serpentine (O'Donoghue, 2006).

In Italy, gem-quality serpentine occurs in various deposits in the Alps and the Apennines. This study aims to provide a gemological and mineralogical characterization of serpentine from Pizzo Tremogge, Val Malenco, Central Alps, which is one of the most known Italian source for "noble" serpentine (Bedogné et al., 1993). At Pizzo Tremogge serpentine minerals are included in forsterite-bearing marbles Paleozoic in age.

The suite of rough and cut gem-quality samples from this locality, kindly provided by Mr. P. Nana (Sondrio, Italy), were investigated by means of gemological analyses, X-Ray Powder Diffraction, EMP chemical analyses, and Raman spectroscopy.

The gemological properties of serpentine from Val Malenco are in the range of typical gem-quality serpentine. In particular, the specimens have all a massive and opaque aspect, with a color ranging from green to yellowish green, sometimes with white veins and black spots. The refractive index, measured by the distant vision method, is about 1.55, whereas the specific gravity ranges from 2.49-2.67, with variations related to the occurrence of other phases. The samples are inert to UV (254 and 366 nm) radiations and have a Mohs hardness of ~4. Four different samples have been analyzed by X-ray powder diffraction and Raman spectroscopy, which are considered the more efficient methods for identifying different species of serpentine. The identified phases are: lizardite, antigorite, calcite, dolomite, brucite and chlorite. In addition EMP analyses allowed us to evidence chemical differences between lizardite and antigorite that mainly arise from the extent of cationic substitution: lizardite is always Al and Fe -enriched (0.10-0.18 and 0.11-0.16 a.p.f.u., calculated on the basis of seven anhydrous oxygens respectively) in respect to antigorite (0.02-0.08 and 0.04-0.08 a.p.f.u, respectively). Minor amounts of Ti (0.001-0.008 a.p.f.u.) and trace amounts of Ca, Cr, Ni, and Zn have been also detected.

The compact and fine-grained microstructure and the typical green color confer to the serpentine from Pizzo Tremogge an agreeable aspect and make it noteworthy as gemological material.

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Berillium diffusion in treated corundum: analysis and identification

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Keywords: Be-treated corundum, LA-ICP-MS, Single-crystal X-ray diffraction and polarized Raman spectroscopy.

At the end of 2001, unprecedented amounts of saturated orange and orangy pink (the so-called "padparadscha") corundums became widely available to the worldwide jewelry market. Many studies subsequently revealed that the light element beryllium (Be) had been diffused into a wide range of corundum gems in order to alter/produce their color. The Be diffusion process requires heating at high temperature (over 1750 - 1800°C) in oxidizing atmosphere, using beryllium-bearing additives (chrysoberyl or beryllium oxide). At the present, a full range of colors, including yellow, blue and red, have been produced or altered by Be treatment, sometimes used in combination with traditional heating. The beryllium diffusion process is surely the most broadly applicable treatment to induce coloration in corundum so far achieved, explaining the extraordinary effect on the market. Consequently, the analysis and identification of Be diffused corundum and its separation from untreated or traditionally heated counterpart has become a major issue in the gem trade.

The observation of Be-diffused corundum at optical microscope can result useful for identification. Diagnostic evidence is an anomalous color distribution, characterized by a layer of surface-conformal color induced by Be-diffusion, which however is not visible when the corundum was colored throughout. Other microscopic evidences indicative of an exposure to very high temperatures, as those typically used for Be-diffusion, are features of inclusions significantly altered, melted or internally recrystallized during the treatment (e.g., highly altered zircon inclusions with whitish crusts of baddeleyite). Spectroscopic techniques (e.g. UV-Vis-NIR, IR, Raman) have been employed to provide identification criteria, but they do not allow a separation from the natural or traditionally heated corundum. At the present, the only reliable identification of Be-diffused corundum is based on the detection of trace levels of beryllium, by means of advanced chemical analyses, such as secondary ion mass spectrometry (SIMS), laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and laser-induced breakdown spectroscopy (LIBS). The detection of Be amounts >1 wt ppm (generally 4-15 wt ppm, rarely up to 50 wt ppm) allows us to surely identify the stone as Be-diffused and the laboratory report should state that the gem shows "indication of heating and color induced by diffusion of a chemical element from an external source". Single-crystal X-ray diffraction and polarized Raman spectroscopy were used to provide additional identification aids, but structural parameters (i.e., cell parameters, bond distance, thermal displacement parameters) and Raman spectra do not change significantly between Be-diffused and untreated specimens.

Green andradite (demantoid variety) from Muslim Bagh, Zhob District, Balochistan, Pakistan: gemological and mineralogical characterization

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Keywords: andradite, demantoid, Pakistan.

Andradite garnet ($Ca_3Fe_2Si_3O_{12}$) is a rock-forming mineral, typically found in metamorphic rocks, such as serpentinites and skarns. Green andradite, often described with the varietal name "demantoid", represents one of the most appreciate and precious gemstones among the garnet group minerals, due to its color, brilliance, and rarity.

The traditional green andradite sources are Russia and Italy (Val Malenco, Central Alps), whereas recently new commercially important deposits were found in Madagascar, Iran, Pakistan (Kaghan Valley), and Namibia (Adamo et al., 2011).

Recently, gem-quality green andradite crystals indicated to come from Muslim Bagh, Balochistan (Pakistan) are occasionally available in the Peshawar gem market. The transparent and fine gem-quality dodecahedral crystals show an attractive fancy green color, although they are very small, rarely exceeding 1 ct in weight. The Muslim Bagh area shows a nearly complete ophiolite sequence, mainly composed by peridotites (harzbugite and dunite), partially to completely serpentinized. Many outcrops of dunites contain podiform chromite deposits (Kakar et al., 2013).

A suite of gem-quality samples from this locality, provided by the collector S. Hanken (Germany), has been investigated by means of standard gemological methods, SEM-EDS, and EMP chemical analyses. All the samples (0.18-0.98 ct) are transparent, with a fancy medium green color. They are all single refractive with moderate to strong anomalous birefringence and refractive indices >1.79. The measured density ranges from 3.80 to 3.90 g/cm^3 and the gems are inert under ultraviolet radiation. These gemological properties are characteristic of andradite, demantoid variety. The samples contain "horse-tail" inclusions and opaque whitish crystals, chemically identified as chrysotile and antigorite, respectively. Opaque blackish crystalline inclusions of chromium-bearing magnetite are also present. The specimens show various growth structures and, in a few cases, dodecahedral twinning. The chemical composition of garnet results in almost pure andradite (Adr≥96 mol%, generally ~98-99 mol%), with minor amounts of Mg, Al, Cr, Ti, V, and Mn. In particular, chromium ranges from below detection limit to maximum 0.92 wt% as Cr_2O_3, this latter measured near the Cr-rich magnetite inclusions. Chromium causes, along with the major constituent Fe^{3+}, the bright green color of this andradite, such as typical for demantoid associated with serpentinites (Bocchio et al., 2010).

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Mogok: Mysteries and Secrets of the Legendary Valley of Rubies

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Keywords: Mogok, gemstones, Myanmar.

This presentation will provide a comprehensive update about the most famous and mysterious colored gemstone gem mining district in the world. Videos and photographs that have never been released to the public will be shared with attendees so that a better understanding of the source, from a miner's perspective, will develop. This aspect of gemology, whilst not scientific in form will nevertheless be invaluable to those in attendance whilst a little humorous at times. Federico's tour of Myanmar's premier gem source, and certainly the world's foremost natural ruby source, is not to be missed!

Identification of the cromophores in Corallium rubrum gem quality corals by HPLC/UV and ^{1}H NMR spectroscopy

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Keywords: Corallium rubrum, HPLC/UV, NMR.

Gem corals are technically non-vertebrate biomaterials. They derive from the branched skeletons of the colonies of marine invertebrates (polyps) belonging to the classes Hydrozoa and Anthozoa of the phylum Cnidaria. According to the main taxonomical characteristics, the Anthozoans have been subdivided into two subclasses: Octocorallia (or Alcyonaria) and Hexacorallia (or Zoantharia) (Bayer, 1956). From a compositional point of view, corals are biocomposites with key components of minerals (calcite or/and aragonite) and organic macromolecules. Structural characterization of the chromophore pigments was carried out by means of HPLC combined with UV and MS (Cvejic et al., 2007) and by Raman spectroscopy (Merlin et al., 1986; Rolandi et al., 2005; Fritsch et al., 2008; Brambilla et al., 2012). Nevertheless, the nature of the cromophores in Corallium rubrum is still under discussion. Corallium rubrum corals live in the Mediterranean Sea and belong to Anthozoa class, subclass: Octocorallia. Their colour varies from dark red to red, orange-pink, bright rosé, pale fresh pink, and sometimes white. The first attempt to determine the chemical composition of the cromophores in the red corals from Marseille revealed the presence of the canthaxanthin carotenoid (Cvejic et al., 2007). Using Raman spectroscopy Fritsch et al. (2008) explained that pigments in Corallium rubrum and in other corals are due to unsubstituted polyenes, characterized by the lack of methyl groups in the carbon chain, as already indicated by Merlin et al. (1986). More recently, Brambilla et al. (2012), by means of the ECC theory in Raman spectroscopy, stated that the Raman spectrum of Corallium rubrum turns out to be an interesting puzzle because it lies in between the spectra of carotenoids and psyttacofulvines (fully de-methylated). Therefore such pigment does not belong to the class of unsubstituted polyenes nor to carotenoids, but it could have a composition with a partially methylated polyenic chain. To confirm and complete such theoretical results, the Authors tested a group of rough specimens of colony skeletons of Corallium rubrum. The cromophore pigments were extracted by incubating ground corals in chloroform for 5 days at 4°C, under agitation. By exploiting ^{1}H NMR spectroscopy the composition of several specimens was investigated. With the purpose to obtain resolved and diagnostic signals, the specimens were further purified by means of HPLC, using a C18 column eluted with acetonitrile/methanol. On the separated pure fractions ^{1}H NMR spectroscopy was again performed. Results are still under investigation.

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Colouring mechanisms in natural spinels

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Keywords: Spinels, Colour, UV-VIS-NIR spectroscopy.

Natural minerals belonging to the spinel group are actively sought as gemstones because of their wide range of intense colours, high mechanical resistance and high thermal and chemical stability. Causes of colour in spinels may be different, most of them being related to transition metal ions, their valence and their coordination. However, more complex colouring mechanisms are difficult to characterize and often remain unexplained. A detailed study on the causes of colours in spinels is lacking in literature.

To shed light on the origin of colour in spinels, a large set of about thirty multi-colour natural samples was explored by Electron Microprobe Analysis and UV-VIS-NIR-MIR spectroscopy. On basis of chemical characterization, the analysed spinels exhibit a dominant spinel *s.s.* ($MgAl_2O_4$) or gahnite ($ZnAl_2O_4$) composition. The different colours do not depend on the end-member composition. In detail, samples having spinel *s.s.* composition show a wide range of colours, while those with gahnitic composition exhibit colours in blue hues.The various colours are caused by different combinations of two or more minor transition metal cations such as Co^{2+}, Fe^{2+}, Fe^{3+} Cr^{3+} and V^{3+}, occupying tetrahedrally (T) and/or octahedrally (M) coordinated sites in the spinel structure.

Optical spectra of natural spinels were recorded in the UV/VIS to NIR spectral range (32000–2000 cm^{-1}). Red, orange and magenta coloured spinels show similar absorption spectra with main absorption bands at ~25500 cm^{-1} and ~18500 cm^{-1} assigned to spin-allowed *d-d* transitions in Cr^{3+} and V^{3+} at the M site. When the contents of Cr^{3+} predominate over the contents of V^{3+}, the spinels appear as red, otherwise they are orange. Magenta spinels with appreciable Cr-contents and secondary amounts of Fe show a red shift of the band at ~ 18500 cm^{-1}, with respect to the red coloured samples.

The pink, blue and dark green spinels, in spite of exhibiting very different colours, show similar absorption spectra characterized by a strong UV-edge absorption at energy >> 30000 cm^{-1} due to the $O^{2-} \rightarrow Fe^{2+}$ and $O^{2-} \rightarrow Fe^{3+}$ charge transfer transitions and a series of weak absorption bands in the visible range mainly related to spin-forbidden *d-d* transitions of Fe^{2+} at the T site. The peak of maximum absorption in the range 20000 and 10000 cm^{-1} moves from ~18000 cm^{-1} for the pink spinels to ~15500 cm^{-1} for the green spinels (with the blue spinels showing an intermediate situation) depending on an increase in total iron content and thus also on Fe^{3+} content. In fact, the latter interacts with Fe^{2+} producing a Fe^{2+}-Fe^{3+} intervalence charge transfer band at 15500 cm^{-1} in the green samples. The optical absorption of the light blue and blue coloured spinels in the range 18000-15000 cm^{-1} is strongly influenced by the presence of very low contents of Co^{2+} (up to 600 ppm) ordered at tetrahedrally coordinated sites.

Natural vs. synthetic quartz: review and new data

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Keywords: quarta, natural, synthetic.

Quartz, and its most important gem quality varieties (amethyst, citrine, smoky…), are widely produced in laboratory. The hydrothermal technique used for this purpose is known since 1905, when Giorgio Spezia, for the first time, was able to produce a lab-grown crystal of quartz.

Since 1970, when synthetic gem quality quartz became commercially available, gemologists had the problem of identifying the origin of the material.

At the present this problem still exists; therefore it is necessary to keep revising the diagnostic criteria for separation and enlarging the natural and synthetic sample database.

A multi-methodological study, resulting from the combination of conventional gemological analysis and other more sophisticated techniques (i.e. infrared spectroscopy, LA-ICP-MS chemical analysis, single-crystal X-ray diffraction), was made in order to provide a review of the methods commonly used for the distinction of natural and synthetic stones.

Some microscopic features, like various crystalline inclusions, polysynthetic lamellar twinning on the Brasil law, the “zebra-stripe” fluid inclusions, provide evidence of the natural origin.

Synthetic samples, instead, can be distinguished by the presence of seed-plate and “bread-crumbs” inclusions.

In the case of flawless stones, more advanced analytical techniques are helpful.

The presence of the infrared absorption band at 3595 cm^{-1} is considered the most consistent feature of natural origin.The chemical analysis by LA-ICP-MS allow us to detect a gallium enrichment in natural quartz compared to its synthetic counterpart. Also a significant cobalt content (>30 ppm) and high concentration of potassium (>1000 ppm) are typical of synthetic citrine.

In addition some preliminary results from single-crystal X-ray diffraction show that there are slight, but systematic, difference between theunit-cell parameters of natural and lab-grown amethyst [average volume 113.12(2) $Å^3$ in natural vs. 113.23(2) $Å^3$ in synthetic] and citrine quartz [average volume 113.03(2) $Å^3$ in natural vs. 113.16(2) $Å^3$ in synthetic].

The separation of natural vs. synthetic quartz is possible in most of the cases using a combination of various analytical techniques.

We are currently increasing our database with chemical, crystallographic and spectroscopic features of natural and synthetic quartz in order to provide a protocol for a non-ambiguous identification.

On the state of the art of synthesis processes of colored gems: An Overview

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Keywords: synthetis, melt, solution.

In this contribute, we will present an overview on the state-of-the-art of the synthesis protocol of the main colored gems. Synthetic gem crystals have been manufactured since the late 1800's, and their production is often marked by a need for them in industrial applications outside of the jewelry industry. During the last century, researchers have developed a number of different ways to create synthetic gem materials in the laboratory. Most of these methods fall into two major categories: melt or solution. In melt processes, the chemical composition of melt is the same as the composition of the resulting crystal. In solution processes, the solution or melt has chemical composition than that of the resulting crystal. Constituents are dissolved in the solution or melt at high temperature, and the crystal forms initially on a seed crystal as the melt temperature is lowered. The three most important synthesis processes from melt are: 1) the flame fusion (Verneuil method), 2) the "pulling method" (Czochralsky method) and 3) the floating zone method. The flame fusion is the least expensive and most common way to make gems such as synthetic corundum and spinel. Gems synthesized by "pulling method" include e.g. corundum and alexandrite. The floating zone method makes possible to create synthetic corundum. The two most important synthesis processes from solution are: 1) the flux-growth and 2) the hydrothermal growth. Some synthetic gems, e.g. emerald, ruby, sapphire, alexandrite and spinel (red and blue) can be created through a flux-growth method. The hydrothermal growth process is slow and expensive, but it is one of the best method to create emerald, aquamarine, red and blue beryl, quartz, or colored corundum.

In the market, gemstones are often available without any gemological report, leaving open questions about their origin (i.e., natural, synthetic). As synthetics for jewelry applications can be "made to order", they are likely to be much less rare than natural gems of equal size, clarity and saturation of color. Only by an accurate gemological investigation is possible to distinguish natural and synthetic stones and, in addition, the synthesis protocols among those previously described.

Natural and enhanced colours in natural and synthetic corundum. Is it always possible to detect them?

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Keywords: micro-Raman Spectroscopy, heat treatment, OH defects.

Corundum, especially rubies, are some of the most important gems in the nowadays gemstone trade.

Due to their high demand, frequently extracted stones that do not show the most appreciated characteristics, undergo to different treatments to improve color and clarity: heat treatment, lattice diffusion and Be-diffusion treatment, fractures Pb-glassy-filling. These treatments are common for corundum and well known in literature. Recently, Pb+Co glassy-filled treated blue sapphires have been submitted to several gemological laboratory, engendering many discussions at international level and especially about nomenclature problems, because the color is due to Cobalt.

One of the requests to the gemological laboratory, is to reveal the geographic origin (Bgasheva T.V., et al., 2012; Pattamalai K. & Hansawek R., 2007). However some of these treatments, like heat treatment or Be-diffusion, can significantly modify the spectroscopic information (i.e. Uv-Vis/NIR spectrum) and make the data collection difficult. Moreover both treatments can be quite difficult to be proved with standard gemological tests. For example, in some cases after heat-treatment we can observe an alteration in the intensity of OH-defect vibrational absorption band by FTIR spectroscopy (Beran & Rossman 2006), but the interpretation of the data is ambiguous, due to the fact that this alteration is closely related with the treatment environment (oxidative or reductive).

The aim of the present study is the opportunity to characterize, with non-destructive analytical methods, the colors of natural stones and treated corundum.

We analyzed several different stones: natural rubies, blue sapphires, yellow corundum and polychrome corundum, each and all untreated, with different geographic and geologic origin. We perform different tests and, particularly, we applied micro-Raman spectroscopy to evaluate the possibility of characterization of the natural chromophore group, responsible of the different colors of the analyzed stones. All data have been compared with those collected from heat treated and Be-treated corundum as well as from synthetic corundum, with different colors.

Moreover, to complete the spectroscopic set of data, FTIR spectroscopy was applied to the characterization OH-defect absorption, with the aim to compare untreated vs treated stones with the same geological origin.

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Characterization of the new gemstone Pezzottaite $Cs(Be_2Li)Al_2Si_6O_{18}$

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Keywords: Pezzottaite, Cs-beryl, chemical analysis, single crystal X-ray diffraction.

Pezzottaite is a rare Cs-bearing mineral with ideal composition $Cs(Be_2Li)Al_2Si_6O_{18}$, discovered in November 2002. It is considered as a member of the “beryl group”, along with beryl *sensu-scricto* ($Be_3Al_2Si_6O_{18}$), bazzite ($Be_3Sc_2Si_6O_{18}$), stoppaniite ($Be_3Fe_2Si_6O_{18}$) and indialite ($Mg_2Al_3(AlSi_5O_{18})$).

We have performed a multi-methodological study of pezzottaite (sample from Ambatovita, central Madagascar), highlighting the main differences with Cs-rich beryl (sample from Monte Capanne, Isola d’Elba, Italy). The two samples have been characterized by electron microprobe analysis in wavelength dispersive mode (EMPA-WDS), single-crystal X-ray diffraction and Raman spectroscopy (Gatta et al., 2012; Lambruschi et al., 2014).

Chemical analysis showed an high amount of cesium (Cs_2O 12.91 wt%) for pezzottaite with respect to Cs-beryl (Cs_2O 1.27 wt%).

As regards the crystal structure, the pezzottaite has a trigonal symmetry (space group *R3c* with a~15.9 and c~27.8 Å), while beryl is hexagonal (space group *P6/mcc*, with a~9.2 and c~9.2 Å).

The Raman spectrum of pezzottaite over the extended region 100-3650 cm^{-1} was collected for the first time, and compared with the spectrum of Cs-beryl. Cs-beryl shows only an intense peak at 3604 cm^{-1}, ascribable to H_2O stretching vibrations. In the pezzottaite sample, two weak Raman bands at 3590 and 3545 cm^{-1} are observed, which could be assigned to the fundamental H_2O or OH stretching vibrations respectively, despite the mineral should be nominally anhydrous. The Raman spectra are useful to distinguish the type of H_2O channel (i.e., type “I” or type “II”) and then to evaluate the presence of alkali in the channels. In addition, the Raman spectrum of pezzottaite shows two intense and characteristic bands at 111 cm^{-1} and 1100 cm^{-1}, which are not present in the beryl spectrum.

The use of a non-destructive technique like Raman spectroscopy provides a quick and inexpensive protocol to distinguish between beryl and pezzottaite.

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Collector gemstones: their evolution, their rarity

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Keywords: gemstones, collector.

We could spend hours talking about the crisis that has mined the gems and jewelry market, or about the difficulties in finding top quality untreated gemstones, or about the diffusion of new treatments and simulants that are compromising the confidence of gems consumers... but we prefer to talk about something else! We prefer to illustrate a brilliant and innovative gemstone approach, to show a new niche in the gemological field, to tell a beautiful story concerning original and natural gemstones , to report a way to survive in this chaotic gemological jungle.

A decade ago the 90% of gem and jewelry market belonged to the diamond, the 9% to ruby , sapphire, emerald and pearl, and the remaining part was shared by twenty other stones . There was also a very small niche of gem collectors interested in maybe other eighty faceted gems. Today, by attending international mineralogical and gemological exhibitions, surfing on internet and reading the major gemological magazines, it is possible to count more than 600 mineral species faceted as gemstones. To better understand this changing in gem market, we have to know why a mineral usually can't be faceted : 1) It is too ugly, 2) the existing rough material is too small to be faceted, 3) the cut is too difficult, 4) there is not a buyer for the gem.

The number 1) does not deserve any comment: if a mineral was not enough attractive ten years ago, then is also not attractive today, and it won't be cut; also point 2) is not responsible for the demographic explosion of new gems, it is true that new minerals have been discovered in the last 10 years, but the new minerals that could be used in gemology are less than ten. So we need to focus more carefully on the points 3) and 4). At the present the faceters improved the cutting techniques and are able to facet materials that couldn't cut few years ago: it is actually possible to see around amazing gems of sulphur , barite, apophyillite, cerussite, Celestine, halite and other minerals really uncommon as precious stones! But someone had to buy these unusual gemstones, that's the meaning of point number 4.

Many gem and jewels collectors already had in their collections all the most famous stones and were looking for something else. This, combined with the difficulty in finding amazing natural stones, untreated, convinced them and the sellers to place on the market different materials; so is actually possible to find in many jewelries earrings and pendants mounting trapiche emeralds or dinosaur bones!

Minerals as benitoite, hackmanite, vayrynenite, taaffeite, jeremejevite which were used only in endless conversations between systematic mineralogy addicted, will be the subject of a gemological presentation.

Believe it or not! During this gemological presentation, there will be also discussed minerals as calcite, barite, cerussite, celestine, halite and sulphur, minerals that have been recently faceted due to the improvements in cutting techniques. There will be also presented new gemstones with optical effects and rare inclusions, that appeared in the gem market to supply the growing demand of the gemstones collectors: color-change diaspore , 12 rays star corundum , reversed trapiche emeralds, quartz with amazing inclusions, rainbow garnet and many other unique gemstones.

Gem production and gem-market in Madagascar in recent years

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Keywords: Madagascar, gem-mining, gem-market.

Madagascar experienced in recent years s period of political instability, consequent to a coup d'état in 2010, and the formation of a "transitional" government up to December 2013, when new democratic elections occurred. Because of such political troubles, the mining sector in Madagascar suffered administrative uncertainty, with the result that many gem-mining and gem-trading companies left the country and productions diminished. Security problems in the county, with armed group of bandits, sometimes connected with the militaries, increase the risk of mining and trading gem in the field and outside towns. Nevertheless, the I.G.M (Gemological Institute of Madagascar), created in 2003 by a project financed by the world Bank, and directly connected with the Mining Ministry, remained active and it represents a reference point for gemology teaching and gem-testing in the island. Moreover, after the recent elections and the establishment of a government recognized by the international community, many Asian, European and African companies of the gem-trading sector returned back to Madagascar renewing their activity. Here is the information about gem-discoveries, mining and trading in Madagascar in the last years: - The production of sapphires of many different colors, including blue, pink, *geuda*, etc., and many associated gemstones, continued in the last years in the large Ilakaka deposit, in southern Madagascar. Most of the mechanized operations stopped and several tens of thousand miners, distributed over and area of several hundreds square kilometers, are still working with primitive and manual tools. Most of the production (if not all) leave Madagascar to be cut, heat treated, and treaded in Bangkok. - Sapphires and ruby, even in rough stones of large size, were discovered at the beginning of 2011 at Ididy, in a remote area covered by rain-forest between Andilamena and Tamatave, in central-east Madagascar. - Much less production of corundum gem-varieties occurred in the last years in some classic or relatively new deposits such as Ambondromifehy (basaltic sapphires), Vatomandry, Maroloambo and Andilamena (ruby), Andranondambo and Ranotsara (sapphires). - New discoveries of high quality aquamarine occurred in the last years in: Fidirana (2010, west of Betafo); Ambatofotsy-Carolle (2011, north of Betafo); Vangaindrano (since 2012, typical blue-green color, heat-treated to produce a very nice blue color). - Very significant production (over 25 tons) of low grade multicolored tourmaline, suitable for the Indian market, occurred in 2011 and 2012 in Ikalamavony. Carving qualities mostly of red color were produced in Tsitondroina (2012-2013), Valozoro (2009-2010), Nanidhizana (2008), and Vohitrakanga (2010-2013). Very limited gem-tourmaline production occurred in the Ikalamavony area and in the Sahatany valley. - Demantoid production, after the huge production occurred after the discovery in 2009, diminished greatly up to rather no production in 2013. Future of the mining activity at the place is at present uncertain. - All the other classic gemstones of Madagascar (e.g. emerald, alessandrite, morganite, danburite, kunzite, scapolite, cornerupine, moonstone, iolite, marolambo garnet, mandarin garnet, malaia garnet, tsavorite, green-blue apatite, opal, amethyst, etc.) are still produced through occasional finds and in small quantities.

Structural and spectroscopic analysis of Baltic amber

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Keywords: succinite, succinic acid, IR spectroscopy, x-ray diffractrion, thermal analysis.

Amber is a fossilized tree resin appreciated since antiquity for its unique aesthetic qualities in the production of small decorative objects. Its chemical composition is strongly related to the origin of the resin, but Baltic amber is synonymous with the chemical name butanedioic acid ($C_4H_6O_4$), more commonly known as succinic acid (Beck, 1986). $C_4H_6O_4$ is also a natural constituent of plant and animal tissues which has been used in Europe as a natural antibiotic and general curative for centuries. It has been stated, for example, that succinic acid isolated from Baltic amber can stimulate human and plant organisms, and can contribute to an increase in the yield of some cultivated plants (Matuszewska and John, 2004). In the literature it was reported that not all Baltic ambers contain succinic acid (Matuszewska and John, 2004).The primary goal of this study was to characterize succinite, a Baltic amber characterized by levels of succinic acid ranging from 3 to 8%. The selected succinite samples - (Palmnicken, Baltic Coast, and Prussia amber) consisted of opaque pale brown to nearly dark red-brown rounded masses of this amber variety. For comparative purposes, our tests were also carried out on a number of reference materials, including amber from Danzig Region, Poland, and commercial specimens. Standard gemological methods were used to document the samples' colour, hardness, refractive indices, fluorescence to long and short-wave ultraviolet radiation, and inclusions. X-ray powders patterns were collected before and after adsorption on a Bruker D8 Advance diffractometer equipped with SOL-X detector. Thermal analyses (TG and DTA) were performed in air up to 900°C at 10°C min^{-1}. According to Shashoua et al. (2006), IR techniques have been shown to identify the provenance of the amber beyond the basic Baltic/ non-Baltic distinction. In this study, infrared spectra collected on a Thermo Electron Corporation FT Nicolet 5700 Spectrometer FTIR spectra revealed characteristic spectral differences that make it possible to positively identify Baltic amber.

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Ferropericlase included in diamond: lower or upper mantle origin?

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Keywords: Ferropericlase, diamond, lower mantle, geobarometry.

Ferropericlase [(Mg,Fe)O] is a common oxide found as inclusions in diamonds considered to be of lower mantle origin (i.e. from below 660 km depth). Indeed, ferropericlase is often associated with low-Ni enstatite and such enstatite could be the inversion product of MgSiO3 perovskite. Nonetheless, ferropericlase is stable over the entire mantle P-T range and its relative abundance as inclusions in diamonds with respect to possible inverted MgSiO3 is much higher than expected based on high-PT experiments. In order to provide new and stronger evidence of lower mantle origin for ferropericlase inclusions, we are investigating four diamonds from Juina (Brazil). By measuring the residual stress on the inclusions, and combining it with knowledge of the EoS of the diamond and the inclusion, it is possible to determine the isomeke that defines possible minimum P and T of entrapment (Angel et al., 2014). This elastic measurement could thus contribute to resolve the question as to whether ferropericlase inclusions in diamond originate entirely in the lower mantle, whether or not enstatite inclusions are also present.

Angel R.J., Mazzucchelli M.L., Alvaro M., Nimis P., Nestola F. 2014. Geobarometry from host-inclusion systems: the role of elastic relaxation. Submitted as Letter to American Mineralogist.

Micro-Raman mapping: a powerful method to ivestigate gemological mysteries

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Keywords: micro-Raman Spectroscopy, Sapphire, Mineral phase, Heat-treatments.

Micro-Raman Spectroscopy is an analytical technique with a lot of applications in many scientific and industrial fields. Amongst its main features there are: fast analysis, no sample preparation and non-destructive test.

All these characteristics make Raman spectroscopy a very powerful analytical tool to study gems and related materials. Raman spectroscopy, in fact, characterizes different mineralogical phases on the basis of the vibrational modes of the chemical group.

Thanks to the recent innovations in advanced optics, electronics and mechanics, the last generation of Raman spectroscope is able to generate Raman images, on the basis of the scattering vibrational modes of the samples.

In this research work, we present some of the first results obtained by the application of these innovative technique, applied on the study of corundum inclusions and their relatively crystallinity after heat-treatments.

In fact, the heat-treatment in Corundum is used to enhance the color and to modify the clarity, and it is commonly accepted by the gem trade. Undesirable dark color shades in rubies can significantly reduce their value, and, on the other hand, a combination of light tone and low saturation can make the difference between a ruby and a pink sapphire (Bgasheva et al., 2012; Pattamalai & Hansawek, 2007). To detect heat treatment in Corundum sometime, when the standard gemological tests are not decisive, it is necessary to analyze the stones applying advanced analytical techniques. In some cases the heat-treatment is responsible for the modification of the spectroscopic response. In these cases it is necessary to know, or hypothesize, the original color of the stone.

For this study we have used ultra fast and high spatial resolution Raman Imaging techniques, allowing also 3D characterization with ULWD microscope objectives.

We have characterized several untreated corundums, analyzing, not only the inclusions, but also the hypothetic chromophore group, responsible for the stone color. For this purpose, we analyzed several untreated gems quality corundums from North Madagascar (basaltic origin – courtesy of Mr. Drera B.) and all the data were compared with treated corundum from GECI collection.

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Application of Laser Induced Breakdown Spectroscopy on gem quality minerals: some cases of study

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Keywords: Gemstone, LIBS, Chemical Zoning.

The application of the Laser Induced Breakdown Spectroscopy (LIBS) to gemmological materials is well known for the gemstone treatment detection but LIBS can also provide a useful contribution in mineralogical studies in which the chemical analyses is essential, playing a key role in the studies on the origin of minerals (Agrosì et al., 2014). The possibility to detect simultaneously all elements, including also light elements such as boron, lithium, and beryllium in a fast way and without sample preparation its clearly a great advantage of the LIBS. Moreover this technique is able to detect chromophorous elements even if they are in very low concentration. Nevertheless the main problems affecting LIBS are the difficulties to perform quantitative analyses and the partial destructivity of the method. Recently, with the development of the technique and in particular with the development of a new softwares there is also the possibilities to perform quantitative analyses with or without calibration. The last examples are the standard Calibration-Free LIBS and the One Point Calibration LIBS, CF-LIBS and OPC-LIBS respectively (Cavalcanti et al., 2013). The improvement of the instrumentation performance and the possibility to focalize the laser beam with an optical lens of a microscope allow to obtain an high resolution and a low destructivity of the sample. Moreover, the use of a double-pulse laser produce a signal enhancement useful for the quantitative chemical analyses guaranteeing a minimal sample damage. In this way we may obtain a considerable improvement on the detection limit of the trace elements, whose determination is essential to define the origin of gemstones. In the mineralogical studies the μ-LIBS appear very attractive because the possibility to select the smallest sampling areas ensures a better reconstruction of the chemical zoning and consequently allows to stimate the rock forming condition because the chemical zoning is sensitive to the changing of the physical and chemical parameters. Some cases of study have been performed on beryls and corundums with different objectives and the results will be discuss.

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Reconfiguration of pre-existing defects in natural diamond lattice: spectroscopic evidence

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Keywords: Diamond, defects, treatments.

Diamond is doubtless the most important gem in the jewellery industry due to its exceptional physical properties, luster and value. The world that revolves around the diamond, from mine to market, is really complex and fascinating at the same time. Nowadays diamond based materials are the target research of many specialized laboratory in the world, and their legitimacy allowed to reach great scientific results. From a gemmological point of view understanding the diamond on the atomic scale is becoming the only way to solve many problems that affect the gemstones market. Complex treatments and synthesis techniques, developed during the last decades, allow to obtain colourless or fancy diamonds very similar to the natural ones. The human eyes and the standard gemmological instruments are often not useful for discerning natural from synthetic or treated diamonds, usually advanced spectroscopic analysis are essential to achieve this goal. This work is a review of what is known regarding natural diamond lattice defects, and how they can be drastically changed by artificial treatments. It is well known that diamond structure consists in carbon atoms each of which is tetrahedrally bonded to four other carbon atoms with covalent bonds, forming a compact lattice belonging to the cubic system. However atomic impurities, vacancies and structural defects are present in crystal structure of diamond in the 99% of cases. The scientific classification of diamond is based on the individuation of nitrogen and boron atoms, and their configuration in diamond lattice (Breeding & Shigley, 2009). Starting from a poor colour quality IIa crystal (for example brown) it is possible to obtain colourless diamond trough HPHT (*High Temperature High Pressure*) processes (Fisher et al., 2000). Another complex and diffused procedure is to irradiate with ionizing radiation and anneal type I diamonds, to obtain coloured diamonds very similar to the natural ones (Collins, 2007). The aforementioned treatments, performed in prohibitive experimentally conditions, produce a reconfiguration of pre-existing defects, with the aim of creating or destroying particular colour centres in diamond lattice. Therefore the diamond colour can be definitively improved modifying the starting defects involving nitrogen atoms, and create new ones which optical properties are drastically different (Collins, 1992).

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SESSIONE S16

Rock-forming minerals and their bearing to petrogenetic processes

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X-ray topographic study of a diamond from Udachnaya: implications for the genetic nature of inclusions

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Keywords: diamond, olivine inclusions, x-ray diffraction topography.

In recent years, several studies have focused on the growth conditions of the diamonds through the analysis of the mineral inclusions trapped in them. In these studies, it is crucial to distinguish between protogenetic, syngenetic and epigenetic inclusions. X-ray topography (XRDT) can be a helpful tool to verify the genetic nature of inclusions in diamond. This technique characterizes, in a non-destructive way, the extended defects within a mineral and reconstructs the growth history of the sample (Agrosì et al., 2013). With this aim a diamond from the Udachnaya kimberlite, Siberia, was investigated. The diamond crystal was the one previously studied by Nestola et al. (2011) who performed in-situ crystal structure refinement of the olivine inclusions to obtain data about the formation pressure. Optical observations revealed an anomalous birefringence in the adjacent diamond and the inclusions had typical "diamond-imposed cubo-octahedral" shape for the largest olivines. The diffraction contrast study shows that the diamond exhibits significant deformation fields related to plastic post growth deformation. Section topographs revealed that no dislocations nucleated from the olivine inclusions. Generally, when a solid inclusion has been incorporated in full-grown state in another growing crystal, the associated volume distortion needs of a number of dislocations to ensure a better connection between the inclusion and the host phase. In some cases, complex twinning can be developed (Agrosì et al., 2013). In our case, the olivine assumes the morphology imposed from the diamond and, consequently, it does not produce volume distortion and the nucleation of dislocations is not necessary. This process generally occur during the simultaneously growth of the two minerals, confirming what was already stated by Bulanova (1995). However, the syngenetic nature of inclusions generally implies epitaxial relationship between diamond and inclusions that in our sample can be ruled out because the orientations of these olivines are random (Bruno et al., 2014). Therefore, the specific and significant results that characterize this sample will be discussed in detail.

Agrosì G., Tempesta G., Scandale E., Harris J.W. 2013. Growth and post growth defects of a diamond from Finsch mine. Eur. J. Mineral, 25(4), 551-559.

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X-ray diffraction topography of brown diamonds from Argyle and Udachnaya

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Keywords: diamond, x-ray topography, micro-laminations.

Two crystals of brown diamonds, coming from Argyle and Udachnaya, were studied, in a non-destructive way, by means of X-Ray Diffraction Topography (XRDT) with the aim to elucidate the relationships between the structural defects and the growth history. The sample from Argyle mine, labelled Br11, was a light-brown diamond with an irregular tetrahedral morphology and free of inclusions. Br11 shows a complex intergrowth phenomenon: the analyses of the diffraction contrasts and the optical observations reveal that the sample is really formed by two individuals twinned by the well-known spinel law. These individuals, in turn, are formed by different sub-individuals with different orientation, piled up along the [111] direction. An aggregation of numerous and thick lamellae parallel to the triangular morphology of the (111) face characterizes each sub-individual. Moreover, the XRDT images show partial dissolution followed by a final overgrowth. The sample from Udachnaya, labelled Ud02, was a light-brown diamond with an octahedral morphology that exhibits several large inclusions and fractures partially healed by dark epigenetic microinclusions. The analyses of the diffraction contrasts of the Ud02 sample show extended deformation fields, growth bands parallel to the octahedral faces and, in addition, a micro-lamination parallel to (1-1-1) that across the whole sample irrespectively of the different growth sectors. These laminations represent a polysynthetic twinning commonly observed in diamonds, which have undergone plastic deformation and are considered post-growth defects (Agrosì et al., 2013). No dislocations nucleated from the inclusions were observed. The analysis of the structural defects allows a reconstruction of a complex growth history of these samples characterized by a sequence of alternating episodes of growth, dissolution and plastic deformation. Lastly, the common feature of the micro-laminations was related to the origin of brown colour.

Agrosì G., Tempesta G., Scandale E., Harris J.W. 2013. Growth and post growth defects of a diamond from Finsch mine. Eur. J. Mineral, 25(4), 551-559.

Trace elements in olivine from Italy convergent margin and inferences on the mineralogy of the mantle wedge

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Keywords: olivine, trace elements, subduction.

Major and trace elements in forsteritic olivine from mafic igneous rocks has proven a valuable tool to infer on metasomatic processes that affect the mantle-source of magmas prior to melting. The deviation of some compatible trace elements (e.g. Ni, Co, Cr) and their ratios to major elements (Fe, Mg), from the values of olivine from MORB, has been used to quantify the contribution of an olivine-free mantle source in the origin of some OIB. Despite the potential of this approach, very few studies exist on olivine from convergent settings, leaving a gap in our knowledge of magma genesis in the mantle wedge.

Here we present the first comprehensive set of major ant trace elements analyses of high-Mg olivine crystals from the Plio-Qyaternary magmatic rocks of the Italian Peninsula. The samples are among the most primitive members of the relevant petrographic series: from Ca-alkaline to strongly alkaline rocks ('ultrapotassic') with lamproitic and leucititic affinity. Olivine crystals were analyzed for major (EPMA) and a wide palette of trace elements (EPMA and LA ICP-MS).

The olivine crystals display a wide variety of Ni, Cr, Mn and Ca contents, which encompass the whole spectrum of magmatic olivines worldwide. Olivines from the lamproite family have remarkably high Ni (up to 5.000 ppm) and Cr, low Ca and Mn/Fe. These values are consistent with a contribution from a mantle source that had undergone depletion and then silica- and K-rich metasomatism prior to melting, leading to olivine-consumption in favour of orthopyroxene. Conversely, the olivine crystals from the rocks of the leucititic family have diametrically opposed trace elements contents. These olivines have variably high Ca (up to 4.000 ppm), Mn/Fe, and low Ni (less than 2,000 ppm) and Cr. This is compatible with a metasomatic reaction in the presence of excess Ca, that would stabilize olivine and clinopyroxene at the expenses of orthopyroxene.

Olivine crystals from both groups are characterized by remarkably high-Li contents (consistently above 5 ppm), pointing toward the involvement of crustal material that have been subducted and then recycled into the mantle wedge. Our results provide further evidence that two different types of sediments are responsible for the two metasomatic processes depicted above: silico-clastic sediments in the source of the rocks of the Lamproite group, carbonate-rich sediments in that of the rocks of the Leucitite group. This duality is strictly linked to the geodynamic of the subduction front beneath Italy and to its changes with time and space.

Core-to-rim chemical zoning and compositional evolution of tourmaline in the granitic pegmatite of the Cruzeiro mine, Minas Gerais, Brazil

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Keywords: Tourmaline, chemical zoning, granitic pegmatite.

Core-to-rim evolution of a large color-zoned tourmaline crystal from the Cruzeiro pegmatite has been accurately described in terms of site population at the Y site (Al, Fe, Li etc.) and at the O1 site (O, OH, F). Four crystals were extracted from the color-zoned tourmaline and investigated by an integrated multi-analytical approach (crystal-structure refinement, electron microprobe analysis, Mössbauer spectroscopy and optical absorption spectroscopy). Compositional evolution from schorl to fluor-elbaite, with minor contribution of fluor-schorl, oxy-schorl and elbaite, has been proved to occur from core to rim. Comparison with previous studies (Federico et al. 1998; Bosi et al. 2005, 2013) revealed that the observed evolution reflects tourmaline compositional variation across the Cruzeiro pegmatite. In particular, black schorl/fluor-schorl (in the Border and Wall zones) is followed by blue-green fluor-elbaite (which only crystallizes in the Intermediate zone) and may locally evolve into multi-color elbaite (in the miarolitic cavities, shaped by fluid phase ex-solution).

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Equation of state of hercynite spinel, $FeAl_2O_4$, and high-pressure systematics of Mg-Fe-Cr-Al spinels

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Keywords: hercynite, diffraction, pressure, diamond.

Due to their abundance in several geological environments, spinels cover a crucial role in geology. A high number of scientific papers have been published on their stability and behaviour and, more recently, several works focused on their elastic behaviour under extreme conditions of temperature and pressure, which can be used to retrieve the conditions at which spinels crystallize. In detail, spinels of high-pressure mantle origin represent one of the most common inclusions found in diamonds and therefore they can provide strong indications about the diamond formation environment. In this specific case, the most common spinels are represented by the Cr-spinels, mainly by solid solutions constituted by magnesiochromite, $MgCr_2O_4$, and chromite, $FeCr_2O_4$. However, the hercynite component, $FeAl_2O_4$, is not negligible at all in high-pressure spinels with percentage reaching 10-15%, whereas the spinel s.s., $MgAl_2O_4$, only represents some unit percentage.

However, whereas the high-pressure behaviour of $MgCr_2O_4$, $FeCr_2O_4$ and $MgAl_2O_4$ has been definitively investigated even very recently (i.e. Nestola et al., 2014; Nestola et al., 2007), the elastic behaviour of hercynite remains still to be studied and compared with that of the other end-members in order to understand which is the effect of the Al for Cr substitution under high-pressure conditions on the elasticity of Cr-rich spinels. In our knowledge the only datum on the bulk modulus of hercynite was published 42 years ago by Wang and Simmons (1972) by ultrasonic measurements. Wang and Simmons (1972) reported a K_s value of 210.3 GPa. Here we have investigated a synthetic single crystal of pure hercynite, $FeAl_2O_4$, by X-ray diffraction under high-pressure conditions and room temperature using a diamond-anvil cell up to about 7.5 GPa in order to verify if the very old data can be still valid. For purpose of comparison we used the same experimental approach used in Nestola et al. (2014) on $MgCr_2O_4$ and $FeCr_2O_4$ and Nestola et al. (2007) on $MgAl_2O_4$. Our results could be crucial in determining correct stability field calculations, which are based on thermodynamic properties, like the bulk modulus.

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Diffusive fractionation of chemical elements during planetary differentiation processes

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Keywords: Diffusive fractionation, Processes of differentiation, Glass inclusions.

Magmatic masses show strong compositional heterogeneity on many scales of observation. These are the result of the development in space and time of chaotic dynamics that, during their evolution, generate structures with scale invariance properties, e.g. fractals.

The development of this physical process, which is expressed through the mechanism of stretching and folding, involves an intimate contact between fluids and the genesis of a compositional gradient, which propagate at many length scales. This induces molecular diffusion generates a new process of differentiation due to the mixing between compositionally different melts which are formed during the evolution of the magma: the diffusive fractionation process.

This process can occur during any process of differentiation (two end-member mixing, fractional crystallization, partial melting, etc..) and can potentially mask their effects making the interpretation of the compositions of igneous rocks very problematic.

In this work a detailed analysis of all works in the literature reporting the concentrations of trace elements measured on glasses and glass inclusions hosted in mineral phases like Olivine or Quartz has been performed in order to assess the impact of this new process of differentiation on present knowledge of igneous systems. We considered only this two mineral phases because trace elements do not enter in their crystal lattice so their concentrations is not influenced by secondary processes.

With these data we have build element vs element plots, using La as reference for estimating the very variable correlation (R^2) between pairs of chemical elements. Furthermore we have created graphics (R^2 vs Δri; ri being the ionic radius of each element) which show a progressive loss of the linear correlation with increasing difference in the ionic radius.

The results showed that, for all collected data, both on terrestrial (igneous rocks with different evolution degree) and extraterrestrial (chondrites and Martian Shergottites) samples show a clear evidence of the presence of the diffusive fractionation process, highlighting that the petrogenetic interpretations advanced so far for the petrogenesis of these rocks may be subject to uncertainties and/or oversimplifications.

The results of this work shed new light on the processes responsible for the generation of compositional heterogeneities in igneous systems and provide a new dimension of knowledge that may have a decisive impact on knowledge of the processes of magma evolution and planetary differentiation.

Thermodynamics, stability and liquidus phase relations of sapphirine at high pressure and temperature: a computational study

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Keywords: Sapphirine, ab initio, thermodynamic properties.

Sapphirine is widely recognized as a key mineralogical phase in ultra-high temperature metamorphism of amphibolite to granulite facies rocks. Nevertheless, its stability extends over a wide range of P-T conditions and diverse bulk rock compositions as well. In spite of its geological and mineralogical significance, the thermodynamic and thermophysical properties of this mineral are poorly defined and largely unknown. In the last two decades a number of thermodynamic assessments appeared in the literature trying to give a quantitative appraisal of the stability relations of sapphirine-bearing assemblages in multicomponent systems (e.g. Jung et al., 2004). Although all these assessments are internally-consistent, the inferred thermodynamic properties are model-dependent and affected by evident drawbacks. In this contribution, we present a density functional theory (DFT) based ab initio computational study on the thermodynamic and equation of state parameters of sapphirine end-members in the join $Mg_4Al_8Si_2O_{20}$-$Mg_3Al_{10}SiO_{20}$ (Belmonte et al., 2014). The MgO-Al_2O_3-SiO_2 (MAS) ternary system was taken as reference phase diagram to define the topology of the primary stability field of sapphirine up to pressures of about 20 kbar and model its liquidus phase relations and high-pressure crystallization processes. First principles calculations have been coupled with the Hybrid Polymeric Approach (HPA) for multicomponent liquids to compute and minimize the Gibbs free energy of liquid and solid phases through the convex-hull analysis of equipotential surfaces. According to our computational investigation, sapphirine turns out to have a small field of primary crystallization in the MAS ternary diagram at 1-bar pressure, which becomes larger due to pressure effects up to 10 kbar, then progressively shrinks and disappears above 21 kbar. The inferred liquidus phase relations allow to get new insights into the stability relations of sapphirine at high-pressure and temperature conditions. First of all, our study supports the evidence that less aluminous compositions are stabilized by increasing pressure. Furthermore, the survival of a noticeably large primary field of crystallization of sapphirine in MAS system up to relatively high-pressure conditions strengthens the hypothesis that sapphirine could be a primary liquidus phase in basaltic magmas at high pressure, as supported by few experimental works (Milholland & Presnall 1998; Liu & Presnall, 2000) and a recent natural finding of igneous sapphirine (Giovanardi et al., 2013).

Belmonte D., Ottonello G. & Vetuschi Zuccolini M. 2014. Ab initio thermodynamic and thermophysical properties of sapphirine end-members in the join $Mg_4Al_8Si_2O_{20}$-$Mg_3Al_{10}SiO_{20}$. Am. Mineral., in press, doi: http://dx.doi.org/10.2138/am.2014.4833.

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Milholland C.S. & Presnall D.C. 1998. Liquidus phase relations in the CaO-MgO-Al_2O_3-SiO_2 system at 3.0 GPa: The aluminous pyroxene thermal divide and high pressure fractionation of picritic and komatiitic magmas. J. Petrol., 39, 3-27.

Effect of crystal chemistry on cleavage process in micas: petrogenetic implications

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Keywords: micas, cleavage, cluster.

Crystal chemistry and topology of the interlayer in micas were detailed by several authors and readily appeared not only to be sensitive to the composition, but to reflect also the topology of other sites occurring in the mica structure as well as crystallization conditions.

The aim of this work is to relate the crystal chemistry of the cleavage surface, mostly occurring at the interlayer, to cation ordering and genetic processes. In particular, cleavage can be related to the electrostatic potential of basal oxygen atoms that is the individual distance of the interlayer cation to a basal oxygen atom, where the influence of layer crystal chemistry is implicit in these distances.

A similar approach commonly leads to a remarkable overestimation of cleavage energy with respect to experimental observations. Better agreement can be obtained if considering cleavage as a consequence of stress values directed along the layer and normal to the layer. i> can thus be expressed as a function of virtual in plane displacements, thus directed along in plane directions, as defined by X and Y fractional coordinates along (100) and (010), respectively, thus allowing the identification of preferential cleavage directions and, along these latter, to the definition of local maxima and maxima points, surrounding the equilibrium configuration. The difference among maximum and minimum values, that represent the energy required to induce cleavage following a pure shearing mechanism, is significantly less than the potential at equilibrium configuration, which represents in turn the energy required to induce cleavage following a pure normal stress approach.

A better matching of experimental to theoretical data, for what concerns cleavage energy, may thus be explained by introducing a combined shear to normal stress cleavage process. The lower is the difference between maximum to minimum point, the more the crystal is unstable, from a mechanical viewpoint, since small energies, associated with in-plane stress and strains, can cause the crystal to cleave. If the difference between the point of minimum to the point of maximum is small, than the structure is expected to be very brittle, cleavage surface very well defined, since the smaller is the displacement to cause cleavage the less likely is the activation of structural defects eventually present in crystal structure.

All these values changes as a function of chemical composition and of crystal structural features. The relevance of these interdependences may be significant for explaining clustering of given elements at crystal surface, thus imparting a different chemical composition at crystal surface with respect to the bulk and to indicate mechanical stability fields for phyllosilicates with given crystal chemical and crystal structural features.

Ca-Zn substitution in clinopyroxenes: anomalous solution behavior and implications for mantle petrology

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Keywords: Ca-Zn pyroxenes, high pressure synthesis, crystal structure, Zn partitioning in clinopyroxenes.

Growing interest was recently paid in Zn substitution in clinopyroxenes. Although Zn is an element present in trace amount in silicates, Zn partitioning in clinopyroxenes, olivine and orthopyroxenes provides a clue to interpret the origin of mantle related differentiates. For instance it was found in peridotite xenoliths that Zn/Fe ratios are equally fractionated between olivine, orthopyroxene and melt, but strongly fractionated when garnet and clinopyroxene are considered (Le Roux et al., 2010). These differences can be explained by the crystal structure where these metal transition ions are hosted. In clinopyroxene Zn has a higher preference for the eight-fold-coordinated M2 site, involving a substitution of Zn for Ca, which can be studied in the $CaZnSi_2O_6$-$Zn_2Si_2O_6$ series; experimental data are however lacking. We have therefore synthesized a set of Ca/Zn pyroxenes along the series, and studied their crystal structure by single crystal X-ray diffraction. The pyroxenes were synthesized after three hours of solid state reaction at T = 1200°C and P = 5 GPa, by means of a multi anvil Walker-type press. A single phase clinopyroxene, together with a small amount of coesite, was invariably found; no evidence of a two pyroxene assemblage was observed, indicating that a solvus, if any, is present at lower temperature. Single crystal XRD and Rietveld analysis of powder patterns showed that the symmetry is *C*2/*c* for the whole series. No phase transition with composition is found. Changes in volume are linear and rather small, in spite of the remarkable difference in ionic radius between Ca and Zn (1.0 vs 0.74). Differently from Ca-Co, Mg and Fe pyroxenes the volume decreases much less than we would expect assuming that changes in volume are only due to differences in ionic radius (Mantovani et al., 2014). Single crystal XRD shows a strong M2-M2' splitting, with Ca and Zn splitted by 0.5 Å. The coordination of Zn in the M2 cavity is four-fold, even in Ca richer samples. The different behavior of Zn respect to Ca, Mg and Fe clinopyroxenes was related to the covalent character of Zn, most apparent in the M2 cavity. The different cation behavior in the M2 site respect to other metal transition elements explains then the different partitioning for Zn in garnets and clinopyroxenes respect to olivine and orthopyroxenes.

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The cooling kinetics of plagioclase revealed by electron microprobe mapping

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Keywords: andesite, plagioclase, EPMA map, cooling, crystallization, thermometer.

In this study we have used electron microprobe mapping to investigate plagioclase compositional evolution due to cooling kinetics. We re-analyzed five run-products from a prior study (Iezzi et al. 2011), crystallized by cooling a natural andesitic melt from 1300 to 800 °C at 25, 12.5, 3, 0.5 and 0.125 °C/min under atmospheric pressure and air redox state. As the cooling rate decreases, the texture of large plagioclases changes from skeletal to hollow to nearly equant. In this study, we use x-ray map data to obtain a database of 12275 quantitative chemical analyses. The frequency of An-rich plagioclases showing disequilibrium compositions substantially increases with increasing cooling rate. At 25 and 12.5 °C/min the distribution is single-mode and narrow, at 0.5 and 0.125 °C/min is single-mode but very broad, whereas at the intermediate cooling rate of 3 °C/min two distinct plagioclase populations are present. This intermediate cooling rate is fast enough to cause departure from equilibrium for the crystallization of the An-rich population but also sufficiently slow that An-poor plagioclases nucleate from the residual melt. We interpret our findings in the context of time-temperature-transformation (TTT) diagrams, and infer the crystallization kinetics of plagioclase in the experiments. Compositional trends and our inferences regarding TTT systematics are consistent with two discrete nucleation events that produced separate populations of plagioclase (i.e., An-rich and An-poor populations) at 3 °C/min. Using plagioclase-melt pairs as input data for the thermometric reaction between An and Ab components, we find that plagioclase mirrors very high (near-liquidus) crystallization temperatures with increasing cooling rate. These results have important implications for the estimate of post-eruptive solidification conditions. Lava flows and intrusive bodies from centimeters to a few meters thick are characterized by a short solidification time and a significant thermal diffusion. Under such circumstances, it is possible to crystallize plagioclases with variable and disequilibrium chemical compositions simply by cooling a homogeneous andesitic melt. X-ray element maps enrich the study of plagioclase compositional variations generated under conditions of rapid cooling.

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Fluorophlogopite and F-rich phases in limestone clasts from the Campanian Ignimbrite quarried at Fiano (southern Italy): mineralogical, geochemical and volcanological insights

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Keywords: Campanian Ignimbrite, southern Italy, Fiano xenoliths, F(Mg)-rich minerals, crystal chemistry.

Fluorine-rich metamorphosed xenoliths associated to the distal Campanian Ignimbrite (CI) tephra (Campania region, southern Italy) have long attracted the interest of the mineralogical community (i.e. Scacchi, 1890; Zambonini, 1919; Masi & Turi, 1972; Balassone et al., 2002). These rocks derive from the Mesozoic carbonate lithotypes of the Campanian Apennine, embedded in the pyroclastic flow and presently resting at the bottom of the tuff formations. The sedimentary protoliths suffered from the action of hot, volatile-rich pyroclastic flow, and consequently were affected by thermal metamorphism to various degrees. Their peculiarity is the occurrence of F- and Mg-bearing phases, with an ubiquitous presence of neoformed fluorite. The occurrence at Fiano quarries (the so-called "*Tufare*") is the classical locality for these rock xenoliths. Similar rocks were also found in the CI of the Caserta area, and in the Latium region (Colli Albani). This research aims both at a crystal chemical study of fluorophlogopite occurring in the Fiano xenoliths, and at a geochemical and volcanological survey, to constrain the petrogenesis processes related to this rare F-, Mg-rich assemblage and to CI.

The analysed samples belong to two lithotypes: mica-bearing clasts and variably metamorphosed carbonate blocks. The former lithotype is represented by abundant fluorite, followed by fluorophogopite, F-rich chondrodite, fluoborite, diopside and (Fe,Mg)-oxides. Minor to trace contents of calcite, humite, tremolite, and grossular also occur. Carbonate rocks can show calcite only, or also trace amounts of fluorite. The Fiano micas composition approaches that of the Vesuvius micas from the 1872 eruption (Balassone et al., 2013). The micas belong to the 1*M* polytype and have crystal chemical features typical of fluorophlogopites i.e., low *c* lattice parameter (~ 10.13 Å), (~ 2.060 Å) and (~ 3.135 Å) distances. New data on minor to ultratrace elements amounts found in the studied clasts, together with Carbon and Oxygen isotope data will be reported and interpreted in a petrogenetic and volcanological frame.

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A Raman spectroscopic study of Cr-bearing natural spinels with 0.03 < Cr < 1.68 apfu

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Keywords: Cr-spinels, Raman spectroscopy, structure.

Cr-bearing spinels can be found in different geological environments, usually related to mafic and ultramafic rocks. In nature, several cations can enter into the structure originating a solid solution with a general formula (Mg, Fe^{2+})(Al, $Cr)_2O_4$. Other cations such as Fe^{3+} or Ti can be present in low amounts - although in some cases the Fe^{3+} content can be very high. They can also be found in metamorphosed rocks, and in sedimentary rocks as a detrital mineral, due to its high resistance to weathering and breakage. In the last decade some Raman spectroscopy studies took into consideration natural Cr-spinels found in meteorites, in mafic rocks and in archaeological stone artifacts. In all natural spinels and almost all of the synthetic ones, even if the vibrational modes are easily assigned, the presence of several cations within the structure has generated difficulties of interpretation of the Raman shifts due to the possibility for several cations to enter the octahedral and tetrahedral sites. Lenaz and Lughi (2013) verified the effects on Raman shifts of Fe^{2+} and Fe^{3+} for two synthetic series. The first one, $MgCr_2O_4$ - $Fe^{2+}Cr_2O_4$, is characterized by the sole substitution of Mg by Fe^{2+} into the tetrahedral site, while in the second, $MgCr_2O_4$ - $MgFe^{3+}{}_2O_4$, Fe^{3+} substitutes for Cr.

For this study we analyzed more than 300 different natural Cr-bearing spinels with 0.03 < Cr < 1.68 atoms per formula unit coming from mantle xenoliths, alpine peridotites, ophiolites, layered complexes and meteorites in order to better define the behavior of the Raman modes according to the chemical composition and structure of these crystals. In many cases, the studied spinels had been previously analyzed by single crystal X-ray diffraction and electron microprobe; in this study, we will attempt to correlate the Raman results to the order-disorder phenomena and the chemistry of spinels.

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Clinopyroxenes from Pico Volcano (Azores Island, Portugal): crystal chemistry and water content

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Keywords: clinopyroxenes, volcanic rocks, water content, IR, SC-XRD.

The Pico volcanic island is located in the central Azores archipelago (Portugal). It is formed by a perfect conical stratovolcano and an enlonged ridge constituted by cinder cones aligned along NW-SE trending faults, and associated to fissural eruptions.

Clinopyroxenes, as an early forming phase, can incorporate H^+ that may be used to calculate the volatile content and contribute to the knowledge of evolution processes during magma crystallisation and ascent.

We focused on cpxs from this area of the island due to the particularly high content of this phase in erupted material. Samples are millimetric euhedral phenocrysts from a cumulitic lava flows and centimetric euhedral crystals from the Pic16 mugearite lava flow erupted during the 1718 eruption. We performed polarized FTIR, Mössbauer, SC-XRD, EPMA on the same cpx crystal.

Diopside (Wo45-46 En45-48 Fs06-09) in composition, the cpxs showed very weak or absent OH^- vibrational bands in the IR spectra (except in Pic16) with a H_2O content ranging from 0 to 91 ppm.

These low contents indicate H^+ loss during ascent to surface or post eruptive re-equilibration, which may occur via the redox reaction $Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + ½H_2$. In order to restore H^+ that was possibly lost, we performed thermal annealing experiments under H_2 gas flux at 700°C and 800°C. All the samples increased their hydrogen content and saturated after 65-83 hours, depending on crystal thickness. The new range of water thus obtained is 93-170 ppm for the cumulitic lava and 182 ppm for Pic16.

Mößbauer analysis gave a Fe^{3+}/Fe_{tot} ratio for untreated cpxs between 18.8-25.8%, after the thermal annealing the ratio remains constant or slightly decrease.

Using the H-saturation values and the partition coefficients of Wade et al. (2008) we calculated 0.75-1.21 H_2O wt% in melt, which is slightly lower than the range measured in melt inclusions in olivines from the Pico fissural eruptions (Metrich et al. 2014).

The Pico primary magmas were produced at 3GPa and 1352-1362°C, by a very low melting degree of a mantle source with 350 to 630 ppm of H_2O, then melts ascended up to 18 km, where olivine and clinopyroxene crystallised and accumulated in a storage areas (Zanon & Frezzotti 2013). The crystal chemistry of cpxs suggests that they crystallized at 18 km depth and that the H^+ loss occurred during the ascent or a late stage of eruption.

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Diamond-olivine host-inclusion system: crystallography and depth of formation

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Keywords: Diamond, olivine, depth, pressure, diffraction, orientation.

Diamond is probably the most deepest and oldest material able to reach the Earth's surface. Thanks to its ability to include any type of inclusion during its ascent it provides the unique direct sampling of our planet interior. Indeed, much of what is believed about the genesis and distribution of diamond in the Earth's mantle has therefore been deduced indirectly from the characterisation of its mineral inclusions. However, there is still an important debate about the temporal growth relationships between diamond and its inclusions and about the real depth at which diamonds can form. In detail, it is often assumed that the inclusions were formed at the same time as the host diamond (i.e. *syngenetic*), and do not represent pre-existing material that was passively incorporated into the growing diamond (i.e. *protogenetic* inclusions). Two main arguments have been used in favour of syngenesis. (1) It has been claimed that inclusions normally exhibit specific orientations relative to the diamond hosts. (2) Inclusions often display a morphology of the diamond host (i.e. typical "cubo-octahedral" shape).

We have measured the crystallographic orientation of 47 inclusions of olivine in 21 different diamonds by single-crystal X-ray diffraction. We found no recurrent crystallographic orientations between olivine and diamond (as instead reported in some literature data) ruling out any possible epitaxial relationship. However, multiple olivine inclusions in a single diamond often show similar orientation to one another.

Concerning the depth at which the diamonds form it is reported that about 94% of diamonds are subcratonic, with depths of formation ranging between 120 and 250 km, and only 6% of them could be considered "super-deep diamonds" (see recent paper on Nature, Pearson et al., 2014). However, it is very difficult using chemical geo-thermobarometer approach to provide the real depth of formation of diamonds and recent the method based on inclusion-host elasticity (see Angel et al., 2014) is representing an extremely valid alternative to get the pressure of diamond formation.

We have measured the pressure of formation on four of the above 21 diamonds from Udachnaya applying the method based on inclusion-host elasticity to the diamond-olivine pair and found a pressure of formation very similar for all the diamonds, which could suggest that at Udachnaya diamonds form under the same pressure.

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How deep (and hot) is a diamond? The current state of diamond thermobarometry

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Keywords: diamond, thermobarometry, Earth's mantle.

A good understanding of the distribution of diamond in Earth's mantle provides constraints for the evaluation of diamond potential of economic targets and for the assessment of the deep carbon cycle in ancient Earth. Much of what we know about the depth distribution of diamond is derived from the study of rare mineral inclusions that are amenable to conventional two-phase thermobarometry. However, non-touching inclusions were not necessarily in equilibrium at their encapsulation time, whereas touching inclusions could reequilibrate after entrapment. Moreover, since diamonds can form under a wide range of redox conditions, the unknown Fe^{3+}/Fe_{tot} ratios in the inclusions may lead to large uncertainties on T estimates based on Fe–Mg exchange thermometry and, in turn, on P estimates.

The development of single-mineral thermobarometers applicable to isolated inclusions has in part overcome the equilibrium issue. However, as yet only chromian clinopyroxene allows to estimate both P and T with a precision comparable, if appropriate analytical conditions are used, to that of conventional methods. In fact, no effective barometers exist for some of the most abundant inclusion types, such as olivine and the eclogitic minerals.

An additional problem is whether the inclusions are syngenetic with diamond or they represent passively captured pre-existing material. In the latter case, incomplete chemical resetting during rapid diamond growth may prevent determination of the conditions of diamond formation. Recent studies suggest that the imposition of diamond morphology on the inclusion (the most widely used criterion for syngenesis) is not unique to syngenetic inclusions, casting doubts on the real significance of P-T data extracted from many reported "syngenetic" inclusions in diamonds.

The determination of the remnant P on the inclusion, e.g., using data from X-ray diffractometry, birefringence analysis or Raman spectroscopy, provides an alternative way to diamond barometry using elasticity theory. Application of this methodology is still at its infancy, because of uncertainties in the thermoelastic behaviour of the minerals, potential non-elastic relaxation and technical limitations. It is a field of on-going development, which may eventually allow evaluation of the depth of provenance of diamonds containing minerals that are chemically insensitive to P, such as the abundant upper-mantle olivine or the super-deep ferropericlase.

Although available data suggest that lithospheric diamonds may come from any depth below the graphite–diamond transition, owing to the above limitations recognition of subtle inhomogeneity in the vertical distribution of diamond (or of specific diamond populations) remains challenging. Further development of conventional and non-conventional thermobarometric methods may allow us to increase the statistical significance of the diamond P-T record and may eventually contribute to refine models of diamond formation in the sub-cratonic mantle.

Zircon beyond geochronology: inherited and antecrystic zircons as igneous petrogenesis tools

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Keywords: Tuscan Magmatic Province, zircon, U-Pb geochronology.

Advances in U-Pb zircon geochronology led to the awareness that zircon crystals in an igneous rock commonly belong to different populations issuing from complex diverse histories. Thus, dates from autocrysts (that are associated only with the latest pulse of magma) indicate crystallization age, while dates on populations of antecrysts (that crystallized from an earlier pulse of magma and which are incorporated in a later pulse) or of inherited crystals/cores (that survived several processes, from sedimentary to anatectic) can give informations about former processes.

The aim of this study is twofold: (i) using dates obtained for inherited zircon crystals/cores in anatectic rocks to unravel the nature/age of the continental crust involved in anatexis; (ii) using dates obtained for antecrystic zircons to shed light on the temporal evolution of the igneous process.

This study has been carried out on a young igneous system, the Tuscan Magmatic Province, which is mostly composed of anatectic acidic and hybrid rocks. The analysed samples are from intrusive bodies (Monte Capanne and Porto Azzurro monzogranites) and hypabissal rocks (San Martino and Portoferraio porphyries) from Elba Island, as well as from volcanic centres from southern Tuscany (San Vincenzo and Roccastrada rhyolites). Internal morphologies have been investigated by SEM-cathodoluminescence and they have been used as a guide for the selection of potential antecrysts or relict crystal cores where to determine U-Pb ages by means of high-resolution laser-ablation ICP-MS.

After a careful screening of analytical data, the obtained dates have been grouped into two sets: “young” ages, close to the established emplacement age, interpreted to represent antecryst ages, and significantly older ages from inherited zircons.

Inherited zircons and cores have an overall age distribution including components that have all been found in detrital zircons from the Tuscan Metamorphic Basement (studied in a companion work), such as neat Panafrican (late Neoproterozoic-Ordovician) and Variscan signatures. The known Tuscan Basement is thus a plausible candidate as a source rock for anatectic melts.

For “young” antecryst ages, a time gap is observed between zircon ages from the same sample, and between these ages and the final solidification/eruption age as well. Such an age distribution of most of the antecrystic zircon grains has been interpreted in recent works (Fish Canyon Tuff, Colorado) as an evidence for the assembling of magma bodies over a timescale hundreds of ky by the amalgamation of small pulses of magma. Among the Tuscan Magmatic Province, the San Vincenzo rhyolite is the best example of magma that was stored as a crystal mush and repeatedly fed, undergoing local thermal oscillations that enabled zircons to grow intermittently over an extended period of time.

Compositional variations of sapphirine in metamorphic rocks

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Keywords: sapphirine, metamorphism, P-T conditions.

Based on compilation of published microprobe analyses of sapphirine and coexisting phases from metamorphic rocks worldwide (now available as an open Internet database at http://database.iem.ac.ru/sapphirine), compositional variations of this mineral have been considered in terms of petrogenetic conditions. Being associated with aluminium- and/or magnesium-rich minerals such as spinel, orthopyroxene, cordierite, garnet, clinopyroxene, olivine, kornerupine, osumilite, plagioclase, K-feldspar, biotite, gedrite, chlorite, talc, clinohumite, sillimanite, kyanite, mullite, and corundum, sapphirine occurs in both silica-saturated and silica-deficient in rocks that have undergone different tectono-metamorphic histories. The Fe^{3+}/Fe ratio for sapphirine, as calculated from the total iron content according to stoichiometric criteria (Droop, 1987), is normally higher than that for coexisting Fe-Mg minerals, including spinel. No correlation between Fe^{3+}/Fe and Mg/(Mg+Fe) ratios have been traced for the compiled compositions of sapphirine. The extensive Tschermak substitution characteristic for this mineral is demonstrated by drastic changes from its rather low Si contents in eclogite assemblages to relatively silica-rich compositions in high-temperature granulites. The P-T range of formation of sapphirine-bearing assemblages have been estimated from below 700°C and 5 kbar to above 1000°C and 10 kbar. Controversial thermodynamic models of sapphirine solid solution (Wheller & Powell, 2014; Podlesskii, 2010) arising from insufficient experimental data seem to allow too much freedom for interpreting the P-T-X phase relations.

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Phase diagrams for $CaCO_3$ and $CaCO_3$+H_2O and their bearing on the genesis of carbonatitic melts

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Keywords: calcite, aragonite, carbonatite.

Phase transformations in the system $CaCO_3$ and $CaCO_3$ + H_2O have been of primary concern for Earth scientists since early XIX century. Sir J. Hall performed the first investigations in this system in 1798 and pursued various attempts at defining decarbonation reactions and melting of calcite with water in externally heated gun barrels, successfully performing the first high pressure experiments in geoscience.

Despite two centuries passed, experimental results on phase transformations in $CaCO_3$ are still extremely contradictory. Discrepancy between *ex-situ* and *in-situ* determination of the reaction calcite = aragonite is in the order of 3 GPa at 1200 °C. Experimental data on melting of calcite with an aqueous fluid differ by 300 °C and aragonite melting is unknown. Uncertainties on the phase diagram for $CaCO_3$ and $CaCO_3$ + H2O have profound consequences in predicting the fate of altered oceanic crust and of metasedimentary materials re-introduced in the mantle at subduction zones.

Multianvil experiments were performed at 4.2 GPa on a model bulk composition in the system CaO-Al_2O_3-SiO_2-H_2O-CO_2, obtained from natural calcite, $Al(OH)_3$ and silica. Stoichiometric proportions are intended to produce at run conditions kyanite + $CaCO_3$ + an aqueous fluid. Al_2SiO_5 saturation prevents the formation of portlandite and offers a basis for modelling melting of impure marbles. Furthermore the usage of $Al(OH)_3$ in the starting material allows an accurate control of H_2O added, fixed at 10 wt% in the present study. This amount is expected to produce largely H_2O-undersaturated melts, on the basis of solubility data determined at low pressure.

Aragonite + kyanite + fluid, and minor lawsonite and grossular form at 700 °C and 800 °C, respectively. At 900 °C a complex sequence of quenching textural features is observed; "chains" and dendrites of $CaCO_3$ grow nucleating from liquid-solid interface; they are followed by growth of Si-Al-bearing fibres; finally spheres of silica precipitate from the residual fluid exsolved from the liquid carbonate phase.

Estimates of liquid – solid proportions, retrieved by image analysis, at known bulk H2O content, along with the solid – pore volume proportions in the liquid region of the run charge provide constraints for H_2O solubility in $CaCO_3$ liquid. Contrarily to early suggestions of supercritical behaviour in the system $CaCO_3$ – H_2O above 4 GPa, our data still support the occurrence of a univariant solidus reaction with clear distinction between fluid and liquid phases in the model system investigated.

The model system investigated here and the minimum temperatures of melting found represent the upper bound of the formation of hydrous Ca-carbonate melts able to metasomatise the mantle at subduction zone environments generating carbonate pyroxenites, a fertile CO_2 source for volatile-rich magmatism.

Crystal-chemistry of Cr-diopsides included in spinel-peridotite mantle xenoliths from Cameroon, Libya and Morocco (Africa): petrogenetic implications

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Keywords: Cr-diopsides, mantle-xenoliths, Africa.

Three series of C2/c clinopyroxenes (cpx) enclosed in spinel peridotite xenoliths from Lake Nyos (Cameroon; CA), Waw-En-Namus (Libya; LB hereafter) and Tafraoute and Bou-Ibalrhatene (Morocco; MOR) have been investigated by single-crystal X-ray diffraction, and electron microprobe, to provide a new knowledge of the mantle beneath North-Western Africa continent. These cpx were also compared with previously studied cpx from Mt. Nji (Lnji) and other cpx worldwide.

The here studied cpx have been selected considering that the mantle xenoliths sampled by alkaline lavas are coming from different geological occurrences. In fact MOR should reflect cratonic conditions and LB metacratonic while CA are from the Cameroon volcanic line whose products outcrop within a polycyclic mobile belt.

The compositional and structural studies reveal that the three series have: 1) comparable chemistry in terms of major elements (Ca = 0.729-0.835; Mg = 0.795-0.919 a.p.f.u.), 2) are hosted in protogranular textured xenoliths and 3) have pressure equilibration ranging between 10 and 21 kb (Mercier formulation).

T site volume decreases with Al^{IV} content and LB cpx show lower volume and Al content with respect to those from MOR and CA. Samples from MOR and CA have Al^{IV} content similar to Lnji cpx even if these latter show a slightly higher V(T). Notably, the high V(T) and Al^{IV} content of Lnji cpx was interpreted as the effect of a crystallization at high pressure of alkaline magmas, which intruded, as small-volume melts, peridotite mantle.

V(M1) site volume increase is well related to the decrease of R^{3+} content. In particular LB and MOR cpx span from 0.157 to 0.251 a.p.f.u, whereas CA and Lnji cpx from 0.221 to 0.257 a.p.f.u.. CA cpx behavior is similar to those of Lnji cpx trending towards cpx crystallized in mantle condition, and not like peridotitic cpx residual after basaltic extraction.

As far as concern the V(M2) site volume for MOR and CA cpx it is positively related to Ca+Na content, whereas for LB and Lnji cpx it increases with virtually constant Ca+Na content (about 0.920 and 0.910 a.p.f.u., respectively).

Inter-crystalline temperature and pressure conditions, calculated through Mercier formulation, are in the range 850-1100 °C and 10-21 Kbar for all investigated cpx. Intra-crystalline temperature, are different for the three cpx suites, (700-1000, 579-700 and 450-780 for LB, MOR and CA cpx, respectively), and this may reflect different cooling history and/or equilibration temperatures into the mantle suffered by the host rocks.

In summary, the three cpx suites show characteristics for some aspects similar each other and also similar to those of Lnji cpx, suggesting they were brought to the surface from a heterogeneous mantle. This heterogeneity may be related to the "small-volume melt metasomatism" which enriched the sub-continental lithosphere during the Pan African event.

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Structure, composition and origin of yangzhumingite and phlogopite from the Kvaløya lamproite (North Norway)

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Keywords: Lamproite, Kvaløya Island, Yangzhumingite, Tetraferrifluorphlogopite.

This study reports the first single crystal structure refinement of a natural yangzhumingite found in a lamproitic dyke at the Kvaløya Island (North Norway), as well as a complete structural characterization of the associated phlogopite. Specifically, three types of micas (yangzhumingite, light brown phlogopite and dark brown phlogopite) underwent petrographic and crystal chemical analyses by integrating multiple analytical techniques: electron microprobe, single crystal X-ray diffraction, inductively coupled plasma mass spectrometry, Mössbauer and micro-Fourier Transform infrared spectroscopy.

The micas are separated into three different groups on the basis of the ^{VI}Fe and Mg versus Si content. Yangzhumingite composition is intermediate between those of $KMg_{2.75}(Si_{3.5}Al_{0.5})O_{10}F_2$ and $KMg_{2.50}Si_4O_{10}F_2$ synthetic compounds studied by Toraya et al., 1976, 1978, respectively. Light and dark brown phlogopite are both Mg-rich tetraferrifluorphlogopite, the latter having a greater Fe content. The main features of the infrared spectra of yangzhumingite and the light brown phlogopite show the occurrence of OH^- absorption bands respectively at: ~3586 cm^{-1} which correlates well with the measured F content: 3707 cm^{-1} and 3686 cm^{-1} assigned mainly to $3Mg^{2+}$-K^+- OH^- (phlogopitic) environment.

Structural analyses, performed only on yangzhumingite and the light brown phlogopite because dark brown phlogopite is poorly crystallized, show that both samples are 1*M* polytypes with the expected space group *C*2/*m*. Yangzhumingite has cell parameters a = 5.2677(3), b = 9.1208(5), c = 10.1652(6) Å, b = 100.010(4)° whereas light brown phlogopite has a = 5.3202(3), b = 9.2128(4), c = 10.1971(5) Å, β = 100.080(4)°. Crystal chemical features are compatible with the following major substitution mechanisms: $2^{XII}K^+ \leftrightarrow {}^{VI}R^{2+} + {}^{VI}[]$ (where R^{2+} = Mg, Fe), $OH^- \leftrightarrow F^-$ for yangzhumingite and $2^{VI}R^{2+} \leftrightarrow {}^{VI}Ti^{4+} + {}^{VI}[\ ]$ (Ti-vacancy), $OH^- \leftrightarrow F^-$ for light brown phlogopite.

The three types of mica reported here formed at relatively constant low pressure, but over a large temperature range in equilibrium with a grain boundary fluid that underwent significant changes in composition during reaction progress. Light brown phlogopite cores and dark brown phlogopite rims formed during crystallization from the lamproitic magma, while yanzhumingite formed as a result of reactions between the already formed phlogopites and the highly reactive fluid that was derived from the volatile-rich lamproite magma.

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A FESEM-FIB-EDS investigation on fibrous and acicular volcanic orthopyroxenes from Etnean products, Italy

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Keywords: etnean minerals, fibrous pyroxenes.

Present work concerns the continuation of the study of these particular ferroan orthopyroxenes, which have been investigated by Field Emission Scanning Electron Microscopy (FESEM) combined with Focused Ion Beam (FIB) and with Energy Dispersive X-ray Spectroscopy (EDS). These analytical techniques have allowed a detailed study of the external morphology, besides to compositional variations from the surface to the internal parts of the crystals, thanks to the FIB cutting. The study revealed differences in morphology and composition between the fibrous and the acicular orthopyroxenes. The crystals with acicular habit (width ≈ 2-3 µm), often twinned and sometimes flattened, has a ferroan-enstatite composition with an iron content higher than the fibrous crystals, and are characterized by the presence of parallel lamellae exolutions between them, which extend along the "c" axis of the mineral growth. The exolutions are often visible on the surface of the crystal, making striated morphologies, and their chemical composition, even tough with similar spectrum EDS of ferroan-enstatite, presents an iron content higher than the host mineral. In effect, these exolutions could be simple iron oxides in following to element migration. The fibrous orthopyroxene variety (thinner than the prismatic type - width ≈ 0,5 µm) shows an internal compositional homogeneity with a lower iron content (FeO ≈ 1 wt%). From these new experimental evidences on morphologies, dimensions, chemical compositions and iron behaviour, we can advance further hypothesis on the crystallization process: 1) a secondary process of alteration interested the prismatic and acicular crystals, which allowed migration of iron and formation of exolutions; 2) consequent formation of oxides with iron 3+ (hematite); 3) high speed of crystallization during the final stage of the magmatic process, with fibrous enstatite formation and low iron content.

A crystal-chemistry study of the acicular and fibrous opx is necessary to confirm or not these hypothesis.

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Natural evidence of kimberlite-garnet reactions in the upper mantle

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Keywords: Garnet, Kimberlite, Trace elements.

Percolation of melts in the Earth's upper mantle leaves geochemical and mineralogical imprints on both the melts and the mantle rocks that need to be interpreted using the available natural samples. Kimberlites, which have the deepest origin of all terrestrial magmas, provide the unique opportunity to study the melt-rock reactions down to the deepest portions of the cratonic lithospheric mantle. The imprints of these reactions are potentially recorded in the kimberlite-hosted mantle xenoliths and in the kimberlitic melts themselves, but they are often obscured by the processes occurring during and after the kimberlite eruption. Garnet and clinopyroxenes, which are two important constituents of the peridotitic mantle, are more resistant to these processes and are in fact commonly found in kimberlites as xenocrysts derived from the disaggregation of the former mantle rocks. Here we focus on the garnet xenocrysts suite of the Zagadochnaya kimberlite (Yakutia, Russia). This is a good case study to investigate the melt percolation processes in the upper mantle, because these samples preserve the clear evidence of garnet-melt reactions occurred at mantle depths shortly before the kimberlite eruption.

All analysed garnet grains are of peridotitic origin and most of them are strongly zoned, showing domains where the original (Ca, Cr)-rich garnet has been replaced by (Ca, Cr)-poor garnet + clinopyroxene + spinel (± phlogopite ± amphibole ± Ti oxides). These domains are often located at the edges of the grains and in some cases extend pervasively throughout the entire grain. The trace element contents of the secondary garnets, which are systematically higher with respect to the primary hosts, are compatible with equilibrium with the Zagadochnaya kimberlite. This observation, combined with other supporting textural and mineralogical evidence (Nimis et al., 2009; Ziberna et al., 2013), indicate that these replacement reactions were driven by melts closely related to the host Zagadochnaya kimberlite and that they occurred at mantle depths shortly before the eruption. The wide spectrum of textural, mineralogical, and major and trace element features of these microxenoliths makes this case study suitable for the application of forward modeling of petrogenetic processes. Therefore numerical simulations of trace element transfer will be tested, which can potentially help to identify the melt-rock reactions that occurred in the mantle shortly before the eruption of the kimberlite.

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SESSIONE S17

The oceanic lithosphere: formation, evolution and fate

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Modes of ophiolite emplacement in the Tethyan Belt: Implications for palaeogeography and geodynamic reconstructions

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Keywords: Ophiolite emplacement, Tethyan belt, palaeogeography.

Ophiolite belts cropping out in mountain ranges have classically been considered as evidence of the closure of a former ocean since the early days of Plate Tectonics (e.g., Dewey, 1977). The articulate mountain belt that extends from the Mediterranean region to the Himalayas, and further to the east, has been shaped by the convergence towards Eurasia of a set of southern plates (chiefly Africa, Arabia, and India), ultimately leading to continental collision. The oceanic Tehyan realm, originated during the breakup of Pangea, was consumed during this long-lasting process of plate convergence, leaving sparse vestiges of its original complex palaeogeography (e.g., Sengor, 1985). The Mediterranean Tethyan belt, in particular, offers many examples of ophiolite units dotting the Alpine mountains. Although these ophiolite units originated within the same oceanic realm, they display different ages and geochemical affinity, ranging from MORB to SSZ. But a feature that is perhaps more relevant for palaeogeographic reconstruction is the nature of ophiolite emplacement. Along the MediterraneanTethyan belt two main types of ophiolite occurrence can be encountered, in spite of some local variety.

In one instance the ophiolites appear as large slivers which have been emplaced onto a passive margin sedimentary succession, and have been capped and sutured by shallow water carbonate sediments. Ophiolites of this type crop out in the Dinarides and Hellenides, with Jurassic age. These ophiolites come from the upper plate and show little or no metamorphism. The age of metamorphic soles indicates that these ophiolites were originated by intra-oceanic subduction, and their emplacement do not mark a collisional suture.

The other major type of emplacement is related to continental collision, when a subductive accretionary wedge is shoveled onto a passive continental margin. A subduction initiatially located at the continental margin is the premise for this type of emplacement. The ophiolite rocks of this type are typically coming from the lower plate, and suffer from variable degree of metamorphism during accretion. Disrupted ophiolites, in blocks of various size often arranged as melange, are accreted in the frontal part of the accretionary wedge. Larger slabs of ophiolite are present in the deeper part of the accretionary wedge; these rocks experienced HP/LT metamorphism in the subduction channel, before being underplated and eventually exhumed. Ophiolites of this type are typically present in the western Mediterranean (Alps, Apennines and Corsica).

The two modes of ophiolite emplacement imply that subduction initiated at different position within the Tethyan ocean, and this issue has major relevance on palaeogeographic reconstructions and geodynamic interpretations.

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Subsolidus and partial melting experiments on a natural pyroxenite at 1-1.5 GPa

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Keywords: Experimental Petrology, pyroxenites, mantle partial melting.

Pyroxenite layers embedded in mantle peridotites represent a diffuse lithological heterogeneity in the upper mantle and they are often invoked as a minor but important component in the mantle source of oceanic basalts, as main responsible for their chemical and isotopic variability (e.g. Lambart et al., 2013). Pyroxenite layers in ophiolitic mantle sequences of the Northern Apennines (NA, Italy) have been recently interpreted as the result of deep infiltration of low-MgO melts in the peridotites, thus representing a natural portrait of the so-called "stage 2 pyroxenite", a potential enriched component in the basalts mantle sources (Mallik & Dasgupta, 2012; Lambart et al., 2012). This study aims to define i) the subsolidus phase assemblage, ii) melt productivity and iii) composition of partial melts of a stage2-type pyroxenite by high pressure and temperature synthesis of a natural NA pyroxenite. Experiments were carried out at P from 1 to 1.5 GPa and T from 1100 to 1330°C, using both single-stage and end-loaded piston cylinders. As starting material we used a glass obtained by complete melting of rock powder sample in a furnace at 1500°C (at FMQ fO_2 conditions) and rapid quench in dry ice. Resulting glass has X_{Mg}=0.83, CaO=14.4 wt%, Al_2O_3=10.1 wt% and Na_2O=0.3 wt%, similar to bulk compositions of several worldwide pyroxenites. To promote the nucleation of the minor phases in subsolidus experiments, gel is seeded with 1% of a mixture of synthetic pure spinel (50%) and Dora-Maira pyrope (50%). A layer of carbon vitreous spheres (dMg in olivine and pyroxenes) and first mass balance calculation support approach to equilibrium. At near-solidus T, a spinel-bearing assemblage is stable at 1.0 GPa, whereas garnet+spinel-bearing assemblage is stable at 1.5 GPa. Glass appears in experiments between 1150-1200°C at 1.0 GPa, and 1200-1250°C at 1.5 GPa. At 1 GPa, pyroxenite GV10 produces i) very low melt fraction (F > 5 wt%) at 1200°C, ii) a low-X_{Mg} (≅ 0.43), Al-rich melt for low melt fraction (F = 8.9 wt%; T = 1250°C), iii) a high-X_{Mg} high-CaO melt for high partial melting degrees (F = 56.7 wt%), iv) melt fraction of about 80 wt% at 1330°C. Preliminary results of this study indicate that high degrees of partial melting of a stage2-type pyroxenite produces melts with composition close to that of near-solidus partial melts from fertile peridotites (Falloon et al., 2008).

Borghini G., Rampone E., Zanetti A., Class C., Cipriani A., Hofmann A.W., Goldstein S.L. & Godard M. Chemical and isotopic heterogeneity in meter-scale pyroxenite-peridotite mantle sequences from Northern Apennine ophiolites (Italy). This conference.

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Chemical and isotopic heterogeneity in meter-scale pyroxenite-peridotite mantle sequences from Northern Apennine ophiolites (Italy)

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Keywords: small-scale mantle heterogeneity, pyroxenite-peridotite sequence, isotope geochemistry.

Deep melt intrusion and melt-peridotite interaction are considered the most efficient processes in creating small-scale heterogeneity in the upper mantle. Pyroxenite-peridotite mantle sequences of External Liguride Units (Northern Apennines, Italy) record the chemical and isotopic variability inherited from their deep lithospheric origin representing an excellent study case to investigate the origin of pyroxenites and how their emplacement modify the chemical and isotopic composition of the upper mantle. Pyroxenites range from spinel-bearing websterite to clinopyroxenite and occur as cm-thick layers (up to 40 cm) parallel to tectonite foliation. In spite of partial subsolidus low-P re-equilibration (spinel- to plagioclase-facies), most of the pyroxenites record chemical features inherited from a precursor garnet-bearing assemblage. Mass balance calculations provide up to about 40% of garnet in the original mineralogy, thus supporting that pyroxenites originated from melt segregation in mantle peridotites at rather high pressures ($P > 1.6$ GPa). Tholeiitic affinity and rather low X_{Mg} (<62) of the pyroxenite parental melts suggest that these latters were produced by partial melting of an heterogeneous (SE)pyroxenite-bearing mantle, then reacted in-situ with the host peridotite. Melt-peridotite interaction is indicated by chemical modification of wall-rock peridotites which show i) modal orthopyroxene enrichment at the expense of olivine, ii) higher Al, Ca, Si contents and slightly lower Mg# of bulk rocks, and iii) Al-richer spinel and lower-Mg# pyroxenes, with respect to the pyroxenite-free country peridotites. In the modified peridotites, clinopyroxene porphyroclasts record a trace element gradient resulting from percolative reactive flow of pyroxenite melt up to about 20 cm from the pyroxenite-peridotite boundary. Sr and Nd isotopic compositions fall within the MORB field ($^{87}Sr/^{86}Sr = 0.7023\text{-}0.7029$; $^{143}Nd/^{144}Nd = 0.5134\text{-}0.5128$). $^{143}Nd/^{144}Nd$ ratios in peridotites and pyroxenite on few meters scale cover almost the entire Nd isotopic variability documented in abyssal peridotites. Pyroxenite intrusion modified the host peridotites, lowering their $^{143}Nd/^{144}Nd$ as a combined effect of the systematic LREE enrichment (i.e. Nd/Sm increase) and radioactive decay (Borghini et al., 2013). Sm/Nd errorchrons defined by pyroxenites and modified peridotites yield a small range of ages between 424-452 Ma (errors < ±50 Ma). This constrains the timing of pyroxenite emplacement that widely predates the low-P evolution related to rifting and opening of Jurassic Ligurian Tethys, as indicated by plagioclase-clinopyroxene-whole rock Sm-Nd internal isochrones (178 ±25 Ma). Hf isotope analysis performed on separated clinopyroxenes from the same set of samples indicate that $^{176}Hf/^{177}Hf$ ratios of pyroxenites and peridotites well correlate with the $^{143}Nd/^{144}Nd$ ratios, showing a large variability at the massif scale.

Borghini G., Rampone E., Zanetti A., Class C., Cipriani A., Hofmann A.W. & Goldstein S.L. 2013. Meter-scale Nd isotopic heterogeneity in pyroxenite-bearing Ligurian peridotites encompasses global-scale upper mantle variability. Geology 41, 1055-1058.

Age and geochemistry of chert-basalt associations in the ophiolitic complexes of the Izmir-Ankara Mélange (East of Ankara, Turkey)

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Keywords: Ophiolites, Izmir-Ankara Mélange, Turkey.

In this work, we present the preliminary age data of the radiolarian cherts deposited on the top of basalts belonging to the Eastern Ankara Mélange (part of the Izmir-Ankara Mélange). Petrological studies on basalts were carried out in order to constrain the tectonic setting of formation of the studied basalt-chert sequences. Nine sections were sampled to the East of Ankara and twenty seven samples were collected for biostratigraphic and geochemical analyses.

The oldest radiolarian cherts dated in the present paper are referrable to Late Triassic (Section 6: late Norian) and are associated with basaltic rocks with OIB character. OIB type volcanic rocks are also found in other sections and are associated with cherts of Late Jurassic (Section 3: middle-late Oxfordian to late Kimmeridgian-early Tithonian) and Early Cretaceous (Section 1: late Valanginian to latest Valanginian-earliest Hauterivian) ages.

E-MORB type rocks are associated with radiolarian cherts of Cretaceous age (Section 4: late Barremian and Section 7: Valanginian to middle Aptian-early Albian), whereas the oldest N-MORBs were found in a section of Late Jurassic age (Section 5: early-early late Tithonian). Other N-MORBs are associated with radiolarian cherts of Early Cretaceous age (Section 8: late Valanginian-early Barremian). P-MORBs type rocks were found only in a section of Middle Jurassic age (Section 2: early-middle Bajocian to late Bathonian-early Callovian age).

In this work, we document the occurrence of OIB-type rocks of Late Triassic and of rocks showing different geochemical affinities (N-, E-, P-MORBs and OIB) generated in the same time span (Middle-Late Jurassic - Early Cretaceous). N-MORBs are compatible with composition of melts generated by partial melting of a depleted MORB mantle source. In contrast, OIBs are compatible with partial melting of enriched-type mantle source. E-MORBs may have derived from mantle source slightly enriched with respect to DMM source, whereas P-MORBs are compatible with melts generated from a mantle source significantly enriched, compared to DMM.

The chemical differences shown by the distinct rock-types can be related either to differences in source composition or different tectonic settings of formation, which may have existed during the Late Jurassic - Early Cretaceous time span.

Multistage asthenospheric melt/rock reaction in the ultraslow eastern SWIR mantle

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Keywords: SWIR, mantle partial melting, melting modelling, trace element.

Very small amounts of melt are produced during mantle upwelling beneath the ultraslow spreading South West Indian Ridge. Sectors of this Oceanic Ridge are characterized by nearly amagmatic spreading with rare limited eruptions of basalts spotting a mantle-derived serpentinitic crust. A large peridotite dataset was recovered during the Smoothseafloor French expedition leaded by D. Sauter and M. Cannat in 2005 (Sauter et al., 2013). Mantle-derived rocks show a significant modal variability from the sample to the dredge scale with frequent occurrences of millimetric to centimetric spinel-bearing pyroxenitic veins. Mantle residua record a multistage reactional history between small amount of transient melts and variably depleted mantle parcels. Incomplete mineral replacements are widespread showing that both pyroxenes are repeatedly dissolved and recrystallized leaving poekilitic pyroxene and spinel textures. Reacting conditions are modelled assuming an incremental open-system melting model under variable critical porosity/F ratios (Seyler et al., 2011; Brunelli et al., 2014). Incoming melts result to be generated by low degrees of melting in the garnet field then reacting with the rock under near-batch conditions, i.e. at low rates of melt extraction with respect to the actual rock porosity. As a consequence Na (and LREE) countertrends with melting indicators as mineral Cr# and concentration of the moderately incompatible elements (HREE, HFSE). This results in rotation of the REE patterns around a pivot element instead of showing progressive depletion as expected after suboceanic mantle decompression.

Brunelli D., Paganelli E. & Seyler, M. 2014. Percolation of enriched melts during incremental open-system melting in the spinel field: A REE approach to abyssal peridotites from the Southwest Indian Ridge. Geoch. et Cosmoch. Acta, 127, 190–203. doi:10.1016/j.gca.2013.11.040.

Sauter D., Cannat M., Searle R. 2013. Continuous exhumation of mantle-derived rocks at the Southwest Indian Ridge for 11 million years. Nature Geosci., 6(4), 1–7. doi:10.1038/ngeo1771.

Seyler M., Brunelli D., Toplis M. J. & Mével C. (2011). Multiscale chemical heterogeneities beneath the eastern Southwest Indian Ridge (52°E-68°E): Trace element compositions of along-axis dredged peridotites. Geochem. Geophys. Geosyst., 12, Q0AC15. doi:10.1029/2011gc003585.

Astenospheric processes beneath the ultraslow Smoothseafloor region in the eastern South West Indian Ridge

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Keywords: mantle partial melting, smoothseafloor, South West Indian Ridge, peridotite, trace element.

Mantle melting at ultraslow spreading ridges is constrained by the low potential temperature and thicker-than-normal LID that limits the extent of the melting column. As a result very small amounts of melts are produced inhibiting the formation of a "normal" oceanic lithosphere and leading to a purely tectonic seafloor extension dominated by serpentinization: the recently investigated Smoothseafloor type spreading (Sauter et al., 2013). At depth the reaction of very small amounts of percolating melts and host asthenospheric mantle leaves traces of the melt/rock reactions as incomplete mineral replacement and strongly variable modal distribution at short scale (dm). Enstatitic, and to a less extent diopsidic, pyroxenes appear to be repeatedly dissolved and recrystallized leaving poekilitic pyroxene and spinel leftovers. Melts enriched in incompatible elements are possibly generated in the garnet field then reacting with the rock under near-batch conditions, i.e. at low rates of melt extraction with respect to the actual rock porosity (Brunelli et al., 2014). Prolonged pyroxenes' dissolution-recrystallization results in enhanced enrichment of the most incompatible elements in the percolating melts that only occasionally are extracted from the system. As a consequence Na (and LREE) countertrends with the melting indicators as mineral Cr# and concentration of the moderately incompatible elements (HREE, HFSE). Accordingly the associated basalts are characterized by a strong Na enrichment and compositional trends separated from those generated in the surrounding regions.

Brunelli D., Paganelli E. & Seyler M. 2014. Percolation of enriched melts during incremental open-system melting in the spinel field: A REE approach to abyssal peridotites from the Southwest Indian Ridge. Geochimica et Cosmochimica Acta, 127, 190–203. doi:10.1016/j.gca.2013.11.040

Sauter D., Cannat M., Rouméjon S., Andreani M., Birot D., Bronner A., Searle R. 2013. Continuous exhumation of mantle-derived rocks at the Southwest Indian Ridge for 11 million years. Nature Geoscience, 6(4), 1–7. doi:10.1038/ngeo1771.

Rare occurrences of Early Jurassic radiolarian cherts in the Dinaric-Hellenic Belt, an open problem

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Keywords: Maliac-Vardar Ocean, Dinaric-Hellenic belt, Early Jurassic.

The Dinaric-Hellenic mountain belt formed through the closure of the Maliac-Vardar Ocean and the collision of Adria with microplates (Tisia, Dacia) positioned between Eurasia and the main branch of the Neo-Tethys. The ophiolites derived from the Maliac-Vardar Ocean are now scattered over different tectono-stratigraphic units (Bortolotti et al., 2013): i) a mélange below the major ophiolite nappe (sub-ophiolitic mélange); ii) a unit of Triassic ocean-floor ophiolites; iii) metamorphic soles underlying the major ophiolite nappes; within the major ophiolite assemblage; iv) a Jurassic fore-arc ophiolite unit (with MOR and SSZ magmatic sequences); v) a Jurassic intra-oceanic-arc ophiolite unit (with only SSZ magmatic sequences) and vi) a Jurassic back-arc basin ophiolite unit (with BABB and CAB magmatic sequences).

During the last 30 years, several authors studied the Dinaric-Hellenic ophiolite sequences where radiolarian cherts are overlying or interbedded with basalts in several locations, e.g. Serbia (Zlatibor), Albania (Mirdita), Greece (northern Pindos Mountains, Vourinos, Othrys, Koziakas, Argolis, Evvia, Guevgueli), aiming at reconstructing the geodynamic history of the Dinaric-Hellenic belt. Numerous sections were studied and rich faunas of Triassic and Jurassic age were found in the radiolarian cherts; however, only in two stratigraphic sections, at Angelokastron and Vothiki (Argolis), radiolarites of *Early Jurassic* age were found.

At Angelokastron, the Early Jurassic cherts were found in a small quarry, where, included in a matrix of dark reddish-brown cherty shales, fragments of chert and chert nodules impregnated by ferro-manganese oxides occur (Chiari et al., 2013). The examined samples indicate four age groups for the nodules, and a Middle Jurassic (middle Bathonian) age for the siliceous matrix in which they are embedded. The first age group includes radiolarians of Late Triassic (late Norian–Rhaetian) age; the second group of Early Jurassic (late early to late Pliensbachian and probably middle-late Toarcian) age; the third group comprises species of early Middle Jurassic (Aalenian-Bajocian) age; the fourth group finally consists of late Middle Jurassic (Bajocian-Bathonian) taxa. The Mn-impregnated chert nodules indicate that from Late Triassic to Middle Jurassic a deep oceanic basin existed in the area.

Only another small outcrop in the Argolis Peninsula gave a very poorly preserved radiolarian assemblage of probable Early Jurassic age. The sample comes from a thin, tectonized chert horizon intercalated in a massive basalt in a little quarry near the village of Vothiki, and has been dated as ?Sinemurian.

The scarcity of Early Jurassic cherts in the entire Dinaric-Hellenic belt poses some significant questions: is the extreme scarcity of Early Jurassic radiolarites due to stratigraphic or tectonic causes? More specifically, is this scarcity due to a lack of sedimentation or secondary tectonic elimination? In the first hypothesis, we should look for paleoenvironmental and/or paleoceanographic changes that may have controlled Early Jurassic radiolarian productivity and deposition. In the second case, the tectonic evolution of the basin may have caused subduction of some Early Jurassic parts of the Vardarian oceanic basin, with the possible incorporation of the Early Jurassic portions of the radiolarite sequences into the Middle Jurassic metamorphic soles, where radiolarites could not thus far be dated.

Bortolotti V., Chiari M., Marroni M., Pandolfi L., Principi G. & Saccani E. 2013. Geodynamic evolution of the ophiolites from Albania and Greece, (Dinaric-Hellenic Belt): one, two or more oceanic basins? International Journal of Earth Sciences (Geol. Rundsch.), 102, 783-811.

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Crustal velocity model for the Ionian Sea inferred from new OBS/H data: evidences of Ionian upper mantle serpentinization?

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Keywords: Ionian Crust, upper mantle serpentinization, P- and S-wave arrival times inversion.

The lack of seafloor stations in the Ionia Sea not allowed to locate moderate magnitude earthquakes and characterize the regional seismogenetic structure in this area (D'Alessandro et al., 2011a, 2011b, 2013a). Within the monitoring activities carried out in cooperation with the Dipartimento di Protezione Civile (Italy) and within the European project NERIES (activity NA6), the Istituto Nazionale di Geofisica e Vulcanologia (Italy) deployed in May 2007 three broadband OBS/H in the Southern Ionian Sea (D'Alessandro et al., 2009, 2012, 2013b). Simultaneous inversion of P- and S-wave arrival times, collected during a long time OBS/H monitoring campaign, yields 1D P- and S-wave velocity models for the Ionian lithosphere. The 1D model highlights the presence of a two layers with high seismic P-wave velocity (S1 and S2, 6.3-6.7 and 7.5 km/s, respectively) in the Ionian lower crust. This two layers, whit thickness of about 3.3 km and 5 km, respectively, are characterized by low values of the S-wave velocity (S1=3.05-3.2 km/s, S2=3.85 km/s) and high values of V_P/V_S (S1=2.06-2.09, S2=1.95). This is characteristic feature often encountered in passive continental margins and are generally interpreted as partly serpentinized peridotite. The V_P, V_S and V_P/V_S values of S1 are consistent with 55-65% serpentinization while that of S2 are consistent with 15–25% serpentinization of the mantle. Water needed to serpentinize peridotites may be supplied from the continental lower crust, through cracks and faults from above or from the rising plume.

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Experimentally-derived Ca-Na partitioning between plagioclase and clinopyroxene: a new geobarometer for mantle rocks

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Keywords: Plagioclase-peridotites, mantle exhumation, geobarometer.

The crystallization of plagioclase-bearing equilibrium assemblages in mantle peridotites is commonly considered witness of lithospheric mantle exhumation at shallow depth. Previous experimental works have found systematic compositional variations in coexisting minerals at decreasing pressure within the plagioclase stability field, similar to what observed in equilibrated plagioclase peridotites. In particular Ca-Na partitioning between plagioclase and clinopyroxene is strictly dependent on pressure, with plagioclase composition varying significantly (An=59-83) in a narrow pressure range, thus envisaging a potential geobarometer to estimate plagioclase-facies equilibrium pressures. Nevertheless, the composition of plagioclase at variable bulk Na_2O/CaO ratios has been not fully discerned yet, making this approach directly applicable to a limited bulk composition range. Here, we present the results of new experiments on a Na-enriched lherzolite (bulk Na_2O/CaO ratio = 0.13), representative of many refertilized lithospheric peridotites at extensional settings, thus enlarging significantly our investigated compositional spectrum (Na_2O/CaO = 0.08 – 0.13).

The starting bulk compositions have been selected in order to cover the variability of natural occurrences. A fertile lherzolite, FLZ, and a depleted lherzolite, DLZ (Borghini et al., 2010) correspond to a spinel lherzolite from Suvero (External Liguride ophiolites, Northern Apennine, Italy) and to a Depleted MORB Mantle (Wasilenky et al. 2003) respectively. In order to investigate the effect of the bulk Na_2O/CaO on the plagioclase to spinel transition, an extra-fertile bulk composition was considered by adding Na_2O to FLZ (HNa-FLZ).

As expected, the increase of bulk Na_2O/CaO extends plagioclase stability to higher P as compared with FLZ; in HNa-FLZ the plagioclase-spinel transition occurs between 0.9-1.0 GPa, 1100°C.

Ca/(Ca+Na) decreases with pressure in plagioclase and clinopyroxene in all the investigated bulks, suggesting a sensitive pressure dependent relation. A slight dependence on bulk Na_2O/CaO might be envisaged. However, the unexpected occurrence of amphibole in HNa-FLZ needs to be taken into account as additional Ca,Na-bearing phase.

Thermodynamic modelling fails in reproducing in details the isopleths of $XCa_{(plag)}/ XCa_{(cpx)}$. This is likely due to the fact that available solution models for orthopyroxene do not consider CaO, which instead might be present in experimental and natural orthopyroxenes (from about 0.4 to 1.6 wt.%).

Experimental data suggest that Ca-Na partitioning between plagioclase and clinopyroxene is only slightly affected by the bulk Na_2O/CaO: at 1100°C: the ratio $XCa_{(plag)}/ XCa_{(cpx)}$ of 0.65 translates into an equilibrium pressure of 0.7 GPa for HNa-FLZ and about 0.8 GPa for FLZ, with a difference of less than 0.1 GPa.

Borghini G., Fumagalli P., & Rampone E. 2010. The stability of plagioclase in the upper Mantle: subsolidus experiments on fertile and depleted lherzolite J. Petrol., 51, 229-254.

IODP Expedition 345: Primitive Layered Gabbros From Fast-Spreading Lower Oceanic Crust

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Keywords: IODP, Integrated Ocean Drilling Program, Ocean Crust, Lower Gabbros, Layered Gabbros.

The lower ocean crust formed at fast-spreading ridges is composed of plutonic rocks whose mineral assemblages, textures and compositions record the history of melt transport and crystallization between the mantle and the seafloor. Owing to the nearly continuous overlying extrusive upper crust, sampling in situ the lower crust is challenging. Integrated Ocean Drilling Program (IODP) Expedition 345 recovered the first significant sections of primitive, modally layered gabbroic rocks from the lowermost plutonic crust formed at a fast-spreading ridge, and exposed at the Hess Deep Rift (Gillis et al., Nature, 2014, doi:10.1038/nature12778). The primary science results were obtained from coring of two ~110 m deep reentry holes and one 35-m-deep single-bit hole, all co-located within an ~100-m-wide area on the southern slope of the inrarift ridge.

Olivine gabbro and troctolite are the dominant rock types recovered, with minor gabbro, clinopyroxene oikocryst-bearing gabbroic rocks, and gabbronorite. All rock types are primitive to moderately evolved, with Mg# 89-76, and exhibit cumulate textures. Spectacular modal and grain size layering, prevalent in >50% of the recovered core, confirm a long held paradigm that such rocks are a key constituent of the lowermost ocean crust formed at fast-spreading ridges.

Geochemical analysis of these primitive lower plutonics, in combination with previous geochemical data for shallow-level plutonics, sheeted dikes and lavas, provides the best constrained estimate to date of the bulk composition of crust formed at a fast-spreading ridge. Simple crystallization models using this bulk crustal composition as the parental melt accurately predict the composition of both the lavas and plutonics. However, the recovered rocks show unanticipated early crystallization of orthopyroxene, challenging current models of melt extraction from the mantle and mid-ocean ridge basalt differentiation.

The core recovered at Site U1415 originated at a stratigraphic level at least 2 km beneath the sheeted dike–plutonic transition, representing intervals of the lower half to one third of the EPR plutonic crust. A more precise depth cannot be assigned as the results of Expedition 345 (e.g., magnetic inclinations) and site survey indicate that the sampled units are tilted, mass-wasted blocks. However, sampling four large blocks of relatively fresh rocks proved facilitated observations of the wide variety and complexity of rock types and textures present in fast spread primitive lowermost crust.

The Tethyan seawater retained in serpentinites of the Hyblean basement (south-eastern Sicily): its role in the igneous activity, tectonic behaviour and oil settings

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Keywords: Hyblean Plateau, Serpentinite, Permian Tethys, Hydrocarbons, Igneous activity.

The study of the xenolith suite found in the Hyblean diatremes (SE Sicily), Upper Tortonian in age, revealed that the unexposed Permo-Triassic basement of the region consists of serpentinized peridotites and minor gabbros, suggesting the development of oceanic core complex structures (Scribano et al., 2006a,b) in the Paleo-Mesozoic, ultra-slow spreading, Ionian-Tethys Ocean. A recent interdisciplinary study pointed out that serpentinites are the dominant rocks forming the Hyblean-Pelagian basement down to a mean depth of 19 km, representing the Moho interpreted as a serpentinization front (Manuella et al., 2013). The basaltic magma-serpentinite interaction could be responsible of various geochemical and rheological modifications of the former. The serpentinite dehydration originated pressurized vapour whose violent expansion generated the Hyblean diatremes (Scribano et al., 2007). At the regional scale, repeated events of hydration/dehydration generated volume changes of huge masses of serpentinites, which can account the vertical tectonic style of the Hyblean area through geological time. Finally, the finding of hydrocarbons in some Hyblean mafic and ultramafic xenoliths suggests that serpentinization process promoted the abiogenic production of hydrocarbons via Fischer-Tropsch reaction (Ciliberto et al., 2009; Scirè et al., 2011). Thus, serpentinites may represent both source and reservoir rocks of hydrocarbons in south-eastern Sicily.

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Tectonic setting and geochemical characteristics of the basic rocks from the Intra-Pontide Suture Zone in Northern Turkey

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Keywords: ophiolite, Intra-Pontide suture, Turkey.

The Intra-Pontide Suture Zone (IPSZ) is the less known one among the suture zones present in Turkey. The IPSZ is well exposed along the Daday-Arac-Kursunlu and Tosya – Emirköy geotraverses where several tectonic units can be recognized. Most of these units are characterized by the occurrence of basic rocks reflecting distinct tectonic origins and geochemical signatures. The study of the basic rocks emerges as an important tool for the geodynamic reconstruction as it can reveal the occurrence of of different types of oceanic basins, the development of a magmatic arc or the presence of rifting-related magmatism. The study of the geotraverses indicates that the imbricate stack of the IPSZ consists of four distinct tectonic units whose successions bear basic rocks: the Aylı Dağ ophiolite Unit, the Arkot Dağ Mèlange and two metamorphic units, referred to as Daday and Devrekani Units. This imbricate stack is probably the result of several episodes of out-of-sequence thrusts that affected the whole IPSZ.

The Aylı Dağ Unit includes an about 5 km-thick ophiolite sequence topped by the middle Bathonian to early Callovian radiolarian cherts. In addition, a metamorphic sole is present at the base of the serpentinized peridotites. The geochemical evaluation of pillow-basalts and dykes highlights subduction-related characteristics, similar to IAT- and BABB-type lavas generated above intra-oceanic subduction systems.

The Arkot Dağ Mèlange consists of an assemblage of slide-blocks, with different size and lithology, enclosed in a Late Santonian sedimentary matrix. The slide-blocks also include ophiolitic lithologies, mainly represented by basalts, but gabbros and peridotites are also found. The slide-blocks of basalts display affinites to IAT- and BABB-type magmas, signifying the involvement of subduction component, whereas no MORB-like basalt have been found.

The Daday unit is characterized by metasedimentary and metabasic rocks deformed under blueschist to sub-greenschist metamorphic facies conditions. The metasedimentary rocks include mica-bearing schists, fine-grained marbles and black quartzites. The metabasic lithologies, on the other hand, comprise actinolite-bearing schists and Na-amphibole-bearing varieties possibly derived from basaltic and gabbroic protoliths. The metabasic rocks have a wide range of chemical compositions, displaying N-MORB-, E-MORB-, OIB- BABB- and IAT-type signatures.

The Devrekani Unit is represented by an assemblage of amphibolites, marbles and micaschists showing a metamorphic climax developed under upper amphibolite facies in the Late Jurassic time. The amphibolites display E-MORB-, OIB- BABB- and IAT-type signatures.

The geochemical signature of the studied basic rocks provide the evidence that all the basic rocks from the tectonic units of IPSZ are derived by a supra-subduction zone. This finding can provide new insights for the recostruction of the geodynamic history of the Intra-Pontide domain.

Petrographic and geochemical characteristics of the Mt. Pollino ophiolitic rocks (Basilicata, Southern Italy)

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Keywords: Mt. Pollino, Ligurian Tethys, Serpentinized peridotite, Ophiolitic rocks.

In Italy, ophiolites occur in scattered outcrops located mainly in the Western Alps and Northern Apennine. In Southern Apennine, ophiolite outcrops are very rare, occurring only in Southern Campania, Basilicata and Northern Calabria. Southern Apennine ophiolites consist of a serpentinized peridotite basement and a reduced crustal sequence characterized by lack of sheeted-dyke complexes, relatively small volumes of gabbros intruded in the peridotite basement, and a discontinuous basaltic and oceanic sediments cover. They are believed to represent fragments of Tethys oceanic crust that were obducted on continental crust during the closure of the Ligurian branch of Tethys. A thorough petrological investigation has been carried out on ophiolites that crop out widely on Timpa delle Murge Hill, along the boundary between Basilicata and Calabria, close to Mt. Pollino. All peridotite samples contain large amount of serpentine, and are characterized by millimeter-sized porphyroclasts of olivine and orthopyroxene, varying from anhedral to subhedral and showing internal deformation. Clinopyroxene is present as large crystals or as exsolution lamellae in orthopyroxene. Spinels are typically anhedral. Some peridotites show the presence of anhedral crystals of amphibole in accessory amounts. The REE contents of clinopyroxene are about 10 xChondrite I (CI) in the MREE and HREE regions where the patterns are almost flat, while the LREE contents are considerably depleted, with a significant difference between peridotites with amphibole (La_N = 1-4) and peridotites without amphibole (La_N = 0.05-0.5). Bulk rocks show excellent correlations in major oxides and some trace elements plotted against MgO. Incompatible elements, as well as Al, Ca, Si, Sc, and V show negative covariance with MgO. In contrast, the compatible elements Ni and Co show positive covariance with MgO. The positive relationship occurring between Fo content of olivine and Cr# of spinel confirms that such trends are related to variable degrees of partial melting, i.e. 8% for peridotites with amphiboles and about 20% for peridotites without amphibole. However, the degree of partial melting inferred on the basis of LREE concentrations of clinopyroxenes is much lower than that recorded by spinel-olivine equilibrium (maximum ~4% near-fractional melting of a spinel-facies DM for both amphibole-bearing and amphibole-free peridotites). The observed decoupling between the degrees of partial melting estimated on the basis of bulk rock and clinopyroxene chemistry allow us to interpret the depleted spinel peridotites of Mt. Pollino as the result of a reactive melt/rock interaction with depleted melts of MORB affinity, occurred at spinel-facies conditions after an earlier melt extraction. In places, the already re-fertilised peridotites experienced the percolation of late hydrous melts/fluids that determined the amphibole segregation, in association with further re-enrichment of LILE and LREE in clinopyroxenes.

Refertilization of subcontinental mantle recorded by the lherzolite-websterite-horneblendite association from St. Lucia (Corsica)

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Keywords: mantle, trace element geochemistry, continental margin.

The St. Lucia nappe from Alpine Corsica consists of late-Variscan lower crust exhumed along the European rifted margin of the Ligurian Tethys and Mesozoic sediments (Beltrando et al., 2013). The basement includes a High Grade Mafic Complex and a Granitoid Complex of Early Permian age. The base of the Mafic Complex is associated with mantle slices consisting of mylonitic spinel-bearing lherzolites and mm- to cm-thick websterite and hornblendite layers concordant with the foliation of the host rocks. The mylonite microstructure in the peridotites is characterized by aligned porphyroclasts of pyroxene (± spinel) in a fine-grained polyphase matrix composed of olivine + pyroxenes + spinel. Large exsolved orthopyroxene (Opx) porphyroclasts mantled by neoblastic Cpx + Opx + spinel testify a low-strain spinel tectonite stage predating the mylonite deformation. Major element compositions of olivine, Cpx and spinel porphyroclasts of the lherzolites indicate a fertile geochemical signature. The websterites are Opx-poor rocks containing Al-Ti-rich Cpx porphyroclasts, Cr-poor spinel, disseminated kaersutite and accessory Fe-Ni sulphides. Spinel-facies mylonite recrystallization in both lherzolites and websterites occurred at ~850-900°C. The hornblendites are composed of K2O-rich kaersutite + Ti-rich phlogopite + ilmenite. Cpx porphyroclasts from the lherzolites have heterogeneous trace element compositions pointing to four different geochemical signatures. Type 1 Cpx is strongly LREE-depleted (CeN/SmN down to 0.05) with nearly flat MREE-HREE at 8-10 times chondrite. Type 2 Cpx is moderately LREE-depleted (CeN/SmN = 0.31-0.49), whereas Type 3 has nearly flat LREE. Type 4 Cpxs are weakly LREE depleted, peak at MREE and have variable HREE (YbN = 7-12). The websterite Cpxs display convex-upward REE patterns and higher concentrations of incompatible trace element. The kaersutite from the hornblendites are enriched in Rb, Ba, U, Nb, Ta, LREE and depleted in HREE with respect to the websterite ones. The peridotite protholiths are consistent with residual rocks after low degrees of near-fractional melting of spinel facies DM. Type 4 Cpx from the lherzolites likely reflect equilibrium with percolating MORB-type melts. Putative liquids in equilibrium with Cpx and kaersutite from the websterites and the hornblendites have transitional to alkaline affinity. Our study has evidenced that the St. Lucia mantle slices underwent injections of melts with MORB to alkaline affinity forming different kinds of magmatic layers, which were associated with metasomatic haloes in the ambient peridotite.

Beltrando M., Zibra I., Montanini A. & Tribuzio R. 2013. Crustal thinning and exhumation along a fossil magma-poor distal margin preserved in Corsica: a hot rift to drift transition, Lithos, 168-169, 99-112.

Geologic and petrographic study of the Lower Shear Zone in the Monviso Ophiolitic Massif (western Alps): insights into the subduction dynamics

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Keywords: Monviso Ophiolitic Massif, Eclogitic breccia, Subduction processes.

The Monviso Ophiolitic Massif is one of the best preserved relics of the oceanic crust in the Western Alps that formed during opening of the Mesozoic Western Alpine Tethys and underwent eclogite-facies metamorphism during the Eocene Alpine subduction.

We have performed detailed fieldwork and petrographic studies across a major shear zone of the Monviso Ophiolitic Massif, i.e. the Lower Shear Zone (LSZ) as defined by Angiboust et al. (2011), in the upper Bulè Valley. This shear zone mainly consists of strongly foliated serpentinitic schists hosting numerous blocks and lenses of MgAl-metagabbros, FeTi-metagabbros (eclogites), eclogitic breccias and metabasites, and is interposed between the serpentinites of the Basal Serpentinite Unit and the MgAl-metagabbros of the Lago Superiore Unit.

Both the units and the interposed shear zone show exceptionally well preserved mineral assemblages and microstructures formed during subduction under eclogite-facies conditions. In the FeTi-metagabbros the eclogitic assemblage consists of garnet, omphacite, Mg-chlorite, zoisite and rutile, ± blue amphibole, ± phengite, ± lawsonite. In the MgAl-metagabbros, the Fe-poor bulk composition hampered the growth of garnet in equilibrium with omphacite: the eclogitic assemblage thus consists of omphacite, zoisite, Mg-chlorite, talc, blue amphibole and rutile, ± jadeite, ± phengite.

Eclogitic breccias have been recognized both as blocks within the serpentinitic schists of the LSZ, and as boudinated levels within the MgAl-metagabbros of the Lago Superiore Unit. These peculiar rocks suggest that the metamorphic evolution under eclogite facies conditions was particularly complex. Eclogitic breccias consist of centimetric clasts of milonitic eclogites surrounded by an oriented matrix with omphacite, lawsonite, rutile, ± garnet. This is the evidence that a brittle deformation occurred under lawsonite-eclogite facies conditions and was interposed between two ductile deformation events, both occurred under eclogite facies conditions. These observations are in agreement with those of Angiboust et al. (2011), who described similar eclogitic breccias from the same LSZ, north of the Bulè Valley. However, according to our data, the eclogitic breccias are not only limited to the LSZ, but are locally observed also in the structurally upper Lago Superiore Unit.

The presence of eclogitic breccias in the Monviso Ophiolitic Massif is particularly important for the interpretation of the subduction dynamics, and suggests a local brittle behavior of the oceanic crust during subduction, potentially linked to seismic phenomena.

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Dating HP metamorphism in Zermatt-Saas ophiolites from Valtournanche

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Keywords: Dating HP metamorphism, Zermatt-Saas, Valtournanche.

The Zermatt-Saas (ZS) Zone is a remnant of the Tethyan oceanic crust that was variously affected by oceanic metamorphism prior to subduction and is now part of the orogenic suture that developed in the Western European Alps during the Alpine subduction and collision (Dal Piaz et al., 2001 and references therein). The Zermatt-Saas rocks preserve a dominant HP to UHP metamorphic imprint overprinted by greenschist facies metamorphism. The age of the oceanic protoliths varies between 164 and 153 Ma (Rubatto et al., 1998) whereas the HP metamorphism is constrained between 44 and 40 Ma (i.e. Rubatto et al., 1998; Dal Piaz et al., 2001).

Ophiolite rocks in upper Valtournanche are dominated by a regional S2 foliation mapped with spatial continuity in serpentinite, metarodingite and eclogite. S2 is defined by HP parageneses in all lithotypes, and developed under 2.5 ± 0.3GPa and 600 ± 20°C during Alpine subduction (Rebay et al., 2012). Rarely clinopyroxene and zircon are found in the S2 foliation of serpentinites. Trace element composition of clinopyroxene suggest that they crystallised from a melt in equilibrium with plagioclase; most likely they represent relicts of gabbroic assemblages. The clinopyroxene porphyroclasts show rims indented within S2 with compositions compatible with clinopyroxene grains defining S2, suggesting that they recrystallised during Alpine subduction.

Zircon cores show, under CL, sector zoning typical of magmatic growth. U-Pb dates suggest their crystallisation during Middle Jurassic. Magmatic cores have thin fringe overgrowths parallel to the S2 foliation. U-Pb concordant analyses on these domains reveal an Upper Cretaceous crystallisation. This date likely represents the HP to UHP Alpine re-equilibration.

Therefore, some sections of the ZS have likely experienced HP to UHP metamorphism earlier than previously thought. Remarkably, these new dates are similar to those recorded for the HP re-equilibration in the continental crust of the Sesia-Lanzo Zone (i.e. Rubatto et al.,1999 and refs therein).

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The embryonic oceanic crust from the Balagne ophiolite (Corsica)

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Keywords: basalt-sedimentary succession, Jurassic ophiolite, U-Pb zircon dating.

The Balagne ophiolite is considered a marginal paleo-geographic domain of the Jurassic Ligurian Piedmontese basin, proximal to the European continental margin (Durand-Delga et al., 1997; Marroni and Pandolfi 2003). It preserves a basalt-sedimentary succession characterized by the association of pillow and massive basalts with deposits of ophiolitic breccias and continental-derived sediments. At the top of the succession, the pillow basalts are covered by a sedimentary sequence made up of Middle Jurassic to Early Cretaceous pelagic deposits.

The ophiolitic breccias occur in the lower portion of the basalt-sedimentary succession and contain clasts of clinopyroxene-rich gabbros, gabbronorites, oxide-gabbros, albitites and basalts. In the lower portion of the succession, two levels of siliciclastic sediments are also present. Most massive basalts are present in the upper portion of the basalt-sedimentary succession. The latter is associated with a tectonic slice mainly consisting of an intrusive sequence overlain by pillow basalts. The intrusive sequence is made up of gabbronorites, oxide-gabbros to albitites on top, showing similar structures and compositions to the gabbroic clasts from the ophiolitic breccias.

Preliminary *in situ* U-Pb zircon dates from an albitite of the tectonic slice show a Middle-Upper Jurassic crystallization age for the intrusive sequence, which is coeval to the gabbroic sequences from the ophiolites of the Alpine-Apennine belt. U-Pb geochronology of zircons from the siliciclastic sediments mostly reveals Early to Middle Permian age, thereby suggesting the Corsica batholith as the original source material. The whole-rock compositions of the massive basalts display slight LREE, Nb and Zr enrichment relative to N-MORB and homogeneous initial Nd isotope ratios consistent with an origin from an asthenospheric MORB-type mantle source. Clinopyroxenes from the basalts and the gabbros have nearly parallel incompatible trace element patterns showing slight LREE enrichment relative to clinopyroxene at equilibrium with typical N-MORB.

The parental melts of the basalts and the gabbros from the Balagne ophiolites may have formed by low degrees of asthenosphere partial melting, in conjunction with thick lithosphere and low astenosphere ascent. The early stages of the basalt-sedimentary succession development were most likely characterized by intense tectonic activity with supplies from different topographic highs consisting of lower oceanic crust and of continental-derived material.

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Ghostlike boninitic magmatism in the Cretaceous southern Neo-Tethys. New evidence from the Zagros ophiolites (Iran)

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Keywords: Ophiolite, Zagros belt, Iran.

Ophiolites cropping out along the Main Zagros Thrust Zone (MZTZ) represent portions of the southern Neo-Tethys Ocean, which existed between the Arabian and Eurasian continental margins. Several authors suggested that an intra-oceanic supra-subduction zone setting (SSZ) developed in this ocean during the Late Cretaceous. However, in contrast to many other ophiolites (e.g., Albanide-Hellenide), volcanic rocks, which typically characterize SSZ settings (i.e., island arc tholeiites and boninites) are lacking. Nonetheless, the volumetrically most abundant rock-type in the MZTZ ophiolites consists of very depleted mantle harzburgites, which have chemical features that are typical for residual mantle after boninitic-type melts extraction. Therefore, though boninitic lava flows are lacking in the MZTZ ophiolites, the occurrence of boninitic magmatism at a regional scale can be envisaged. In this contribution, we review the available data on the Kermanshah and Sarve-Abad ophiolites (SW Iran) in search for evidence for the existence of boninitic magmatism in the southern Neo-Tethys.

The Kermanshah ophiolites include SSZ sequences largely consisting of depleted mantle harzburgites, which display a significant depletion in incompatible elements and rare earth element (REE), coupled with a marked LREE enrichment with respect to MREE. REE modeling shows that they may represent a residual mantle after 25 – 30% removal of boninitic-type melts. The mineral chemistry of Cr-spinels also supports this conclusion.

The Sarve-Abad ophiolites include cumulitic lherzolites bearing minor dunite and chromitite lenses in places. The crystallization order in ultramafic cumulates is: olivine ± Cr spinel + clinopyroxene ± orthopyroxene, which is typical for boninitic melts. The mineral chemistry of Cr-spinel, pyroxenes, and olivine is compatible with a genesis from a boninitic-type melt. Indeed, the calculated TiO_2 and Al_2O_3 compositions and Mg# in the parental melt that was in equilibrium with these minerals are consistent with boninitic-type compositions. Whole-rock geochemistry show low incompatible element content and a general enrichment in Th with respect to Ta and Nb. Chondrite-normalized REE patterns are consistent with boninitic-type parental melts. REE petrogenetic modeling indicates that the Sarve-Abad ultramafic cumulates may have formed by small degrees (5-15%) of fractional crystallization from typical boninitic melts.

In conclusion, several lines of evidence indicate that episodes of boninitic magmatism occurred within the southern Neo-Tethys Ocean during the Late Cretaceous. Some hypotheses explaining the lacking of boninitic lavas or dykes in the MZTZ ophiolites can be postulated (e.g., short lived intra-oceanic subduction, transition from intra-oceanic to continental subduction). However, further investigations should be made for testing their tectono-magmatic and geodynamic consistence.

Discriminating between different types of ophiolitic basalts and their tectonic significance using a new method based on Th-Nb and Ce-Dy-Yb

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Keywords: Basalt, Ophiolite, Discrimination diagram, Trace elements, Plate tectonics.

Ophiolites are interpreted to form in a wide variety of plate tectonic settings including oceanic spreading ridges, hot spots, and supra-subduction zone (SSZ) environments, such as intra-oceanic arcs, continental arcs, forearcs, and back-arcs. Hence, different rocks or rock associations found in ophiolitic complexes preserve records of tectono-magmatic events that occurred during distinct phases of oceanic development, from continental rifting to oceanic spreading, subduction, accretion and continental collision. Recognition of the tectonic affinity of ancient ophiolites is therefore a fundamental problem for all scientists working on this topic. To this purpose, tectonic discrimination diagrams based on major and/or trace elements have been a common technique for addressing this problem since the early 70s. In this work, a new discrimination diagram using absolute measures of Th and Nb is proposed and is applied to ancient ophiolites to best discriminate a large number of different ophiolitic basalts. This diagram was obtained using >2000 ophiolitic basalts (spanning in age from Proterozoic to Cenozoic) and was tested using ~560 modern rocks from known tectonic settings. Data consist of ten different basaltic varieties, including two types that have never been considered before, which are: a) medium-Ti basalts (MTB) generated at nascent forearc settings; b) a type of mid-ocean ridge basalts showing garnet signature (G-MORB) that characterizes Alpine-type (i.e., non volcanic) rifted margins and ocean-continent transition zones (OCTZ). In this diagram, basalts generated in subduction-unrelated settings can be distinguished from subduction-related basalts with a misclassification rate <1%. This diagram highlights the chemical variation of oceanic and OCTZ basalts from depleted compositions to progressively more enriched compositions reflecting, in turn, the variance of source composition. Chemical contributions of enriched components (plume-type components) to mantle sources can therefore be identified. Enrichment of Th relative to Nb is effective for highlighting crustal input via subduction or crustal contamination. Basalts formed at continental margin volcanic arcs can be distinguished from those generated in intra-oceanic arcs in supra-subduction zones (SSZ) with a misclassification rate <1%. Within the SSZ group, two sub-settings can be recognized. They are: a) SSZ characterized by chemical contribution from subduction-derived components (forearc and intra-arc) characterized by island arc tholeiitic (IAT) and boninitic basalts; b) SSZ with no contribution from subduction-derived components (nascent forearc) characterized by MTBs and depleted-MORBs. Two additional discrimination diagrams are proposed: a) boninite and IAT basalts can be discriminated with a confidence level >99.5% using a Dy-Yb diagram; b) G-MORBs and N-MORBs can be discriminated using a Ce/Yb-Dy/Yb diagram.

Mantle-crust interactions in the oceanic lithosphere: constraints from minor and trace elements in olivine

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Keywords: olivine, dunite, troctolite.

Minor and trace element compositions of olivines were used as probes into the melt-rock reaction processes occurring at the mantle-crust transition in the oceanic lithosphere. We studied mantle and lower crustal sections from the Jurassic ophiolites of Alpine-Apennine belt, which are considered to be lithospheric remnants of a slow-spreading basin. Olivines from depleted mantle plagioclase-harzburgites and associated replacive dunitic conduits (Fo = 91-89 mol%) and olivines from olivine-rich troctolites and troctolites (Fo = 88-84 mol%) within km-scale gabbroic bodies were analyzed.

Positive correlations among the concentrations of Mn, Ni, Co, Sc and V characterize the olivines from the dunites. These chemical variations are reconciled with formation by melts produced by a mixed source melted under different pressure conditions and made up of a depleted peridotite and a pyroxene-rich, garnet-bearing component. We propose that partial melts extracted from the asthenosphere did not fully aggregate within the mantle before they form the oceanic crust.

The olivines from the olivine-rich troctolites and the troctolites have lower Ni contents and higher concentrations of Mn and incompatible trace elements (Ti, Zr, Y and HREE) than the olivines from the dunites. In addition, the olivines from the olivine-rich troctolites and the troctolites commonly show heterogeneous Ti, Zr, Y and HREE compositions, which produce variable Ti/Y and Zr/Y values. The chemical variations observed for these olivines cannot be only related to fractional crystallization. We correlate these olivine compositional characteristics with events of reactive melt migration occurred during the formation of the primitive lower oceanic crust. The migrating melts may have formed at the mantle-crust transition via interaction with mantle peridotites during periods of low melt supply.

Ultra-depleted peridotites of New Caledonia: a reappraisal

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Keywords: New Caledonia, Peridotites, Ophiolites.

In spite of pervasive serpentinisation and prominent weathering, the New Caledonia Peridotitic Nappe is one of the largest and best exposed supra-subduction mantle section in the world and hence provides a unique insight on upper mantle processes. The sequence is dominated by harzburgite-dunite association and minor lherzolites, but it also includes mafic/ultramafic cumulates.

Recent geochemical studies revealed that harzburgites experienced several phases of melting, melt-rock interaction and re-melting, that led to overall ultra-depletion, making their geochemical characterization an analytical challenge.

This presentation deals with the preliminary results of a reappraisal based upon a new set of unserpentinised, or only slightly serpentinised, peridotite samples collected on the whole island.

Harzburgites are highly refractory rocks, as attested by the absence of primary clinopyroxene, very high Fo content in olivine (90.7-92.9 mol%), high Mg# in orthopyroxene ([Mg/(Mg+Fe)]= 91.0-92.7) and Cr# in spinel ([100 • Cr/(Cr+Al)]= 40-71).

Secondary, interstitial and undeformed clino- and orthopyroxenes have also been observed in harzburgites. These phases indicate percolation after partial melting and re-equilibration at lithospheric conditions. Their chemical compositions, i.e. low Al_2O_3 and CaO contents in orthopyroxene and very low Na_2O and TiO_2 in clinopyroxene, suggest a metasomatic origin by SiO_2-rich fluids and/or depleted melts in a subduction-related setting.

In contrast, lherzolites exhibit a fairly fertile nature, indicated by lower Fo in olivine (88.5-90.0), low Cr# in spinel ([100 • Cr/(Cr+Al)]= 13-17) and relatively high Na_2O (up to 0.80 wt%) and Al_2O_3 (3.1-6.7 wt%) in clinopyroxene.

The peridotites are low strain tectonites with porphyroclastic textures partially overprinted by mosaic equigranular textures. They record an asthenospheric HT origin followed by sub-solidus re-equilibration, as also testified by geothermometric estimates (930–1145°C and 870-1080°C on porphyroclastic assemblages for harzburgites and lherzolites respectively; 830°C-980°C for spinel facies recrystallization in both lithotypes).

Mineral compositional variations (e.g. Mg# (Ol) vs Cr# (Spl), Cr# (Spl) vs Mg# (Spl)), show that most investigated harzburgites plot in the field of fore-arc peridotites, while lherzolites are more akin to (variably refertilized) abyssal peridotites. These features have also been confirmed by whole-rock REE contents, that display U-shaped pattern for harzburgites, commonly attributed to a fore-arc setting and abyssal-type patterns for lherzolites.

These results are consistent with multi-stage history of melting, deformation, recrystallization and melt-rock interaction. Major and trace elements combined with radiogenic isotope analyses (in progress) will provide a clue for deciphering the depletion vs. refertilization evolution of the different peridotite types and will add new constraints on their geodynamical significance.

The magmatic-hydrothermal transition in the lower oceanic crust: clues from the Ligurian ophiolites, Italy

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Keywords: Alpine Jurassic ophiolites, hornblende chemistry, O and Sm-Nd isotopes.

The gabbroic bodies from the Jurassic Ligurian ophiolites are structurally and compositionally similar to the gabbroic sequences from the oceanic core complexes of the Mid Atlantic Ridge. The high temperature cooling evolution of the Ligurian gabbros is locally associated with formation of hornblende-bearing felsic dykes and hornblende vein networks. The hornblende veining is correlated with widespread development of hornblende as coronas/pseudomorphs after the igneous clinopyroxene in the host gabbros. We also found hornblende-rich gabbros as dykes/sills within mantle peridotites.

The hornblendes from the felsic dykes and the hornblende gabbros are characterized by low Mg#, CaO and Al_2O_3, negligible Cl, and high TiO_2, K_2O, REE, Y, Zr and Nb. The whole-rock Sm-Nd isotopic compositions of the felsic dykes and the hornblende gabbros define a Jurassic isochron with a MORB-type initial ^{143}Nd/^{144}Nd ratio. The ä^{18}O of the hornblendes and coexisting zircons from these rocks do not decipher the presence of a seawater component in these melts. We propose that the felsic dykes and the hornblende gabbros formed by SiO_2-rich silicate melts derived from high degree fractional crystallization of MOR-type basalts.

The vein and the coronitic/pseudomorphic hornblendes show high Mg# and CaO, significant Cl and low TiO_2 and K_2O. The coronitic/pseudomorphic hornblendes have trace element compositions similar to those of the clinopyroxenes from the gabbros and ä^{18}O close to that of seawater, thereby documenting an origin by reaction between migrating seawater-derived fluids and the host gabbros. The vein hornblendes commonly show slight LREE enrichment and relatively high values of Nb and ä^{18}O. The crystallization of these hornblendes most likely required the involvement of both seawater and magmatic components.

Relationships between embryonic and slow spreading oceanic crust in the Jurassic Ligurian-Piedmontese basin: constraints from U-Pb zircon geochronology

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Keywords: Ophiolite, rift, seafloor spreading.

The fragments of Jurassic oceanic crust exposed in eastern Liguria (Northern Apennine, Italy) are either associated with continental lithosphere material, or bear structural and compositional resemblances to slow spreading oceanic crust. To constrain time and spatial relationships between these embryonic and slow spreading type domains in the Jurassic basin, we carried out a U-Pb geochronological study of zircons. Zircons were separated from eight intrusive rocks and analyzed for U-Pb isotopes by laser ablation ICPMS and isotope dilution TIMS. Zircons were also investigated for morphology, internal structures, inclusions and chemistry, thereby revealing remarkable similarities to zircons collected from modern oceanic crust. The U-Pb zircon dates indicate a short time span for the formation of the oceanic crust in the eastern Liguria ophiolites, thereby arguing against a ca. 30 Ma time span as previously thought. Implications for the geological evolution of the Jurassic basin are discussed.

SESSIONE S18

The geological cycle of C and Earth degassing: what do we (really) know?

CONVENORS

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New geological, geophysical and biological insights on the hydrothermal system of the Panarea – Basiluzzo Volcanic complex (Aeolian Islands, Tyrrhenian Sea)

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Keywords: Volcanic arc, hydrothermal systems, CO2 degassing.

Since the exhalative crisis of 2002 cruises were carried out to investigate morphology, magnetic and gravity fields, fluid escape, plume anomalies, biological and microbiological activity, benthic fluxes, early diagenesis, mineralogy and geochemistry of water and sediments of the hydrothermal system of Panarea. The volcanic complex was mapped by multibeam, including backscatter analysis, and magnetometric surveys were done to detect low magnetization in areas with hydrothermal activity, i.e., vents, sulphide deposits, chimney fields. CTD by ship and on ROV detected acidic plumes at bottom (minimum pH value 6.5) and mid depths.

An Automatic Benthic Chamber was deployed on a terrace (40m) and in depressions with gas-charged and hydrothermally altered sediments (80m). At the 40m site, strong releases of Dissolved Inorganic Carbon (DIC) and Fe, Mn, Zn (75.7, 2.0, 2.9, 3.4 µmol m^{-2} day^{-1}) were found. Average decrease of pH in the chamber was ~4 units day^{-1} with a H^+ benthic flux of 0.32 µmol m^{-2} day^{-1}). DIC values of seawater had average 2.3, increasing to 3.1 on degassing vents, while 7.5 µmol was measured on top of a bubbling core.

ROV dives explored and sampled several sites; active chimneys (black, red crusts and yellowish-orange precipitates at top) were recovered on the SE flanks of Basiluzzo; pH value of 5 was measured aboard on sediments. XRD and XRF data on the external crust showed Fe-Mn oxyhydroxides, including goethite and opal, with Co, Ce, Sr, Zn and Cu enrichments, whereas the inner part are depleted of Fe, Mn and other metals, mostly under detection limits. SEM imagery shows porous filamentous minerals, probably bacterial in origin. Dives to SW discovered fields of partially or totally relict chimneys at the same depth (~200m). Chimneys are present on the edges of slope failures and settled on areas of relative lower positive magnetic anomaly, indicating possible shallow depth level of hydrothermal alteration. Reddish crusts and sediments, and acid, gas boiling water (pH 5.5) were cored at 90 m depth upslope of the 'active' chimneys; upslope from the 'relict' chimney's fields, oxized-normal sediments were found.

Biological investigations on the sediments revealed a community strongly dominated by the amphipod *Ampelisca ledoyeri (*43.8 % of the total abundance), probably dwelling in the tube-patches. Rare species were detected on the chimney's samples.

The phylogenetic diversity of microbial communities in the precipitates collected on chimneys and on Bottaro vent was analyzed by bacterial and archaeal 16S rDNA clone libraries, showing a dominance of sulfur-oxidazing epsilon and gamma proteobacteria. Very interesting groups of archaea were revealed including methanotrophic Thermoplasmatales and members of SM1 candidate division. Overall prokaryotic diversity was found similar to that of deep sea hydrothermal vents and other sulfidic habitats. White microbial mats were found in an area S of Panarea, on a N-S oriented fracture.

CO_2 release and carbonation of Tuscan serpentinites

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Keywords: magnesite deposits, serpentinites, CO2 release.

Serpentinite-hosted magnesite deposits are known from almost all the serpentinite outcrops in Tuscany (Monti Livornesi, Colline Metallifere, Elba Island). The inland Tuscan magnesite deposits are considerably large, being represented by tens of veins up to 15 m thick and 800 m on strike that were exploited over a vertical extent of at least 100 m. All the ore bodies show similar mineralogy and have a general sub-vertical attitude trending NNW–SSE, coherent with the main extensional, high-angle faults in the region. The deposits are not directly in contact with Neogene–Quaternary magmatic rocks, but they are placed at the northern periphery of the active Larderello–Travale geothermal field where granite intrusions were cored at depth of about 3300–4800 m. These deposits were derived from serpentinite silicification–carbonation of the Ligurian ophiolites, and represent a natural analogue of *in situ* CO_2 mineral sequestration. Serpentinite host rocks were transformed to a brownish friable mineral assemblage of opal, chromian montmorillonite, Fe-rich magnesite and minor iron sulfides and oxides. The pervasive alteration of serpentinite was accompanied by the formation of a network of magnesite and dolomite veinlets, and large magnesite–dolomite veins along major structures. The mineral assemblage observed both in veins and in host rock is indicative of low-temperature hydrothermal alteration driven by Si- and CO_2-rich fluids under relatively low pH conditions.

The origin of the hydrothermal fluid is most probably related to the Tertiary to present Tuscan magmatic activity. In particular, the presence of low temperature fluids could be connected to the peripheral hydrothermal circulation (lateral flow) of high-temperature magmatic-hydrothermal field, as Larderello-Travale geothermal field. Here, we present the geological, petrological and geochemical characteristic of the Tuscan serpentinite-hosted magnesite deposits and we discuss their strict relationship with a peripheral hydrothermal circulation and with a regional release of CO_2.

CO_2 fluxes from Earth degassing in Italy

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Keywords: CO_2 fluxess, Earth degassing, non volcanic emissions, volcanic emissions, gas flux.

CO_2 Earth degassing is contributed by the combined action of two distinct source processes: active volcanoes (volcanic CO_2), and tectonically active areas of the world (non-volcanic CO_2). Even if It has long been recognized that Earth degassing may represent a not-trivial contribution to the global CO_2 budget, also nowadays, the magnitude of both contributions is however poorly constrained.

Central and southern Italy are affected by an active and intense process of CO_2 Earth degassing from both volcanic and non volcanic sources as revealed by recent studies focussed on the quantification of both CO_2 fluxes by point emission and soil diffuse degassing, and on the quantification of deeply derived CO_2 dissolved by the groundwater.

Regional scale studies in non volcanic areas of central and southern Italy, based on mass balance of carbon dissolved by groundwater, highlights the presence of two large CO_2 degassing structures (Tuscan Roman degassing structure, TRDS, and Campania degassing structure, CDS) that, for the magnitude and for the geochemical-isotopic features, were related to a regional process of mantle degassing. Quantitative estimates provided a regional CO_2 flux of about 9 Gt/y affecting the region (62000 km^2), an amount globally relevant, being ~ 10% of the present-day global CO_2 discharge from subaerial volcanoes.

In addition to the large amounts of carbon dissolved by regional aquifers, the TRDS and CDS are also characterised by the presence of many cold gas emissions where the CO_2 is released by both vents and soil disuse degassing. Both anomalous soil CO_2 degassing and CO_2 rich groundwater are different manifestations of the same process. In fact when the deeply produced gas is able to rise toward the surface, it can be dissolved by groundwaters or emitted directly to the atmosphere from gas emissions, depending on the magnitude of the gas flux rate and on the geological, structural and hydrogeological settings.

Measurement performed by the accumulation chamber shows soil CO_2 fluxes of order of magnitude higher than the typical biogenic CO_2 fluxes, characterise different sized areas which extension and shape are mainly relate to tectonic structures. The first on-line catalogue of Italian gas emissions recently realised, reports on the existence of about 270 gas manifestations. Even if for only a limited number (~50) of such manifestations quantitative estimations of CO_2 fluxes are available considering that these contribute for fluxes in the range of some tenths of a some hundreds tons per day, it is likely that the cumulative contribution of the 270 manifestation would be large, and highly significant to the total CO_2 budget.

Large amounts of CO_2 is also discharged by soil diffuse degassing at the quiescent volcanoes. Specific surveys on the Campanian volcanoes pointed out the relevance of this process that in the case of Solfatara of Pozzuoli volcano, provide a CO_2 flux comparable to an erupting volcano.

The estimations of the fluxes of deep CO_2 in Italy points out the relevance of non-volcanic CO_2 degassing and of soil diffuse degassing from volcanoes, suggesting the actual underestimation of the Earth degassing process at global scale, arising from the lack of specific and systematic studies in the numerous "degassing areas" of the world.

MAGA, a new database of gas emissions from natural systems: a collaborative web environment for collecting data

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Keywords: CO2 emissions, gas emissions, CO2 global budget, data science, data base.

The data on volcanic and non-volcanic gas emissions available online are, as today, are incomplete and most importantly, fragmentary. Hence, there is need for common frameworks to aggregate available data, in order to characterize and quantify the phenomena at various scales. A new and detailed web database (MAGA: MApping GAs emissions) has been developed, and recently improved, to collect data on carbon degassing form volcanic and non-volcanic environments. MAGA database allows researchers to insert data interactively and dynamically into a spatially referred relational database management system, as well as to extract data. MAGA kicked-off with the database set up and with the ingestion in to the database of the data from: i) a literature survey on publications on volcanic gas fluxes including data on active craters degassing, diffuse soil degassing and fumaroles both from dormant closed-conduit volcanoes (e.g., Vulcano, Phlegrean Fields, Santorini, Nysiros, Teide, etc.) and open-vent volcanoes (e.g., Etna, Stromboli, etc.) in the Mediterranean area and Azores, and ii) the revision and update of Googas database on non-volcanic emission of the Italian territory (Chiodini et al., 2008), in the framework of the Deep Earth Carbon Degassing (DECADE) research initiative of the Deep Carbon Observatory (DCO).

For each geo-located gas emission site, the database holds images and description of the site and of the emission type (e.g., diffuse emission, plume, fumarole, etc.), gas chemical-isotopic composition (when available), gas temperature and gases fluxes magnitude. Gas sampling, analysis and flux measurement methods are also reported together with references and contacts to researchers expert of each site. In this phase data can be accessed on the network from a web interface, and data-driven web service, where software clients can request data directly from the database, are planned to be implemented shortly. This way Geographical Information Systems (GIS) and Virtual Globes (e.g., Google Earth) could easily access the database, and data could be exchanged with other database. At the moment the database includes: i) more than 1000 flux data about volcanic plume degassing from Etna and Stromboli volcanoes, ii) data from ~ 30 sites of diffuse soil degassing from Napoletan volcanoes, Azores, Canary, Etna, Stromboli, and Vulcano Island, several data on fumarolic emissions (~ 7 sites) with CO_2 fluxes; iii) data from ~ 270 non volcanic gas emission site in Italy.

We believe MAGA data-base is an important starting point to develop a large scale, expandable data-base aimed to excite, inspire, and encourage participation among researchers. In addition, the possibility to archive location and qualitative information for gas emission/sites not yet investigated, could stimulate the scientific community for future researches and will provide an indication on the current uncertainty on deep carbon fluxes global estimates.

Measuring carbon dioxide and heat fluxes at orogene scale: the case of central Apennines

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Keywords: CO_2, heat flux, Apennines.

Geological and geophysical studies hypothesized that the intrusion of Tyrrhenian asthenosphere is one of the factor controlling the Apennine orogenesis. This hypothesis are supported by the researches that we devoted in the last decade to quantify the rate of CO_2 and heat released in the Apennine belt. Carbon dioxide Earth degassing process was quantified on the base of the carbon mass balance of regional aquifers. The deeply derived CO_2 resulted in $\sim 2\text{-}2.5\times10^{11}$ mol/a that represents a significant proportion (2% to 15%) of the estimated present-day total CO_2 discharge from the sub aerial volcanoes of the Earth. The groundwaters enriched in CO_2 systematically display a slight temperature anomaly, which becomes significant when the differences between the water temperatures at the springs and the temperature of corresponding recharging meteoric waters are compared. These temperature differences, together with the hydrogeologic parameters of the different aquifers, have been used to compute the total amount of heat by geothermal warming which results of $\sim 2.1 \times 10^9$ Js^{-1}, implying that a large sector of the Apennines is affected by heat fluxes higher than 300 mWm^{-2}. These are in absolute very high values, for instance they are higher than the average heat fluxes of the famous geothermal provinces of Tuscany and Latium.

This finding is in some way surprising because so far the central Apennines was though to be a cold area. This high heat and CO_2 flux opens a new vision of the Apennines belt and requires the existence, at depth, of a thermal and fluid source such as a large magmatic intrusion. Recent tomographic images of the area confirm the presence of such intrusion visible as a broad negative velocity of seismic waves. This study reveals how the investigations based on groundwater systems are important for a more reliable estimation of both deep CO_2 and heat fluxes in orogenes.

From mantle to magma: a comparison between volatile content in mantle xenoliths, basic lavas and melt inclusions from Northern Victoria Land, Antarctica

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Keywords: Lithospheric mantle, melt inclusions, volatile content, basic magmatism.

The Trans-Antarctic Rift is the most extended continental break up on Earth. However, the origin of the magmatism and the nature of the mantle sources are still poor undertood. This study offers an innovative view on the petrologic features of mantle xenoliths, basic lavas and olivine-hosted melt inclusions (MI) in the same lavas from Northern Victoria Land (NVL). Samples were collected from various localities, such as Baker Rocks, Harrow Peaks, Greene Point, Shield Nunatak, Eldridge Bluff and Handler Ridge during two expeditions funded by the Italian Antarctic Program (PNRA).

Mantle xenoliths are anydrous and hydrous spinel-bearing lherzolites and harzburgites. Few samples are Fe-rich peridotites. Amphibole is the main volatile-beraing mineral, although few crystals of phlogopite were also found. Volatile content in amphibole were determined by SIMS at IGG-CNR laborary in Pavia, while water contents in NAMs were determined at the Department of Erath and Space Science, University of Hefei (China).

Lavas are olivine-phyric (up to 15 %vol) with minor clinopyroxene and plagioclase in a glassy to microcristalline plagioclase-dominated groundmass; opaque minerals are mostly magnetites and subordinately ilmenites. Samples are nepheline-normative basanites (42.4-44.8 SiO_2 wt%; 3.11-6.19 Na_2O+K_2O wt%) and alkaline basalts (44.9-48.7 SiO_2 wt%; 2.81-4.55 Na_2O+K_2O wt%). Samples from Handler Ridge are more primitive and richer in alkaline, with the highest TiO_2 content (3,55-3,65 wt%). They are also enriched in Rb, Ba, Nb, La, Zr despite their primitive features.

Olivine-hosted melt inclusions (MI) were analized for major element and volatiles (H_2O. CO_2, S, F, and Cl) after HT (1300°C) and HP (6 Kbar) homogenization at Rensselaer Polytecnic Institute (New York, USA). They are compositionally comparable to host lavas but show a wider range of variability. At least two populations have been identified, sometimes coexisting in the same sample, following two distinct compositional trends: a high- and a low-Fe-Ti-K trend. Volatile content in MI has been determined by SIMS at Woods Hole Oceanographic Institute (Massachusets, USA). The H_2O content ranges from 0.70 wt% to 1.19 wt% and CO_2 from 25 ppm to 341 ppm ($H_2O/CO_2 \sim 1$). At comparable H_2O contents few samples show a remarkable higher CO_2 values (1322 ppm to 3905 ppm) with a H_2O/CO_2 molar ratio down to 0.8. F and Cl content varies from 990 ppm to 10 ppm and from 570 ppm to 38 ppm respectively.

A comparison between volatile budget in the mantle sources and that analyzed in MI were developed, after modelling the metasomatic and melting processes which affected this portion of the lithospheric mantle. The Fe-Ti-K-rich melt observed in MI was also tentatively proposed as the metasomatic agent responsible for the genesis of the Fe-rich xenoliths.

Metamorphic CO_2 production in scapolite-bearing calc-silicate rocks from the central-eastern Himalaya

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Keywords: orogenic CO_2 cycle, metamorphic CO_2 degassing, scapolite-bearing calc-silic.

The "long-term carbon cycle" operates over millions of years and involves the slow exchange of carbon between rocks and the surficial system; the volume of CO_2 involved in these processes is still far from being constrained. So far, the degassing flux was mainly estimated based on the flux emitted by volcanoes in different geodynamic contexts, and additionally include carbon from the mantle and carbon degassed from subduction zones. This estimated flux does not take into account CO_2 derived from orogenic zones, where organic-rich sediments and limestone may be buried at depths at which CO_2 is formed by metamorphic reactions. However, recent studies suggest that metamorphic degassing from active collisional orogens supplies a significant fraction of the global solid-Earth derived CO_2 to the atmosphere, thus playing a fundamental role, even in today's Earth's carbon cycle (Gaillardet & Galy, 2008).

In order to test if calc-silicate rocks may act as metamorphic CO_2-source rocks, a petrologic study of K-feldspar+scapolite-bearing calc-silicate rocks from eastern Nepal Himalaya has been performed. These rocks occur as tens to hundreds of meter thick levels hosted in anatectic Ky-Sil- bearing gneisses.

Mineral assemblage consists of Kfs + Cpx + Scp + Cal + Pl + Qtz ± Zo, and later Ep and green Amp. Clinopyroxene often shows oriented inclusions of Phl + Scp + Cal ± Mu ± Qtz, whereas zoisite includes Scp + Qtz + Ca + Na-rich Pl and is intergrown with Kfs and Ca-rich Pl. Clinopyroxene is often partially replaced by later green Ca-Amp ± Ep, whereas scapolite is locally partially replaced by symplectitic aggregates of Pl + Cal. In addition to ubiquitous titanite, strongly pleochroic allanite and bluish to colorless tourmaline locally occur, whereas graphite is always absent.

The Kfs+Scp-bearing calc-silicate rocks can be modeled in the NKCMAS-CO_2-H_2O system, including Pl and Scp solid solutions, in addition to a fluid of variable composition. In such complex system, the use of mixed-volatile phase diagram projections (in which the volatile composition of the system is projected onto the P–T coordinate frame: Connolly & Trommsdorff, 1991), is the best approach for simultaneously considering the effects of the three variables P, T and X_{fluid} on phase relations.

Preliminary petrologic data demonstrates that Kfs+Scp- bearing calc-silicate rocks may act as CO_2-source during prograde heating, releasing internal-derived CO_2-rich fluids (XCO_2=0.5-0.6) through Cpx, Kfs and Zo -forming, and Scp -consuming, reactions such as:
Qtz + Cal + Mu + Scp = Zo + Pl + Kfs + F
Qtz + Phl + Scp + Zo + Cal = Cpx + Kfs + Pl + F
Mu + Scp + Phl + Qtz + Zo = Cpx + Kfs + Pl + F

Gaillardet J. & Galy A. 2008. Himalaya-carbon sink or source? Science, 320, 1727-1728.
Connolly J.A.D. & Trommsdorff V. 1991. Petrogenetic grids for metacarbonate rocks: pressure–temperature phase-diagrams for mixed-volatile systems. Contrib. Mineral. Petrol., 108, 93-105.

Carbonate, not carbonatite, at Villamayor volcano (Calatrava Volcanic District, Central Spain)

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Keywords: Carbonatite, Petrology, Leucitite.

The Moron de Villamayor Volcano (~9 Ma) represents the oldest volcanic activity in the Calatrava Volcanic field, Central Spain. The products of this activity have been classified in literature as leucitites despite a minor presence of modal groundmass leucite (<5 vol. %), the low K2O content (average 3.3 wt%) and the low K2O/Na2O ratio (<1.8). The lava flows of this small volcano are strongly porphyritic with the presence of subhedral to euhedral olivine phenocrysts and cumulate crystals. A recent paper (Humphreys et al., 2010) classifies these rocks as leucitites and considers the olivine phenocrysts as mantle debris. The carbonate inclusions are considered to represent the relict of Ca-carbonatitic magma crystallizing calcite and, in one single case, aragonite. We challenge the Humphreys et al (2010) hypothesis for several reasons:

1) The olivine crystals cannot be considered mantle xenocrysts because of their low forsterite content (72-89 mol% Fo) and relatively high CaO (>0.2 wt%).

2) Olivine crystals are considered liquidus phases (euhedral crystals with plateau Mg/Fe ratios to normal zoning) or cumulitic phases remobilized after arrival of new magma batches (subhedral to euhedral shape with plateau Mg/Fe to inverse zoning in the outermost rim).

3) The rare mica occasionally associated with carbonate within olivine has much lower Mg# (73-84) compared to mantle phlogopite (Mg# = 89-95) and is indistinguishable from groundmass biotite.

4) Also the other mineral phases associated with carbonates as inclusions in olivine are chemically indistinguishable from groundmass phases.

5) The calculated leucitite composition (obtained subtracting 30% olivine, considered xenocrysts by Humphreys et al., 2010) is too much MgO-poor (0.52 wt%) for the calculated SiO2 (46.65 wt%). This is not compatible with a mantle melt.

6) The carbonate present in the Moron de Villamayor mantle sources, in equilibrium with the leucititic magma cannot be Mg-free as the Ca-carbonate (calcite and aragonite) found as inclusions in olivine crystals.

7) The SrO content of the carbonate inclusions is generally low (generally <0.2 wt%) and never exceeding 0.54 wt%, values, compatible with sedimentary carbonates.

8) The LAM-ICPMS incompatible trace element contents of calcite indicate nearly sterile compositions, with very low REE contents (La down to 0.01 ppm).

We propose a sedimentary origin for the carbonate mineral inclusions in olivine. In our model sedimentary carbonate is scraped off the country rocks and partially digested by the ultrabasic melt. When in contact with the carbonate xenocrysts the olivine growth is stopped, producing the typical hollow body euhedral shape of the Moron de Villamayor olivine.

Humphreys E.R., Bailey K., Hawkesworth C.J., Wall F., Najorka J. & Rankin A.H.. 2010. Aragonite in olivine from Calatrava, Spain—Evidence for mantle carbonatite melts from >100 km depth. Geology, 38, 911-914.

C-O-H fluids and redox processes at subduction zones

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Keywords: C-O-H fluids, carbonate, diamond, redox state, oxygen fugacity.

C-O-H fluids are released by dehydration, partial melting and/or decarbonation of the slab and transferred to the mantle, where they interact with the surrounding rocks, prompting the growth of carbonates, hydrous minerals and C polymorphs. In the pure C-O-H system, C-saturated fluid speciation is a function of the oxygen chemical potential. Therefore, in natural systems, the fluid speciation can be imposed by the redox state of the rock-forming phases. Alternatively, C-O-H fluids may control the bulk oxidation state of the rock system by redox reactions with the mineral phases. Complexities in the speciation of such fluids are demonstrated by discoveries of hydrates, carbonates and carbon polymorphs in polyphase inclusions, and also by high-pressure H2- or CH4-bearing fluid inclusions in mantle harzburgites, suggesting that the composition of C-bearing hydrous fluids closely relates to the oxidation state of the system. We selected three case studies of garnet-bearing ultramafic rocks (Ulten zone, Italy; Sulu, China; Bardane, Norway), which record metasomatic processes driven by C-O-H fluids at the interface between a subducting slab and the overlying mantle wedge. All these rocks contain carbonates (dolomite-only at $P < 1.9$ GPa at 900 °C, magnesite-only at $P > 2.4$ GPa at 900 °C, dolomite + magnesite in between) and hydrous phases (amphibole, phlogopite) equilibrated at some stages in the garnet stability field. The fO2 values, estimated by analysing the Fe3+ content (skiagite mole fraction) in garnet, indicate that the Ulten and Sulu peridotites record high oxygen fugacities (FMQ to FMQ+2) and a retrograde path with decreasing P and T. The fO2 values obtained for the Bardane garnet websterites, which record a prograde path with increasing T and P, are up to -2 log units lower than the FMQ. When combined with data for subduction-zone systems (arc lavas and their mantle sources), the studied ultramafic rocks define a trend of decreasing fO2 with increasing pressure.

The Bardane websterites contain C-polymorphs in polyphase inclusions, which precipitated from entrapped metasomatic fluids at ultrahigh pressures. The calculated C-O-H fluid phase in equilibrium with the solid phases consists of mixtures of H2O and CO2. Semi-quantitative estimates for the Ulten and Sulu peridotites, in which C-polymorphs have not been found, and petrographic constraints for the Ulten peridotites indicate that the C-O-H component of the fluid could consist of H2O+CO2.

Subduction zones and the deep carbon cycle

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Keywords: subduction, carbon cycle, dissolution.

Most studies conclude that the mantle is gaining carbon because more carbon is subducted than is degassed by volcanism. A key component of these budgetary analyses is the estimation of the carbon lost from slabs and degassed at arc volcanoes. But this hinges on the assumption that there is a 1:1 correspondence between carbon derived from subducting lithosphere and carbon degassed at arc volcanoes, and that the carbon transfer mechanism involves only molecular CO2. Neither of these assumptions is valid. The first is problematic because arc magmas may attain deep fluid saturation, a significant fraction of arc magma does not erupt, and arc crust is permeable to fluids. These considerations point to diffuse loss and deep storage of potentially significant carbon that does not contribute to degassing at volcanic centers. The second problem arises because assessment of the supply of carbon from subducting slabs arbitrarily limits consideration to CO2 in molecular fluids, which underestimates the mass of carbon that can be mobilized. Theoretical and experimental results show that carbon solubilities are likely higher than these models predict. Total dissolved carbon depends on the solubilities of all carbon species (e.g., CO2aq, HCO3-, CO3-2, etc), which are controlled by pH, fO2, halogens, and dissolved cations. Controls on these variables in subduction zones can combine to elevate carbonate mineral solubility. For example, the calculated pH of model slab mineral assemblages of jadeite, white mica and quartz along slab-top geotherms show that the CaCO3 solubility is higher at silicate-buffered pH than at the more alkaline pH of otherwise pure H2O saturated only in CaCO3, or than in molecular mixing models. Carbonate solubility is also enhanced by alkali halide salts. At a given pressure and temperature, calcite solubility increases in proportion to the square of salt mole fraction for NaCl, KCl, LiCl, and their mixtures. At fixed P, T, and Xsalt, solubility decreases as LiCl > NaCl > KCl, consistent with Pearson Hard-Soft Acid-Base rules. Ion pairing and reduction of carbonate or CO2 to CH4 will further increase solubility. Models including the above effects yield carbon solubility approaching 1 wt% in some slab fluids. Carbon carried by subduction-zone fluids and deep degassed magmatic volatiles likely play important roles in the deep carbon cycle, and must be taken into account in assessing the gain or loss of carbon by the mantle.

Hydrous carbonatitic liquids from epidote-dolomite eclogites: new perspectives on carbon transfer at subduction zones

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Keywords: subduction, carbon, carbonatite.

Current knowledge on the solidus temperature for carbonate-bearing rocks suggests that carbonatitic liquids should not form in a subducted oceanic lithosphere, unless anomalous thermal relaxation occurs. For a mildly warm subduction path, COH-bearing basaltic eclogites are expected to loose all H_2O component at epidote breakdown, located at approx. 2.8-3.0 GPa. Above this pressure limit, the solidus is that of a carbonated basaltic eclogite which shows a minimum temperature of 1020 °C at 4.0-4.5 GPa. However, the oceanic crust includes a range of gabbroic rocks, altered on rifts and transforms, with large amounts of An-rich plagioclase. It has been shown that epidote disappearance with pressure depend on the normative anorthite content of the bulk composition considered; we therefore expect that altered gabbros might display a much wider pressure range where epidote persists, potentially affecting the solidus relationships. Notably, this applies to epidosite rocks formed in hydrothermal environments at oceanic settings, then recovered in high-pressure and ultra-high pressure terrains.

New experimental data from 3.7 to 4.6 GPa, 750°C to 1000 °C are intended to unravel the effect of variable bulk and volatile compositions in model eclogites, enriched in the normative anorthite component (An_{37} and An_{45}). Experiments are performed in piston cylinder and multianvil machines apparatus, using both single and, buffered, double capsule techniques.

Garnet, clinopyroxene and coesite form in all syntheses. Lawsonite was found to persist at 3.7 GPa, 750 °C, with both dolomite and magnesite; at 3.8 GPa, 775-800 °C, fluid saturated conditions, epidote coexists with kyanite, dolomite and magnesite. The anhydrous assemblage garnet, omphacite, aragonite, kyanite is found at 4.2 GPa, 850 °C. At 900 °C, fluid-rich conditions, a silicate fluid/melt of granitoid composition, a carbonatitic melt and Na-carbonate are observed. Close to fluid-saturation, 3.8-4.2 GPa, 900 °C, garnet and Na-rich clinopyroxene coexist with a carbonatitic melt, dolomite and aragonite. The carbonatitic melt is enriched in Ca compared to melts previously obtained in dry carbonated experiments. Sandwich experiments, producing large quantities of liquid, demonstrate attainment of equilibrium and the supercritical nature of the carbonate liquid produced.

The subsolidus breakdown of epidote in the presence of carbonates at depths exceeding 120 km provides a major source of COH fluids at subarc depth. In warm subduction zones, the possibility of extracting hydrous carbonatitic liquids from a variety of gabbroic rocks offers new scenarios on the metasomatic processes in the lithospheric wedge of subduction zones and a new mechanism for recycling carbon. Such liquids are expected to be extremely reactive in a percolated mantle wedge, where they generate carbonate pyroxenites, a fertile CO_2 source for magmatism at subduction zones.

Soil gas geochemistry and C isotopic signature in Medolla (Modena) area

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Keywords: soil gas, C isotope.

Several soil surveys were performed in Medolla (Modena), a peculiar area characterized by spotty high soil temperature, coupled to gas emission and lack of vegetation, to determine the origin of these phenomena.

In this area gas fluxes (CO_2 and CH_4) measurements, soil gas concentrations (He, H_2, CO_2, CH_4 and C_2H_6) and their isotopic analyses ($\delta^{13}C$–CH_4, δD–CH_4 and $\delta^{13}C$–CO_2) were performed in October and December 2008, and repeated in May 2012, September 2012, June 2013 afterwards the 2012 Emilia seismic sequences.

Chemical composition of soil gas are dominated by CH_4 that ranges from 0.34 to 764,269 ppmv/v, with CO_2 concentration ranging from 0.024 to 3 %v/v. Very anomalous fluxes (138 g/m^{2}day of CO_2, 51.77 g/m^{2}day of CH_4) and concentrations are recorded in the spot area.

In the surrounding area CO_2 and CH_4 values are very low, within the typical range of vegetative and of organic exhalation of the cultivated soil.

After the seismic sequence the CH_4 and CO_2 fluxes are increased of one order of magnitude in the spotty areas, whereas in the surrounding area the values are within the background. On the contrary, CH_4 concentration decrease (40%v/v in the 2012 surveys) and CO_2 concentration increase until to 12.7%v/v (2013 survey).

Isotopic analysis were carried out only on samples with anomalous values. October/December 2008 data hint a thermogenic origin of CH_4 probably linked to leakage from a deep source. Conversely, 2012/2013 isotopic data indicate a typical biogenic origin (i.e. microbial hydrocarbon production) of the CH_4, as recognized elsewhere in the Po Plain and surroundings.

The d^{13}C-CO_2 value suggests a prevalent shallow origin of CO_2 (i.e. organic and/or soil-derived) probably related to anaerobic oxidation of heavy hydrocarbons.

Obtained results highlight a different behavior before and after the seismic events, proved also by the different carbon isotopic signature of CH_4. These variations could be produced by increasing of bacterial (e.g. peat strata) and methanogenic fermentation processes in the first meters of the soil.

Experimental determination of carbon-saturated COH fluids speciation at 1 GPa

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Keywords: COH fluids, speciation, experiments.

The quantitative assessment of species in COH fluids is crucial in modelling mantle processes. For instance, H_2O/CO_2 ratio in the fluid phase influences the location of the solidus and of carbonation/decarbonation reactions in peridotitic systems (Wyllie, 1978). In the scientific literature, the speciation of COH fluids has been generally assumed on the basis of thermodynamic calculations using equations of state of simple H_2O-non-polar gas systems (e.g., H_2O-CO_2-CH_4). Only few authors dealt with the experimental determination of high-pressure COH fluid species at different conditions, using diverse experimental and analytical approaches (e.g., piston cylinder+capsule-piercing+gas-chromatography/mass-spectrometry; cold-seal+silica glass capsules+Raman). We performed experiments on COH fluids using a capsule-piercing device inspired by Taylor & Foley (1994) coupled with quadrupole mass spectrometry. This type of analyzer ensures superior performances in terms of selectivity of molecules to be detected, high acquisition rates and extended linear response range. Experiments were carried out in a rocking piston cylinder apparatus at pressure of 1 GPa and temperatures from 800 to 900°C. Carbon-saturated fluids were generated through the addition of oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$) and graphite. Single/double capsules and different packing materials (BN and MgO) were used to evaluate the divergence from the thermodynamic speciation model. Moreover, to assess the effect of solutes on COH fluid speciation we also performed a set of experiments adding synthetic forsterite to the charge. To determine the speciation we assembled a capsule-piercing device that allows to puncture the capsule in a gas-tight vessel at 80°C. The extraction Teflon vessel, similar to that described by Manning & Boettcher (1994) for dissolution experiments, is composed of a base part, where the capsule is allocated on a steel support, and a top part where a steel drill is mounted. To release the quenched fluids from the capsule, the base part of vessel is hand-tighten to the top part, allowing the steel pointer to pierce the capsule. The evolved gases are then convoyed to a quadrupole mass spectrometer through a heated line to avoid the condensation of water. Our results suggest that fluid speciation can diverge considerably compared to the thermodynamic model depending on the experimental strategies adopted and on the presence of solutes in complex COH systems.

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COH serpentinites and metasomatic rocks from Cogne (Aosta Valley, Western Italian Alps): Insights into seafloor fluid-rock interactions

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Keywords: COH fluids, magnetite, serpentinite

The serpentinites of Cogne contain magnetite, serpentine, calcite, graphite, brucite, chlorite, diopside, and andradite/hydroandradite garnet. These mineralogical assemblages result from oceanic serpentinization and metasomatic processes, mediated by hydrothermal-vent fluids on the Tethyian seafloor. Â Fluid speciation and redox potential are strictly linked to each other in carbon-saturated COH (GCOH) fluids. If the redox buffer capacity of rocks can be overwhelmed, as in the case of high fluid/rock ratios, COH fluids can control externally the redox potential of rocks. The speciation of the COH fluid and therefore the redox conditions in force during the oceanic serpentinization and metasomatism recorded by the Cogne rocks can be unravelled by the mineral assemblages observed. Thermodynamic modelling of the garnet-forming reaction

magnetite + calcite + lizardite + O_2 + H_2O = andradite + brucite + CO_2

suggests that the formation of andradite at T ranging from 250 to 400 Â°C is possible only for very low XCO_2 [$=CO_2/(H_2O+CO_2)$] in the fluid (log XCO_2 = -5 to -4), which is comparable to the present-day seawater. Â Thermodynamic modelling of GCOH fluids at 500 bar and 350 Â°C shows that this CO_2 content is consistent with fO_2 conditions broadly approaching the FMQ buffer, which well agrees with estimates concerning oceanic hydrothermal vents and with the sulphide parageneses found at Cogne. The constraints to the fluid speciation allowed the construction of a fluid-saturated, isobaric (500 bar) T-X diagram, ranging from two representative bulk-rock compositions: (1) a typical magnetite- and sulphide-bearing serpentinite and (2) an andradite-, diopside- and calcite-bearing metasomatic rock. At composition (1), T-X diagram represents a model for the serpentinization of a peridotite in a pure FMS+COH system. When oceanic peridotite undergoes hydration, it becomes a magnetiteÂ± brucite-bearing serpentinite. Prograde forsterite is expected to grow at the expenses of brucite and lizardite above ~ 400 Â°C. In fact, we observed olivine (Fo98) neoblasts developing after brucite. Towards composition (2), at T below 400 Â°C and for low degrees of metasomatism, the expected association should contain clinochlore and calcite in addition to lizardite, magnetite and brucite. Higher degrees of metasomatism will stabilize andradite at T < 360Â°C and diopside at T > 360 Â°C in brucite-free rocks. Eventually, for (2) andradite and diopside coexist even at T < 360 Â°C, and calcite disappears. At T < 300 Â°C, diopside should be replaced by amphibole, never observed in the investigated samples of Cogne.

In conclusion, thermodynamic modelling suggests that mineral assemblages observed at Cogne match a process of seafloor serpentinization and Ca (Â±Al) metasomatism at 300â€“360 Â°C conveyed by carbon-saturated COH hydrothermal vent fluids characterized by CO_2 contents comparable to present-day seawater, capable to fix the redox potential of rocks close to the FMQ buffer.

Co-seismic carbonate melting along natural faults

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Keywords: Carbonate rock, Pseudotachylytes, Faults.

Seismic faulting in carbonates produces different fault rocks due to competing chemico-physical processes (e.g., mechanical comminution, thermal decomposition and melting), which tend to prevail mainly as a function of ambient temperature and pressure, presence and composition of fluids, and rock material properties. Viganò et al. (2011) recently reported the occurrence of carbonate pseudotachylytes, i.e. products of friction-induced melting of carbonate rocks.

Here we present two examples of natural faults where co-seismic carbonate melting occurred: (i) the Canalone Porta fault (CPF, Grigna Massif, Italy; Viganò et al., 2011) and (ii) the Pietra Grande thrust (PGT, Brenta Dolomites, Italy; Castellarin et al., 1993).

The studied faults developed within dolomitic and marly limestones (CPF) and limestones and dolomitic limestones (PGT) of middle Triassic and Triassic–Early Jurassic age, respectively. At the outcrop scale, faults show reddish infillings forming fault- and injection-veins. At the micro-scale, veins consist of a fine-grained reddish matrix containing carbonate clasts of different size. Veins usually show chilled margins and typical wall rocks vary from fractured carbonate of the damage zone to protocataclasite, cataclasite and fault breccia.

Even if bulk chemical and mineralogical compositions of host rocks and carbonate pseudotachylytes are mostly the same, the fine-grained matrix is characterized by a second-generation nanometer-sized Ca-carbonate aggregates with different compositions compared to clasts. A K-bearing aluminosilicate amorphous phase bounds aggregates and clasts in the fine-grained matrix. We suggest that this glass was obtained by disequilibrium melting of mainly muscovite and quartz of the host rock.

The temperature attained by the Canalone Porta fault by calcite–dolomite solvus geothermometry on nanometer-sized Ca-carbonates is up to 720 °C, above the eutectic melting temperature of dolomite with water at pressure of 0.2 GPa (cf. Lee et al., 2000). Regarding the almost pure calcite composition of the Pietra Grande fault rocks, petrological models similarly suggest a melting temperature of about 740 °C for the join calcite–water system at 1 kbar (Wyllie and Tuttle, 1960).

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SESSIONE S19

Fluids in the Earth's crust and Mantle

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The H_2O content of granite embryos

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Keywords: melt inclusions, granite H2O content, crustal melting.

Quantification of H_2O contents of natural granites has been an on-going challenge owing to the extremely fugitive character of H_2O during cooling and ascent of melts and magmas. Here we approach this problem by studying granites in their source region (i.e. the partially melted continental crust) and we present the first NanoSIMS analyses of anatectic melt inclusions (MI) hosted in peritectic phases of migmatites and granulites. These MI which totally crystallized upon slow cooling represent the embryos of the upper-crustal granites (Cesare et al., 2009; Bartoli et al., 2013). The approach based on the combination of MI and NanoSIMS has been here tested on amphibolite-facies migmatites at Ronda (S Spain) that underwent fluid-present to fluid-absent melting at ~700 °C and ~5 kbar. Small (≤ 5 µm) crystallized MI trapped in garnet have been remelted using a piston-cylinder apparatus and they show leucogranitic compositions. We measure high and variable H_2O contents (mean of 6.5±1.4 wt%) in these low-temperature, low-pressure granitic melts. We demonstrate that, when the entire population from the same host is considered, MI reveal the H_2O content of melt in the specific volume of rock where the host garnet grew. Mean H_2O values for the MI in different host crystals range from 5.4 to 9.1 wt%. This range is in rather good agreement with experimental models for granitic melts at the inferred P-T conditions. Our study documents for the first time the occurrence of H_2O heterogeneities in natural granitic melts at the source region (Bartoli et al., 2014). These heterogeneities are interpreted to reflect the birth of granitic melts under conditions of "mosaic" equilibrium, where the distinct fractions of melt experience different buffering assemblages at the micro-scale, with concomitant differences in melt H_2O content. These results confirm the need for small-scale geochemical studies on natural samples to improve our quantitative understanding of crustal melting and granite formation. The same approach adopted here can be applied to MI hosted in higher-temperature, granulite-facies rocks that represent the parents of many upper-crustal granites. This will result in a better understanding of formation and evolution of granitic magmas.

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The "*spongy*" behaviour of serpentinized mantle rocks at the plate interface setting: geochemical and tectonic implications

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Keywords: High pressure ultramafic rocks, plate interface, fluid-mediated mass transfer.

A "*spongy*" behaviour of serpentinized mantle rocks has been recently advocated to explain fluid and element (e.g. B, Sr, Pb) transfer from slab to mantle in subduction zones (Deschamps et al., 2011). In this scenario, km-thick hydrated layers in the supra-subduction mantle wedge, as well as melanges hosting serpentinized mantle rocks can play a key role. In such environments, mixing of slab derived fluids with mantle and/or geochemical mixing of different element reservoirs in subduction channel melanges significantly affect subduction recycling.

Here we present the study of two plate interface environments: (I) serpentinite-rich, represented by the high-pressure Ligurian serpentinites (Erro-Tobbio, ET, and Voltri Units, VU); (II) metasediment-dominated top slab mélange, represented by the de-serpentinized garnet peridotite and chlorite harzburgite bodies (with eclogite and metarodingite layers) embebbed in metasediments from Cima di Gagnone (CdG, Adula Unit).

The Ligurian serpentinites derive from oceanic slab and mantle wedge tectonically coupled and dragged to depth during Alpine subduction: they may represent the hydrated precursors of the CdG peridotites. The ET serpentinites show high [B], positive d^{11}B and limited enrichment in Pb and Sr isotopic ratio: they are interpreted as supra-subduction mantle flushed by slab fluids. The VU serpentinites show comparable values of [B], d^{11}B and Pb and slightly higher Sr isotopic ratio. This geochemical signature may reflect interaction with slab fluids enriched in heavy B-rich and in crustal radiogenic Sr, suggestive of mantle evolving atop the slab.

High-pressure metaperidotite and mafic rocks from CdG show low [B], negative d^{11}B and high Sr and Pb isotopic ratios. The host metasediments have higher [B], negative d^{11}B and distinctly higher Sr and Pb isotopic ratios. The geochemical signature of the CdG rocks, points to exchange between mantle and sedimentary/crustal reservoirs during prograde subduction burial.

The evidence presented here for a number of Alpine ultramafic rocks suggests that slices of serpentinzed mantle of different size and provenance (slab and wedge) were accreted to plate interface domains since the early stages of subduction. These serpentinized rocks took up slab fluids and elements during burial (spongy rocks) thus becoming key fluid-mobile element reservoirs for arc magmatism.

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Volatile concentrations of silicate melt inclusions: Deep insights into processes in active volcanic systems

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Keywords: Melt inclusions, melt inclusion assemblage (MIA), pre-eruptive volatile contents, magma degassing pattern.

In the last few decades, many volcanologists, petrologists and geochemists have focused on understanding the volatile (H_2O-CO_2-S-Cl-F) evolution of active volcanic systems using silicate melt inclusions (MI). The prominence of MI studies is not surprising because MI often provide the only means to measure directly the volatile contents dissolved in deep, undegassed melts. MI represent aliquots of melt trapped during crystal growth (and, more rarely, during crystal dissolution). Ideally, this aliquot of melt would be considered representative of the melt in equilibrium with the growing crystal at the time of trapping. Thus, the volatile concentrations of MI are commonly coupled with the silicate melt composition to estimate depths of crystal formation based on experimentally derived volatile solubility models. The volatile contents of MI can also be used to infer the magma dynamics of past eruptions, in an effort to better predict the characteristics of future eruptions. Furthermore, volatile concentrations of MI can be used to decipher physical and chemical processes in deep volcanic plumbing systems, such as volatile fluxing from deep source regions to shallow magma reservoirs and to reveal the oxidation state of deep magmas.

One common feature of MI volatile data presented in the literature is the high variability of concentrations observed in a typical dataset. On one hand, such variability can reflect varying pressure, temperature, oxidation state, and/or silicate melt composition during the evolution of the magmatic system, recorded by MI trapped in phenocrysts grown at different stages in the magma reservoir. Such variability itself may thus allow researchers to investigate different magmatic processes using MI. On the other hand, a growing body of evidence suggests that similar variability in volatile concentrations of MI can result from modifications of MI after trapping (e.g., post entrapment crystallization, diffusive loss, etc.). Therefore, in order to draw robust inferences concerning magmatic evolution based on volatile concentrations of MI, methods are needed to distinguish the "primary" signal (representing deep magmatic processes) from potential post-entrapment modification effects.

In this study, we review methods that can be used to assess the reliability and optimize the interpretation of volatile contents of MI. Firstly, we highlight the importance of petrographic examination of MI to collect robust data. We review the concept of melt inclusion assemblages (MIA), representing groups of MI that were trapped all at the same time during the magmatic evolution, and thus, at the same physical and chemical conditions (e.g., MI trapped along a growth zone of a phenocryst). If MI in a single MIA record the same volatile contents, an inclusionist can be confident that those MI faithfully record representative concentrations of the melt in equilibrium with the growing phenocryst. Conversely, if MI in a single MIA show variable volatile concentrations, an inclusionist should be cautious of whether these MI record a representative composition. Commonly, identifying melt inclusion assemblages (especially in juvenile phenocrysts) can be challenging; therefore, we review alternative means to establish time correlations among studied MI (e.g., cathodoluminescence imaging). Next, we highlight the importance of bubbles in bubble-bearing MI, and discuss how we can estimate the original CO_2 concentration of bubble-bearing MI. Finally, we review the importance of major/trace element compositions of MI and mineral hosts for interpreting the volatile concentrations of MI. To demonstrate how data from MI can be effectively interpreted, we include MI data from the Phlegrean Volcanic District in Italy as a case study.

Water in the oceanic lithosphere: a trilogy

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Keywords: water, fluid flow, slab hydration/dehydration, seismological observations, deep earthquakes, mantle.

I will review the geological and geophysical phenomena associated with water in the oceanic lithosphere that can be grouped into three different categories: those related to 1) the storage of water in the oceanic lithosphere at the surface, 2) the subduction of a hydrated slab and 3) its dehydration that ultimately leads to mantle regassing (Faccenda, 2014). Widespread hydration of the uppermost oceanic lithosphere occurs at mid-ocean ridges and more pervasively at the trench-rise system in response to bending-related fracturing and faulting. The amount of water stored in the upper lithosphere appears to be proportional to the spreading slowness and amount of bending. Hydrothermal alteration of the oceanic plate may also occur more locally along transform margins, fracture zones and volcanic ridges. Subduction of a hydrated slab should be observed from a reduction of seismic velocities, anomalous Vp/Vs ratios and seismic anisotropy in its uppermost portions, and shift of the main phase transformation boundaries characteristic of the mantle. Because of the increased buoyancy and weakness, hydrated or wet slabs should tend to stagnate over the 660 km discontinuity, favouring layered mantle convection patterns. Slab dehydration takes place according to the plate thermal regime function of the slab age and sinking velocity. Hydrous minerals in the oceanic crust and mantle are stable down to maximum 300 km and 1200 km depth, respectively, after which minor amounts of water can be retained in nominally anhydrous minerals. There is abundant geophysical evidence for dehydration of the slab crust and sub-Moho mantle, while fragmentary and often indirect evidence supports the presence of water in the lower plane of the Double Seismic Zone and at depths > 300 km.

Faccenda M. 2014. Water in the slab: a trilogy. Tectonophys., 614, 1-30.

Fluid inclusions as tracers for the chemical-physical behaviour of deep-subduction fluids

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Keywords: ultra-high-pressure metamorphism, mantle metasomatism, element recycling.

Fluids released from the slab by progressive dehydration reactions during deep subduction can have strong petrological and geochemical effects, inducing metasomatism into the mantle wedge. Deep-subduction fluids must be considered an integral part of the H*P*-UH*P* phase assemblages and, in the last twenty years, their chemical-physical properties have been subject of experiments, thermodynamic models, and field studies.

Deep-subduction fluids are almost ubiquitously trapped in eclogite-facies crustal suites as inclusions that still preserve firsthand information on their chemical composition and origin. Thus, data from natural fluid inclusions can be combined with those from experiments and thermodynamics to investigate the chemical-physical properties of fluids released during subduction, their solvent and transport capacity, and the subsequent implications for the element recycling.

Three distinct populations of fluid inclusions have been observed in H*P* and UH*P* metamorphic rocks: i) chloride-bearing aqueous fluid inclusions and/or gaseous fluid inclusions, ii) multiphase-solid inclusions, and iii) melt inclusions. Their study reveals that the chemical composition of natural deep-subduction fluids is more complex than that considered by experiments. At forearc depths, moderate concentrations of chlorides, Si, Al, and alkalis, ± non-polar gases are present in water-dominated solutions; at subarc depths, mobile water-rich phases gradually increases the amounts of aluminosilicate components (e.g., Si, Al, Ca, Fe, alkalis, Ti, Zr, $(SO_4)^{2-}$, $(CO_3)^{2-}$) and trace elements at rising temperature. Trace element patterns show enrichments in LILE, U, Pb, LREE, and depletion in HFSE, and result chemically controlled by stabilization/destabilization of some hydrous and accessory minerals. These data are in agreement with experiments of mineral dissolution and element fractionation at deep subduction and also support experiments and thermodynamics on physical properties of deep-subduction fluids. At forearc depths, fluids are supposed to have properties similar to crustal fluids, i.e. dominated by halide ligands. In contrast, element solubility and transport of aqueous fluids released at subarc depths are supposed to be governed by polymerization, which is directly proportional to pressure and temperature. On the contrary, the finding of substantial amounts of dissolved oxidized carbon in natural fluid inclusions from deep-subducted rocks reveals that the deep transport of carbonates by aqueous fluids is a relevant process, and implies a reconsideration of the petrological models supporting liberation of C into the mantle wedge as CO_2.

Although hampered by some analytical difficulties, in the coming years the research on fluid inclusions in H*P*-UH*P* metamorphic rocks will provide exciting new results, supplying the added value to experimental and thermodynamic data.

Melting of continental crust at mantle depth: nanogranites from leucogranulites of the Orlica–Śnieżnik Dome (Bohemian Massif)

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Keywords: Nanogranites, partial melting, granitoids.

Crystallized MI, or “nanogranites” (Cesare et al., 2009; Ferrero et al., 2012), were identified within HP felsic granulites from Orlica–Śnieżnik Dome, NE Bohemian Massif (Walczak, 2011). The investigated samples are Grt+Ky leucogranulites originated from a granitic protolith, with assemblage Qtz+Pl+Kfs+Grt+Ky+Ttn+Rt+Ilm. Nanogranites occur in garnet as primary inclusions, and consist of Qtz+Ab+Bt+Kfs±Ep±Ap. Such assemblage results from the crystallization of a melt generated during a partial melting reaction; the same reaction is also responsible for the production of the host garnet, interpreted therefore as a peritectic phase. Besides nanogranites, former presence of melt is supported by the occurrence of tiny pseudomorphs of melt-filled pores (Holness & Sawyer, 2008) and euhedral faces in garnet. Garnet composition, with Grs =0.28–0.31, phase assemblage (kyanite, ternary feldspar) and classic thermobarometry suggest that partial melting took place at T≥875°C and P~2.4–2.8 GPa, under eclogite-facies conditions. Although other authors reported palisade quartz after coesite in this area (see e.g. Bakun-Czubarow, 1992), no clear evidence of UHP conditions have been identified during this study. Piston cylinder re-homogenization experiments were performed on MI-bearing garnet chips to obtain the composition of the pristine anatectic melt. Data from experiments show that nanogranites can be re-melted through piston cylinder experiments at T≥875° and confining pressure of 2.7 GPa under dry conditions. The homogenized nanogranites can be analyzed by EMP means and they show a syenitic/granitic composition with water ≤8 wt%. Water presence in the glass has been also confirmed by Raman investigation.

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Volatile content in mantle amphiboles from Harrow Peaks, Northern Victoria Land (Antarctica)

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Keywords: amphibole, crystal chemistry, oxygen fugacity, lithopsheric mantle water activity.

This contribution reports a crystal-chemical study of four mantle amphiboles from three spinel-bearing lherzolites and one harzburgite from Harrow Peaks, Antarctica (HP, 74 02.785S 164 47.466E, q. 335m). The experiments were carried out by means of single crystal X-ray diffraction, electron microprobe analyses, secondary ion mass spectrometry (SIMS) and ^{57}Fe Mössbauer spectroscopy.

Amphiboles represent the main hydrous metasomatic minerals and texturally occur both disseminated in the peridotite matrix and/or in fair veinlets.

Their accurate crystal-chemical characterization is crucial to better understand the mechanism of amphiboles formation in relation to water activity (and partitioning) in peridotite ambient and their ultimately effects in controlling the mantle redox conditions.

HP amphiboles are compositionally referred to pargasite (Mg# [MgO/(MgO+FeO) mol%] = 87.5-90.2 and TiO_2 = 2.74-4.20 wt%) and kaersutite (HP164: Mg# 80.1 and TiO_2 = 5.30 wt%). The outcome crystal chemistry was carried out by minimizing the differences between theoretical and experimental site scatterings and it shows high concentrations in Fe^{3+} preferred ordered in C site, a partial vacancy in A site and M4 site disordered with the presence of Ca, Na and Fe^{2+}.

The degree of dehydrogenation determined by SIMS ranges from 0.820 to 0.989 and 0.682 O3(O^{2-}) a.p.f.u. in pargasites and kaersutite. F ranges from 0.020 to 0.042 a.p.f.u and 0.111 a.p.f.u.; whereas Cl ranges from 0.007 to 0.017 and 0.020 a.p.f.u., in pargasites and kaersutite respectively.

The aH_2O was determined from dehydration equilibrium among end-member components assuming that pargasites are in equilibrium with the anhydrous peridotitic phases (at least for Fe/Mg and Ti). This assumption is not applicable to the lherzolite HP164: kaersutite contains too much Ti and Fe^{3+} to be in equilibrium with the metasomatic parageneses (mainly clinopyroxene).The equilibrium temperatures, calculated by ol-sp Fe-Mg distribution (P=15 Kbar) are in the range of 916-966 °C. The aH_2O calculated for HP pargasite-bearing peridotites is in the range of 0.091-0.105. The oxygen fugacity of HP xenoliths is also calculated upon the dissociation constant of water (by oxy-amphibole equilibrium). The HP pargasite-bearing peridotites record fO_2 well below the fayalite-magnetite-quartz (FMQ) buffer (fO_2= -1.61 - -1.75) and show higher water reactivity at comparable (or slightly more reduced) fO_2 with respect to other mantle fragments from the same region.

Notwithstanding this high water activity, the pyroxene water contents, determined by Fourier transform infrared spectroscopy, appear very low, close to the lower limit of the pyroxene water contents of the intraplate mantle pyroxenes. In fact, Their H_2O (ppm) content ranges from 172 to 122 for cpx and from 20 to 63 for opx. These values are comparable with those of the nearby locality of Baker Rocks, where fO_2 is comparable but water activity is much lower.

Slab-derived fluid phase precipitation at high pressures

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Keywords: Polyphase inclusion, epytaxial growth, X-ray diffraction, subduction fluid.

Remnants of the fluid phase at ultrahigh pressure (UHP) in subduction environments may be preserved as primary polyphase inclusions in UHP minerals. These inclusions show the same textural features as fluid inclusions and locally may enclose UHP daughter minerals. Detailed textural studies, as well as experimental attempts to homogenise such inclusions, demonstrate that polyphase inclusions derive from solute-rich aqueous fluids or hydrous melts. However, the mode of precipitation of daughter minerals from these solute-rich hydrous fluids has never been investigated yet.

A case study is represented by garnet orthopyroxenites from the Maowu Ultramafic Complex (China). They derive from harzburgite precursors metasomatised at ~ 4 GPa, 750 °C by a silica- and incompatible trace element-rich fluid phase, sourced from the associated crustal rocks (Malaspina et al., 2006). This metasomatism produced poikilitic orthopyroxene and inclusion-rich garnet porphyroblasts. Solid polyphase primary inclusions in garnet display negative crystal shapes and constant volume ratios of infilling minerals (spinel: 10–20 vol.%; amphibole, chlorite, talc, mica: 80–90 vol.%). Experimental homogenisation of polyphase inclusions demonstrated that derive from trapped solute-rich aqueous fluids (Malaspina et al., 2006).

To constrain the possible mode of precipitation of daughter minerals, significant contribution could be given by the analysis of the growth relationships between host and infillings. As demonstrated by Nestola et al. (2013) for the case of diamond and their olivine inclusions, the use of 'state of the art' single-crystal X-ray diffraction to collect data symoultaneously on both host and inclusion phases, allows to obtain "orientation matrixes" of both phases thus retrieving their reciprocal crystallographic orientation. We performed a single-crystal X-ray diffraction experiment by Synchrotron Radiation at DLS-Diamond Light Source. Combination of the EMPA analyses, Raman Spctroscopy and X-ray diffraction allowed unique identification of each mineral phase and its orientation with respect to the host. Applying this methodology we have been able to infer the possible epitaxial growth of spinel-garnet; gedrite-pargasite and spinel-gedrite pairs which share preferred crystallographic orientation. Such information is crucial to evaluate any recurrent orientation, ruling out epitaxial growth relationships, sheding light on the temporal growth relations between host and inclusion that could not be otherwise evaluated.

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Evidence for strong depletion, followed by multiple refertilisation, in the mantle column of the extra-Andean backarc (Paso de Indios, Argentina)

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Keywords: Mantle xenoliths, Back arc, Refertilisation.

In the central part of the Chubut province, close to the town of Paso de Indios, there are several outcrops of Cenozoic basalts carrying spinel-facies ultramafic xenoliths. In this area, located in the extra-Andean back-arc region, basaltic necks and dikes outcrop between 43º 36′ – 43º 50′ S and 68º 53′ – 69º 02′ W, along with remnants of lava flows divided in two groups of Paleocene and Eocene age. This volcanism was generated by extensional tectonic related to a transform plate margin episode that affected the southern South America active margin from the Paleocene to the Oligocene, as the Aluk plate detached and a slab window opened beneath the study area.

Here, the petrochemical processes experienced by spinel-facies mantle xenoliths, hosted in Eocene basalts of the Matilde lava flow remnants, the León volcano and the Chenque dike, are presented.

The studied samples are mainly spinel-facies harzburgites and clinopyroxene(Cpx)-poor lherzolites, with some dunites. The Chenque xenoliths mainly present porphyroclastic to equigranular texture, whereas those from Matilde and León volcanoes have coarse-grained to porphyroclastic textures. Estimated equilibrium temperatures based on pyroxenes solvus range from 800 to 940°C.

The refractory character of the mineral assemblages is matched by the major element mineral compositions, which are mostly Al poor and Mg and Cr rich. Spinel composition is consistent with melt extraction from 8 to 14% (Chenque and León) and 14 to 18% (Matilde). The estimated degree of melting rises up to 24% considering the literature spinel data. However, the occurrence of melt-related open-system processes is suggested by local trends of positive correlation between Na and Cr# in Cpx, being fully confirmed by the trace element compositions. Cpxs from a harzburgitic sample from León volcano show composition rich in U, Th, Sr and LREE. The Matilde harzburgites ubiquitously show Cpx with transient U-shaped REE patterns. The LREE fractionation is very strong, with La_N up to 100 and minimum at the M-HREE region between 0.1-1xCI. The HREE level content (Lu_N down to 1) is consistent with 20-23% fractional melting of spinel DM. V-to-U-shaped REE patterns are also shown by Chenque lherzolites and harzburgites. Their M-HREE are more fractionated than that expected in residue after spinel facies basal removal, thus suggesting an onset of the partial melting at garnet facies conditions. Other Chenque lherzolites seem to result from a more extensive refertilisation processes led by LREE-enriched to LREE-depleted melts. The latter gave rise to transient LREE-depleted sinusoidal patterns through reaction with the depleted ambient peridotite. It is, thus, concluded that the shallow mantle column beneath Paso de Indios records an incomplete refertilisation of strongly depleted protoliths. This represents a unique example for the Patagonian region, where the mantle is usually completely overprinted by multiple stages of melt/fluid migration.

The interaction between silicate minerals and C-O-H bearing melts in the Earth's mantle

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Keywords: volatiles, kimberlites, incipient melting, H2O partitioning.

Melting processes in the mantle are strongly affected by the presence of volatile species such as H_2O and CO_2. In this study we conducted experiments to investigate the effect of these volatiles on the melting of mantle rocks at conditions corresponding to the deep upper mantle (~180-400 km). Chemical compositions of small degree hydrous melts that would form at 180 km depth and near adiabatic temperatures were determined in a natural mantle peridotite system. The hydrous melt compositions, on a volatile free basis, are found to be similar to group II kimberlites. The H2O concentrations of peridotite mineral phases were measured and the partitioning of H2O between peridotite and melts determined. The results indicate that current estimates for the H2O content of the depleted mantle (50-200 ppm H2O) are insufficient to induce mantle melting at these conditions. Based on inter-mineral H2O partitioning a model is constructed that calculate the distribution of H2O between peridotite phases as a function of depth at H2O-undersaturated conditions. The model indicates that for a fixed mantle H2O content the olivine H2O content will increase with depth solely due to changes in inter-phase partitioning and mineral modes, providing an explanation for the reduction in seismic anisotropy observed at depths >200 km. Experiments were also conducted at 6 and 13 GPa in the simplified systems MgO-SiO2-H2O±CO2. In the H2O-bearing experiments melting phase relations were examined using a thermodynamic model that supports the almost complete dissociation of H2O to OH- bonded to melt silicate components at these conditions, although results for forsterite at 13 GPa are inconclusive. H2O partition coefficients were determined as a function of temperature for forsterite and enstatite at 6 and 13 GPa and very little temperature dependence was observed except for forsterite at 13 GPa. Experiments in the H2O- and CO2-bearing system at 13 GPa were performed to investigate the effect of CO2 on the mineral-melt H2O partition coefficient. These results have implications on the formation of volatile bearing melts atop the transition zone.

The Valdieri marbles: the result of a localised recrystallization and metasomatism related to a focused flow of REE-rich fluids

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Keywords: Dauphinois domain, Hydrothermal circulation, REE enrichments.

In the Maritime Alps, at the northeastern border of the Argentera crystalline massif, close to Valdieri, two kilometre-scale rock bodies of marbles occur within a carbonate succession referable to the Dauphinois domain. These marbles have been quarried in the past as ornamental stones ("Marmi di Valdieri").

The stratigraphic succession in which the Valdieri marbles occur consists of Middle Jurassic-Upper Cretaceous deep water sediments: dark marls (Entracque Marl, Middle Jurassic-Berriasian) followed by micritic limestones with breccia beds (Lausa Limestone, Valanginian-early Aptian) in turn overlain by dark shales and marls (Marne Nere, Aptian-Cenomanian) and by marly limestones (Puriac Limestone, Turonian-Campanian). The Puriac Limestone is bounded at the top by a regional unconformity, overlain by middle Eocene-Lower Oligocene sediments of the Alpine foreland basin.

Recrystallization affects the Lausa Limestone, the Marne Nere, and the lower and middle portions of the Puriac Limestone, whereas the upper portion of the Puriac Limestone, as well as the overlying Alpine foreland basin succession, seems to be unaffected. Laterally, the marbles rapidly pass to poorly recrystallized limestones and marls of the corresponding stratigraphic intervals.

The lower part of the Valdieri marbles, corresponding to the Lausa Limestone, consists of pure white and grey marbles with rare mm-thick elongated and folded domains strongly enriched in muscovite, K-feldspar, albite and quartz. The upper part, corresponding to the Puriac Limestone, is mostly composed of lens-shaped, cm- to dm-thick granoblastic marble portions, interlayered with mm-thick anastomosed greenish to purple levels. The latters are composed of white mica (muscovite-paragonite s.s.), chlorite and epidote with accessory titanite, tourmaline, apatite and zircon. The epidote, locally abundant, occurs as subhedral crystals up to few millimeters across, undeformed to strongly fractured; it often shows a dark (metamictic?) core surrounded by a clear rim and at least locally overgrows the folded S_0 planes. Preliminary SEM-EDS analyses show that the Fe-rich epidote (very close to the epidote end member) is characterized by an irregular zoning, with abundant small patches (few microns across) strongly enriched in HREE (La_2O_3+Ce_2O_3+Nd_2O_3 up to ~13 wt%) and Th (ThO_2 up to ~2.8 wt%). The marbles are crossed by mm- to dm-thick veins commonly filled with calcite, quartz and locally also Fe-rich carbonate. Veins strongly enriched in epidote (+ calcite + quartz) are found in the upper part. All the veins show equilibrium relationships within the host marble.

The stratigraphic setting and the petrographic features of the Valdieri marbles suggest that their formation probably took place in the Late Cretaceous-Eocene time interval and that it was due to a polyphase metasomatic process related to the localized upflow of REE-rich hydrothermal fluids.

Solubility of mantle minerals in high-pressure COH fluids

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Keywords: COH fluids, solubility, subduction.

Fluids play a crucial role in many processes in subduction zones, influencing the melting temperatures and promoting mass transfer from the subducting lithosphere to the overlying mantle wedge. Carbon is a relevant component in deep fluids, as suggested by its occurrence in arc magmas and subduction-related rocks. Compared to H_2O-only fluids, high-pressure COH fluids are substantially unexplored. For this reason we choose to experimentally investigate the dissolution of mantle minerals, represented by forsterite, enstatite and magnesite in graphite-saturated COH fluids at controlled redox conditions. We conducted experiments at pressures from 1 to 1.5 GPa and temperatures from 700 to 1100°C using a rocking piston cylinder apparatus. Synthetic forsterite, enstatite and natural magnesite were used as starting material. A diamond trap was placed between two layers of mantle minerals to collect fluid and solutes. Carbon-saturated COH fluids were generated starting from oxalic acid anhydrous ($H_2C_2O_4$), water (doped with 580 ppm of Cs) and graphite. Redox conditions were controlled employing the double capsule technique and nickel-nickel oxide buffer (ΔFMQ=-0.61 at 800°C; ΔFMQ =-0.98 at 900°C). Thermodynamic calculations predict fluids mainly composed of H_2O and CO_2, characterized by different XH$_2$O contents as a function of P and T. We analyzed the fluid and solutes using the cryogenic laser ablation ICP-MS technique. With this method the capsule is frozen (T=-35°C) prior the opening to allow laser ablation analyses of the frozen fluid. As the temperature reached by the freezing stage is not sufficient to freeze CO_2, the analyzed solute content refers to the aqueous part of the COH fluid. The concentration of an internal standard (Cs), corrected with a dilution model, was used to retrieve the amount of solutes in the fluid, as Cs fractionates completely into water. The use of a dilution model is necessary because the XH$_2$O is not constant and is controlled by the nickel-nickel oxide buffer. The results will highlight the importance of fluids for the mass transport of C, Si and Mg in subduction zones. Comparison with other experimental system (Newton & Manning, 2002) will also be shown.

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Ultra-oxidized redox conditions in subduction mélanges? Decoupling between oxygen fugacity and oxygen availability in a metasomatic environment

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Keywords: manganese, oxygen fugacity, redox.

The manganese ore of Praborna (Italian Western Alps) is embedded within a metasedimentary sequence belonging to a subduction mélange equilibrated at high-pressure conditions (~2 GPa) during the Alpine orogenesis and record environmental conditions typical for a subducting slab setting. The pervasive veining of the ore and the growth of "pegmatoid" HP minerals suggest an open system with large fluid/rock ratio and a strong interaction with slab-derived fluids. This natural case provides an excellent natural laboratory for the study of the oxygen mobility in subducting oceanic slab mélanges at high-*P*, fluid-present conditions. The Mn-rich rocks in contact with the underlying sulphide- and magnetite-bearing metabasites, in textural and chemical equilibrium with the veins, contain braunite ($Mn^{2+}Mn^{3+}_6SiO_{12}$) + quartz + pyroxmangite ($Mn^{2+}SiO3$), and minor hematite, omphacite, the epidote piemontite and spessartine-rich garnet. Similarly to Fe-bearing systems, Mn oxides and silicates can be regarded as natural redox-sensors, capable to monitor a process of fluid infiltration that could fix externally the intensive variable fO_2 (or μO_2). Sulphides are absent in these Mn-rich rocks, sulphates (barite, celestine) occurring instead together with As- and Sb oxides and silicates. On the basis of the observed assemblages, new thermodynamic calculations show that these mélange rocks are characterized by unrealistic ultra-oxidized states (dFMQ up to +12) if the chemical potential of oxygen (or the oxygen fugacity) is accounted for. However, if the molar quantity of oxygen in excess with reference to with reference to a system where all iron and manganese are considered to be ferrous, the ore appears only moderately oxidized, and comparable to typical subduction-slab mafic eclogites. Therefore, oxygen can be hardly considered a perfectly mobile component, even in the most favourable conditions. In the Earth's interior redox reactions take place mainly among solid oxides and silicates, as oxygen is a negligible species in the fluid phase, if any. Therefore, the description of the redox state of petrological systems requires the introduction of the conjugate oxygen molar quantity, becoming the oxygen chemical potential a dependent variable. As a consequence, μO_2, and therefore fO_2, should not be regarded as long-range properties, indicative of the redox state of the entire rock column of a subduction zone, from the dehydrating oceanic crust to the overlying mantle wedge. On a more general basis, the comparison of fO_2s retrieved from different bulk compositions and different phase assemblages may lead to apparent redox heterogeneities. On the contrary, the distribution of oxygen is expected to be much more continuous moving from a maximum in the subducted mafic eclogites, formed from the altered oceanic basalts and gabbros, down (upward) to a minimum in the peridotites of the mantle hanging-wall.

Fluid-induced leaching of organic matter at HP-LT conditions: a new tile in the deep C cycle

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Keywords: Subduction, HP-LT metasomatism, C devolatilization.

At subduction zones, crustal rocks are recycled into the Earth's interior with profound implications for global elemental cycling. This process includes redistribution of carbon from the solid state (e.g. carbonates, graphite, diamond) to the fluid phase (e.g. CO2, CH4), which deeply participates in the global carbon cycle. In subducting oceanic slabs, C in the solid state mainly occurs as carbonates and organic matter (OM). The participation of carbonates in decarbonation reactions at HP-LT conditions has been recently matter of field-based studies, which in part question more consevative thermodynamic and experimental results. On the contrary, much less is known about the evolution and role of OM in the processes of C recycling at HP-LT conditions. The thermodynamic approach has provided important insights on the evolution of graphite-saturated COH (GCOH) fluids. However, natural example of OM recycling at HP-LT conditions in subduction zones is poor.

The progressive transformation of organic matter from a disordered structure to almost pure, ordered graphite is well established. This process occurs in a wide range of T ranging from diagenesis to T exceeding the peak estimates of most oceanic rocks that are back from HP-UHP conditions (ca. 650 °C). This indicates that, in absence of perturbations induced by changing boundary conditions such as changing redox state or interaction with external fluids, subducted OM is expected to persist in the solid state during HP regional metamorphism.

In this contribution we show that impressive fluid-induced leaching of OM may occur at HP conditions. We present natural evidence for C devolatilization during HP metasomatism of ocean-derived blackschists from Alpine Corsica. This process is accompanied by profound chemical and mineralogical variations in the rock, including hydrous phases such as lawsonite, and affects a significant amount of the HP-LT terranes of Corsica from a minimum P-T condition of ca. 360 °C and 1.6 GPa. Mass balance calculations point to significant CO_2 fluxes produced by this metasomatic process and released toward the forearc or subarc wedge.

SESSIONE S20

Magmatism and Geodynamics of the Mediterranean area

CONVENORS

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Subduction-modified and intraplate Neogene magmatism in SE Anatolia

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Keywords: Eastern Anatolia, Neogene Volcanism, Petrology, Isotope Geochemistry.

Widespread igneous activity occurs from Middle Miocene to Quaternary in Eastern Anatolia. Around Elazig, Pertek, Tunceli, Mazgirt and Karakoçan areas calc-alkaline and alkali-basaltic rocks with whole-rock chemical compositions ranging from basalts and trachybasalts to andesite and dacite crop out.

On the basis of geochemical and isotopic data, three main groups of rocks have been distinguished. Rocks of the first group occur in Elazig and Karakoçan areas show high TiO_2 (3.10-1.71), low La/Nb ratios (1.9-0.7), low Sr ($^{87}Sr/^{86}Sr$ = 0.70331-0.70376), high Nd ($^{143}Nd/^{144}Nd$ 0.51290-0.51283) and low $^{207}Pb/^{204}Pb$ isotopic ratios (15.64-15.67), coupled with roughly HIMU-OIB-like pattern in primitive mantle-normalized diagrams, peaking at Nb-Ta. The second group of rocks is found in Tunceli and Bulgurçuk area and marks the transition between intraplate-like and more typical subduction-related magmatic compositions. The TiO_2 content is lower (1.75-1.42), while the La/Nb ratios (2.3-1.3) and $^{87}Sr/^{86}Sr$ (0.70395-0.70491) as well as $^{207}Pb/^{204}Pb$ (15.64-15.67) are higher than the first rock group, coupled with lower $^{143}Nd/^{144}Nd$ (0.51280-0.51268). The third group includes samples from Pertek and Mazgirt area, characterized by low TiO_2 (1.67-0.41), high La/Nb (3.5-2.3), strongly radiogenic $^{87}Sr/^{86}Sr$ (0.70554-0.70682), lower $^{143}Nd/^{144}Nd$ (0.51263 to 0.51257) and higher $^{207}Pb/^{204}Pb$ (15.70-15.72). These features, including positive Pb and K anomalies as well as LILE and Sr enrichment in primitive mantle-normalized diagrams, are compatible with derivation from a subduction-related mantle source.

Despite the supra-subduction tectonic setting of all of the studied samples, rocks of the first group exhibit geochemical and isotope characters typical of mantle source with any or limited modification by subduction-derived fluids. This fact, along with the presence of spatially and temporally overlapping volcanic rocks with very different mineralogical and chemical compositions is a further evidence of the perils in inferring paleotectonic environments on the basis of geochemical constraints only.

The negative correlation of TiO_2 with $^{87}Sr/^{86}Sr$ and $^{207}Pb/^{204}Pb$ ratios, as well as the positive correlation of $^{87}Sr/^{86}Sr$ with Th/Ta and La/Nb speak for the existence of two mantle source end-members, one producing HFSE-rich, LILE-poor, low $^{87}Sr/^{86}Sr$, low $^{207}Pb/^{204}Pb$ intraplate-like magma and the other responsible for the production of HFSE-poor, LILE-rich and radiogenic $^{87}Sr/^{86}Sr$ and $^{207}Pb/^{204}Pb$ melts, generated by subduction processes.

The within-plate Na-alkaline magmatism of the Pelagian Block (Southern Italy): Sr-Nd-Pb and U-series isotope constraints from Pantelleria, Linosa and Pachino-Capo Passero basalts

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Keywords: within-plate continental magmatism, Sr-Nd-Pb isotope, HIMU-FOZO, Common Mantle Reservoir, U-series.

The origin of the mantle sources of the Na-alkaline magmas erupted within the Pelagian Block (southern Italy) are here investigated through the determination of Sr, Nd and Pb isotope ratios on basaltic volcanic from Linosa, Pantelleria and Pachino-Capo Passero. Despite their geographical proximity these rocks were erupted over a large time span (Upper Cretaceous to Quaternary). U-series disequilibria have been measured on the recent products of Pantelleria (120-9 ka) volcano in order to constrain the mechanism of mantle melting in relationship to the geodynamic setting of the studied area.

The isotope data, along with trace element ratios are used to assess the possible role of the interaction with the continental crust and/or the Sub-Continental Lithospheric Mantle (SCLM). The data show little variation in Sr and Nd isotopes and a continuous trend towards more radiogenic Pb isotope composition from Linosa to the oldest mafic activity of Pantelleria (i.e. Paleo-Pantelleria) and Pachino-Capo Passero, with intermediate values measured in the youngest Pantelleria lavas (Neo-Pantelleria). The Sr-Nd-Pb isotope compositions of the studied rocks are also compared with literature data from the Canary Islands, as representative of a putative plume component contaminating the mantle region, but some clear distinction, especially in terms of Pb isotopes are observed.

The increasing FOZO-like character of the studied magmas and the variation of some key trace element ratios is interpreted as a feature of the ambient asthenospheric mantle, due to the extremely widespread process of prolonged subduction and recycling of mafic oceanic crust of variable age and composition.

Pantelleria basalts have ubiquitous ^{230}Th-excess ranging from 7% to 20%. These data suggest the magmas are originated within the asthenospheric mantle, with little or no interaction with either the continental crust or the SCLM.

The Coupled ^{230}Th-^{238}U and ^{231}Pa-^{235}U data in a Pantelleria sample were used to perform quantitative dynamic melting models in order to constrain physical parameters of mantle melting in the Sicily Channel. The combined modelling yielded positive solutions only for high D_U/D_{Th} (≥ 2.5) and low melting rates (-4 kg/m^3/a). These data argue against any important role for amphibole in the genesis of these magmas and are consistent with a peridotite source possibly well mixed with recycled components. The modelled values of melting rate can also be converted into estimates of the upwelling rate of the mantle that are compatible with slow passive upwelling along the Sicily Channel rift.

Metasedimentary and igneous xenoliths from the volcano of Tallante (Betic Cordillera, Spain): a reappraisal based on isotopic analyses

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Keywords: Magmatism and geodynamics, Betic Cordillera, xenoliths.

Deep seated xenoliths entrained by volcanics provide information on the composition, thermal regime and physical properties of deep inaccessible lithologies. Unfortunately, the approach of study is somewhat limited because: i) xenoliths are rare and not ubiquitous in all volcanic centers; ii) in each volcanic center the xenolith population is often monotonous, i.e. mainly represented by a prevalent lithology. The homogeneity of xenolith suites from distinct volcanic sites is ascribed to the uptake mechanism, mainly related to fluid release and bubble nucleation, which trigger discrete event of crack formation and breaking of the surrounding deep rocks. The specific depth of xenolith formation is distinctive of each magma type, and usually Cenozoic alkaline basalts of the Mediterranean region entrain xenoliths from either the uppermost lithospheric mantle (30-50 Km depth) or the lower crust, and sampling from different depths is rare. In this view, the volcano of Tallante (Pliocene) in the Betic Cordillera (Spain) represents a peculiar occurrence, where alkaline basalts uprising from mantle sources exhumed an extremely heterogeneous xenolith association, including protogranular peridotites, felsic metasedimentary rocks, as well as diverse cumulitic igneous rocks such as amphibole-clinopyroxenites and norite-gabbros. Noteworthy, the numerous studies available in the literature mainly focused on the peridotite xenoliths and failed to consider in a coherent framework the total xenolith suite of Tallante and to explain its extreme variability. Only recently, Bianchini et al. (2013) proposed that the extreme xenoliths heterogeneity recorded at Tallante could be related to the specific geodynamic setting, located along a collisioned belt, where the crust-mantle boundary is possibly characterized by an intimate association of crustal and subcrustal lithologies, interlayered as result of orogenic processes. This contribution presents new Sr-Nd isotopic analyses carried out on metasedimentary and igneous xenoliths, as well as in-situ U-Pb dating of a zircon grain from a gabbroic xenolith. The new data, discussed taking into account the most recent geophysical evidence (Thurner et al., 2014) give insights to refine the pre-existing petrological hypotheses, in the general geological framework of the Betic orogenic belt.

Bianchini G., Braga R. & Langone A. 2013. Crustal xenoliths from Tallante (Betic Cordillera, Spain): insights into the crust–mantle boundary. Geol. Magaz., 150, 952-958.

Thurner S., Palomeras I., Levander A., Carbonell R., & Lee C.-T. Ongoing lithospheric removal in the western Mediterranean: Evidence from Ps receiver functions and thermobarometry of Neogene basalts (PICASSO project).

Geochemistry of submarine mafic lavas from Pantelleria Island, Sicily Channel

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Keywords: Pantelleria Island, submarine volcanism, mafic magmas.

Detailed investigations of the submarine portions of Pantelleria were carried out in 2006 and 2008 (aboard R\V Urania) using a 50 kHz multibeam bathymetric system and collecting seafloor samples by dredging, grabbing and coring. In particular, more than 50 dredge samples including scoriaceous and massive lavas were recovered on the NW portion of the volcano. Here, numerous volcanic centers were identified, including the vent of the last known eruption (1891). The NW monogenetic volcanic field likely formed during a discontinuous activity punctuated by several eruptions close in space and, probably, in time.

In order to reconstruct the submarine volcanic activity of Pantelleria, several mafic lava collected from these volcanic cones and along the NW slope have been analyzed in their petrography and geochemistry and compared with the literature data of analogous subaerial products from the NW of the island. Samples from the cones are scoriaceous basalts and basanites with sub-aphyric to porphyric texture (P.I.~5-15vol%) in which plagioclase, clinopyroxene±olivine±oxides occur as phenocrysts, microphenocrysts and microlites. Vesicles of most of these samples are totally or partially filled with secondary minerals (i.e., carbonate and/or motukoreaite). In addition, the composition of scoriaceous lavas is similar to those of 1891 products (Conte et al., 2014).

The massive lavas from the slope are weakly porphyritic basalts (P.I.≤10vol%) with phenocrysts of plagioclase>olivine> clinopyroxene and ± oxides, set in a microcrystalline groundmass made up of the same minerals. Their higher olivine amount respect to the scoriaceous products, along with the higher Mg# and Cr and Ni contents, testify a more primitive character. Noteworthy, the massive basalts are characterized by a lower TiO_2 and P_2O_5 contents than those of the scoriaceous lavas (TiO_2~2.55wt%-P_2O_5~0.55wt% and TiO_2~4.3wt%-P_2O_5~1.80wt%, respectively).

The chemical differences observed between submarine massive and scoriaceous lavas were found respectively in the older (~120 to 50 ka) and younger (~30 to 10 ka) mafic sub-aerial products outcropping in the NW part of Pantelleria, which are characterized by higher TiO_2 (>3wt%) and P_2O_5 (>1wt%) contents, and lower TiO_2 (<3wt%) and P_2O_5 (<0.7wt%) contents, respectively. Therefore, we infer that the massive basalts from the NW submarine slope were fed by magmas similar to the younger sub-aerial products and the scoriaceous lavas of the NW volcanic field, including the historical 1891 eruption products, were fed by a reservoir filled by a magma geochemically very similar to that which had fed the older sub-aerial mafic units.

Conte A.M., Martorelli E., Calarco M., Sposato A., Perinelli C., Coltelli M., Chiocci F.L. 2014. The 1891 submarine eruption offshore Pantelleria Island (Sicily Channel, Italy): Identification of the vent and characterization of products and eruptive style. Geochemistry, Geophysics, Geosystems, accepted May 29, 2014.

Newly discovered submarine volcanoes north of Ventotene extend the Pontine volcanism offshore Gaeta (Tyrrhenian Sea, Italy)

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Keywords: New submarine volcanoes, Pontine islands, arc-related volcanism.

Newly acquired high-resolution bathymetric data covering the upper part of the continental shelf off Gaeta, combined with magnetic data and multichannel seismic reflection profiles, have revealed an elongated partially-buried structural high oriented NW-SE. A 200 m-high cone and an elliptical feature mark the summit of this structure. Morphology and positive magnetic anomalies (> 150 nT) suggest that they are two volcanic edifices. Both volcanoes have flat summits lying at a depth of ~170 m, with a diameter of 1.5 km and with major and minor axis of 5 and 2 km, respectively. A multichannel seismic line runs SE-NW along the axis of the 20 km-long structural high. The seismic line crosses the lower northern flank of the elliptical edifice bounded to the south-east by a major normal fault trending SW-NE that offsets the Ventotene Basin basement by over 1 km. Further to the north the seismic line intersects another normal fault with similar orientation. This fault separates the aforementioned volcanic edifice from the sub-circular volcanic apparatus shaping its southeastern flank. Well stratified contourites cover the flanks of the sub-circular volcanic cone, whereas a ring-like depression due to erosion surrounds the cone.

The newly discovered submarine volcanoes are located 25 km north of Ventotene Island extending Pontine volcanism landward. The Pontine Archipelago forms a 50-km-long chain running parallel to the Tyrrhenian coast and connecting the Vavilov abyssal plain with the continental platform. The western Pontine islands (Ponza, Palmarola and Zannone) are dominated by silica-rich submarine volcanic units. The magmatic activity of Ponza began 4.2 Ma with emplacement of rhyolitic hyaloclastites and ended 1 Ma with a trachytic event. Palmarola island consist of rhyolitic hyaloclastites and domes dated between 1.6 and 1.5 Ma. The eastern Pontine (Ventotene and Santo Stefano) are dominated by alkali-potassic subaerial deposits dated between 0.9 to 0.3 Ma.

The flat, shallow tops of the newly discovered volcanoes are interpreted as wave-cut marine terraces due to lower sea_level in the past. Marine terraces with similar depths have been already noted on the flanks of Ventotene. This, together with the normal polarity of the magnetic anomalies, suggests that volcanic activity in this sector of the Gaeta bay was contemporaneous with that of Ventotene (Middle Pleistocene). Further studies in this new volcanic area, in particular geochemical work, may have important implications on the evolution of the east-directed back-arc-related opening of the Tyrrhenian Sea. In fact, changes in space and time of the Pontine magmatism has been related to the tectonic evolution of the area, with emplacement of volcanic units that range from syn-collisional to post-collisional setting.

The evolution of the magmatic feeding system of the Ustica Island (Southern Tyrrhenian Sea, Italy)

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Keywords: Tyrrhenian Sea, Ustica, Transtensional tectonics.

Volcanism at Ustica has been related to the activation of left-transtensional faults, linked to the anticlockwise rotation of the Italian peninsula and opening of the Tyrrhenian basin. It started more than 1 Ma ago and extinguished at 130 ka. Volcanism on the island can be subdivided in three periods, based on major and trace elements and total alkali variations vs. stratigraphic height.

During the first period (750-475 ky) there was the emplacement of units characterized by poor compositional variations, although showing appreciable intra-formational variability. The second period (around 425 ka) is marked by the only eruption of trachytic magma occurred on the island, whose deposits show a decreasing differentiation degree from base upward, suggesting the existence of a compositionally zoned magma chamber. The volcanic units emplaced during the third period (420 – 130 ky) are the product of less differentiated magmas, although they show a greater compositional variability, mainly in the differentiation degree, between one unit, and the previous and following ones.

Sr isotopic ratios individuate well defined fields for rocks belonging to different periods in the plots vs. SiO2 and P2O5. The rocks of the first period have this ratio on average higher than the rocks belonging to the third period. The most differentiated product of the Ustica volcanic sequence, represented by the trachytic Grotte del Lapillo pyroclastic unit, is characterized by Sr isotopic ratios that vary significantly with the stratigraphic height, suggesting open-system evolution processes. Based on chemical composition of the erupted products, their stratigraphic height, and vent position, each period can be subdivided in cycles in which the first erupted magmas are systematically less differentiated than the final ones.

Taking also into account the absolute ages of the erupted products, it is possible to formulate the following hypothesis on the evolution of the Ustica magmatic feeding system. During the first period, due to the intense tectonic activity related to the opening of the Tyrrhenian sea, almost continuous eruptions were fed by poorly evolved magmas, which had no time to differentiate in shallow- level reservoirs. Only short episodes of stagnation at variable depth could have occurred during this period, accompanied by moderate crystal fractionation and assimilation processes. After a period of quiescence that lasted about 50 ka, the eruption of trachytic magma could be related to a stasis in the regional tectonic activity, which allowed the stagnation of magma and the formation of a compositionally zoned magma chamber.

After this eruption, volcanism renewed with close eruptions fed by poorly evolved magmas, which were however characterized by more efficient differentiation processes, likely related to the formation of small-scale magma chambers.

Subduction-related enrichment of the Neapolitan volcanoes (Southern Italy) mantle source: new constraints on the characteristics of the slab-derived components

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Keywords: Neapolitan volcanic area, Basilicata ophiolites, subduction slab derived melts and fluids.

The Neapolitan volcanic area (Southern Italy) has been the site of an intense Plio-Quaternary magmatic activity with a subduction-related signature. The high-Mg, K-basaltic lithic lava fragments dispersed in hydromagmatic tuff of the Solchiaro eruption (22 ka, Procida Island) are the least evolved volcanic rocks of the Neapolitan volcanic area and provide constraints on the nature and role of both pre-enrichment mantle and subduction-related components. Their average values of HFSE ratios such as Nb/Yb, Nb/Y, and Zr/Hf, relative to typical EMM and Canary Islands OIB, would seem to indicate an EMM-like, spinel peridotite pre-enrichment source for the Procida and, by inference Somma-Vesuvius, mafic magmas. In order to constrain the characteristics of subduction-slab derived components added to this mantle sector, new geochemical and Sr-Nd-isotopic data have been acquired on meta-sediments and pillow lavas from Timpa delle Murge ophiolites, representing fragments of Tethyan oceanic crust obducted during the Apennine orogenesis, and that may be similar to sediments subducted during the closure of Tethys ocean. Based on trace elements compositions (Th/Nd, Yb/Th, Ba/Th) the addition of three distinct subduction components to the mantle wedge underlying the Neapolitan volcanic area can be hypothesized: partial melts from shales, aqueous fluids from shales, and partial melts from limestone. Trace elements and Sr-Nd-isotopic ratios suggest a greater role for melts from pelitic sediments, relative to melts from limestones, and aqueous fluids, whereas seem to rule out a significant role for altered oceanic crust. Modeling based on variations of trace elements and isotopic ratios indicates that the pre-subduction mantle source of the Phlegrean Volcanic District and Somma-Vesuvius was enriched by 2-3% of subducted slab-derived components that might have stabilized amphibole and/or phlogopite in the mantle. The partial melting degree of this enriched source (amphibole-bearing spinel peridotite) should have been 2.5% to generate the Procida primary magmas. Modeling based on trace element contents and 87Sr/86Sr-143Nd/144Nd values constrains the age of the enrichment event to about 45 Ma ago, confirming that the Plio-Quaternary magmatism of the Neapolitan area is post-collisional, and suggesting that the origin of the subduction-derived enriching agents can be related to the closure of Tethys. A model of 1% partial melting of a source with the same chemical composition as that inferred for the PVD, but with different mineralogy (phlogopite-bearing spinel peridotite) reproduces the same trace elements distribution pattern of the olivine-hosted shoshonitic melt inclusions from the 1906 AD lava flow of Somma-Vesuvius. EC-AFC modeling suggests that these primitive melts were subsequently modified at mid-lower crust depth, with assimilation of 1.4% of continental crust.

Mantle dynamic in the Mediterranean

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Keywords: Mediterranean, mantle, tectonics.

The Mediterranean offers a unique opportunity to study the driving forces of tectonic deformation within a complex mobile belt. Lithospheric dynamics are affected by slab rollback and collision of two large, slowly moving plates, forcing fragments of continental and oceanic lithosphere to interact. This paper reviews the rich and growing set of constraints from geological reconstructions, geodetic data, and crustal and upper mantle heterogeneity imaged by structural seismology. We proceed to discuss a conceptual and quantitative framework for the causes of surface deformation. Exploring existing and newly developed tectonic and numerical geodynamic models, we illustrate the role of mantle convection on surface geology.

Petrological characterization of the upper Miocene Rodna-Bârgău sub-volcanic district (Eastern Carpathians, Romania)

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Keywords: petrology, Eastern Carpathians, Rodna-Bârgău, amphibole.

During Neogene, the Eastern Carpathians were the locus of abundant igneous activity with subduction-related geochemical characteristics. Among the various districts, the Rodna-Bârgău sub-volcanic complex represents a potentially key-area due to its peculiar position at the junction point between ALCAPA, Tisza-Dacia and East European plates, the exclusively sub-volcanic nature of its products, compared with the mainly effusive nature of the products from the other districts and the occurrence of a wide range of chemical compositions coupled with xenoliths of various nature, testifying complex low-pressure evolution. Despite this, little attention has been so far devoted to the study of the products of the area, which still remain poorly characterized. The present work is thus aimed to a full petrological investigation of the products of the Rodna-Bârgău district, which will possibly shed some new light on the magma-genetic and geodynamic evolution of the entire Carpathian arc.

The preliminary analyses on representative samples allowed the recognition of numerous petrographic types, ranging from basalt/microgabbro to mainly andesite/microdiorite up to dacite/granodiorite and rhyolite/microgranite. Rock compositions show a well defined calcalkaline serial affinity in which, however, a clear distinction between a low-K and a high-K magmatic suites can be observed. Rocks of the first series are amphibole-bearing andesites/microdiorites, dacites and rhyolites/microdiorites with SiO_2 = 58.0-74.6, MgO = 3.36-0.09 and K_2O = 1.49-2.93 wt.%, whereas rocks of the high-K suite are microgabbros, amphibole-bearing basaltic andesites/andesites and dacites with SiO_2 = 53.4-64.1, MgO = 10.2-2.18 and K_2O = 1.29-3.23 wt.%. Intermediate-evolved terms of the two series are remarkably different also on petrographic grounds, given that 1) low-K rocks (K_2O = 1.71-3.23 wt.%) display a yellow-pale green tschermakite to Mg-hornblende amphibole (Si = 6.01-6.94, K = 0.03-0.09 a.p.f.u.), whereas high-K ones (K_2O = 1.16-1.46 wt.%) feature a green hastingsite-pargasite (Si = 5.82-6.36, K = 0.16-0.34 a.p.f.u.); 2) low-K andesites display rare Na-rich alkali feldspar (Or ~49) in the groundmass, whereas high-K equivalents have higher abundances of a K-richer variety (Or ~70); 3) accessory biotite (Mg# = 0.57-0.61) is present only in high-K andesites and dacites. Incompatible element abundances suggest subduction-modified magma sources and again indicate a clear distinction between the two rock series, with rocks of the high-K suite displaying a stronger enrichment in LILE (e.g., Rb = 34-57 and 56-118 ppm, Ba = 359-631 and 578-819 ppm, in least evolved and intermediate-evolved terms, respectively) and LREE (e.g., La_N = 22.7-31.6 and 30.6-44.4, Nd_N = 12.1-14.9 and 13.0-20.0) with respect to those of the low-K one (Rb = 27-46 and 38-107 ppm, Ba = 158-288 and 253-619 ppm, La_N = 15.3-22.4 and 17.0-42.6, Nd_N = 8.1-11.2 and 9.7-13.4, respectively for intermediate and evolved rocks).

^{40}Ar-^{39}Ar dating of Marsili seamount (Tyrrhenian Sea)

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Keywords: 40Ar-39Ar dating, Marsili seamount, Tyrrhenian Sea.

Marsili seamount, a huge volcanic edifice about 60 km long and 20 km wide, rises from the 3500 m deep seafloor of the homonymous basin to about 500 m below sea level. Its products range from medium- to low K basalts to high-K andesites, the latter sampled only in the summit area of the volcano (Marani & Trua, 2002).

Very few chronological constraints on its development are available in the literature. Poorly defined K/Ar ages, younger than 0.1-0.2 Ma, are reported for shallow lava scoriae by Selli et al. (1977). Cocchi et al. (2009) place the start of the vertical growth of the seamount at the beginning of the Jaramillo subchron and the maximum accretion within the Brunhes chron. Furthermore, the magnetic chronology of the Marsili basin is presently debated (Nicolosi et al., 2006; Cocchi et al., 2009; Florio et al., 2011).

Some fresh samples, dredged in past cruises (Marani et al., 1999), have been selected for ^{40}Ar-^{39}Ar dating, with the aim to attempt to clarify seamount growth. The often altered state of the samples and the inability to place them exactly on the volcanic edifice are limiting factors, constraining the choice of samples and the volcanological interpretation of their results. The only reliable datum obtained up to now is from a calc-alkaline basalt dredged in the NE steep flank, at 3050-2725 m depth. Pooled data from two step-heating experiments identifies an isochron of 213±22 ka (1σ), which represents the first direct dating of Marsili basalts.

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^{40}Ar-^{39}Ar geochronology and evolution of the Cimini volcanic district (Central Italy)

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Keywords: Cimini volcanic district, 40Ar-39Ar geochronology, stratigraphy.

The Cimini volcanic district (CVD) is located in Central Italy and belongs to the Tuscan Magmatic Province (Miocene-Middle Pleistocene). It is characterized by several phases of activity during which lava domes, lava flows and ignimbrites have been erupted (Lardini & Nappi, 1987). Conticelli et al. (2013) indicate that the Cimini volcanic rocks range from ultrapotassic to potassic, where shoshonitic lavas represent the most primitive products and trachytic lava domes are the rocks richest in silica. Although some age determinations were made in the past for the CVD, evidencing a quite long eruptive history (see Fornaseri, 1985, for a review), a great uncertainty persisted on the age, as well as on the stratigraphy of the Cimini volcanic activity. To solve such doubts, a ^{40}Ar-^{39}Ar geochronological study has been performed in the framework of the new sheet No. 345 "Viterbo" of the Geological Map of Italy at 1:50,000 scale. The accurate geological survey at 1:10,000 scale allowed an improvement of the stratigraphy and a detailed and representative sampling of the whole volcanic sequence.

Fourteen ^{40}Ar-^{39}Ar datings evidence an interval of activity of about 0.07 Ma, from 1.36 to 1.29 Ma, a period by far shorter than previously thought. Lava domes, which constitute a well preserved dome field, display the widest age dispersion (1.36÷1.29 Ma), while the ignimbritic and lava flows are all in the age interval 1.31÷1.29 Ma. The integration of geochronological and field data opens up to different interpretations about the eruptive history of the CVD than previously thought. The activity started with the growth of trachytic lava domes, followed by explosive eruptions that gave rise to pyroclastic flows which deposited a thick and widespread ignimbritic cover of latitic to trachytic composition. The building of further trachytic lava domes continued after this explosive stage. Latitic, olivine-latitic and shoshonitic lavas, coming from Mt. Cimino dome, are subsequent to the ignimbritic eruption, but both age data and field evidences are unable to fully elucidate their mutual relations and those with some of the last lava domes. However, some evidences question the allocation of olivine-latites and shoshonites as final products. The new datings enlarge the age gap between the end of the CVD and the beginning of the nearby Vico volcanic activity (0.42 Ma, Laurenzi & Villa, 1987).

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Magmatism in central Mediterranean: can we change the subduction paradigm?

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Keywords: magmatism, subduction, lithosphere delamination, central Mediterranean.

We review geophysical and petrological data that can support an evolutionary model for the Apennine system based on delamination of continental lithosphere. What is classically interpreted as subduction-related magmatism, i.e., partial melting of a mantle wedge metasomatized by coeval subduction, could be instead be considered as partial melting of mantle sources modified by no longer active (Alpine or Hercynian) subduction systems.

This may force a change in the current paradigm that explains the calcalkaline, high-K calcalkaline, potassic and ultrapotassic Cenozoic igneous activity of western Mediterranean in terms of subduction-related processes.

While coeval subduction can explain the early-middle Miocene igneous activity in Sardinia and the late Pleistocene volcanism in the Aeolian Islands, the distribution of many subduction-related igneous districts of western Mediterranean is not consistent with paleogeographic reconstructions. Excluding the naïve geochemical models invoking the presence of alleged mantle plumes, geochemical and petrological arguments simply indicate tapping of mantle sources modified by interaction with crustal lithologies, not a direct connection with active or recent subduction processes.

Magmas generated by subduction-modified mantle sources, not genetically related with coeval subduction systems, are present in the early Oligocene northern Apennines and the late Eocene Provençal-Sardinian margins. The subduction-related igneous activities along the Alpine Chain and in the Algerian Kabylies are tectonically unrelated with subduction (being post-collisional or emplaced too much closer to the trench or even in foreland position). Also the calcalkaline, potassic to ultrapotassic volcanic activity of the Betic Chain cannot directly be explained by subduction processes because these terminated more than 30 Myr before.

So far, high velocity mantle anomalies in tomographic models have been interpreted as remnants of subducted lithosphere, sustaining an East-directed and West-directed subduction-retreat model in the Apennine-Maghrebide and Betic-Rif systems. Consistent traces for prolonged Ionian subduction are outlined by high velocity anomalies in the mantle in the southern Tyrrhenian Sea region only, without continuity with the rest of the Apennines. Geophysical data likely indicate that the Apennines belt is delaminating and continental lithosphere plunges down to 100 km depth in front of a fossil Alpine belt, dismembered during the Tyrrhenian Sea opening. The Pleistocene volcanism is sourced in the hydrated and chemically heterogeneous patches of the uppermost mantle, outlined by high-resolution Vp/Vs models.

Leucitites and leucitites within and around the Mediterranean

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Keywords: Alkaline magmatism, Mediterranean, petrology.

Leucitites crop out in few localities within and around the circum-Mediterranean area: Central Spain (Calatrava), Central Germany (West and East Eifel), Eastern Germany (Saxony; Hammerunterwiesenthal), Czech Republic (Doupovské hory Mts.), Southern Hungary (Bàr), Central Italy (Ernici Mts. and Alban Hills volcanoes), Southern Kosovo (Devaje-Visoča), Western Turkey (Kirka-Afyon-Isparta) and NW Iran (Eslamieh Peninsula). We tentatively differentiate them in "anorogenic" and "orogenic" leucitites, depending on the proximity from active or recent subduction zones. Anorogenic leucitites are characterized by higher TiO_2 (1.9-3.6 wt%), Fe_2O_3tot (9.7-13.6 wt%), MgO (8.5-19.3 wt%), but lower Al_2O_3 (8.5-14.3 wt%), K_2O (0.5-4.3 wt%) and K_2O/Na_2O ratios (0.1-1.9) compared with orogenic leucitites. Compared with orogenic leucitites, the anorogenic leucitites have also lower Rb (13-303 vs. 96-670 ppm), Th (all but two samples 6-41 vs. 14-106 ppm), Pb (all but three samples 6-34 vs. 28-211 ppm), Ba/Nb (6-19 vs 42-193), La/Nb (0.7-1.2 vs. 1.1-9.5), Zr/Nb (1.5-6.5 vs. 4.9-29.8), Th/Ta (1-12 vs. 8-108) higher Nb (54-172 vs. 4-60 ppm), Ta (3.4-9.9 vs. 06-3.4 ppm), Nb/U (all but two samples 19-51 vs. 1-17), Ta/Yb (2.2-4.5 vs. 0.2-1.7) and Nb/Nb* (0.7-3.0 vs. 0.04-0.6).

This survey evidences the following important features: 1) Not all the leucitites are ultrapotassic rocks; 2) Some rocks classified in literature as leucitites are instead leucite-bearing basanites, tephrites, tephriphonolites and K-trachybasalts, given the abundant presence of feldspatic minerals; 3) Some rocks classified as basanites-tephrites should rather be defined leucitites because of the absence or paucity of feldspars; 4) leucitites are not confined in the foidite field of TAS diagram only, but spread towards silica-richer compositions; 5) rocks classified as leucitites emplaced in the foreland of subduction zones or in intraplate settings are not true leucitites. These can be easily distinguished from true leucitites, emplaced above active or recent subduction zones or along ancient sutures on the basis of several major and trace element constraints; 6) Rocks classified in different terms (e.g., leucite-basanite, tephrite, leucitite, leucite-nephelinite, phonotephrite, leucite-lamproite) generally have roughly the same incompatible element content, therefore can be related to similar petrogenetic processes, independently from the given rock name.

The siderite mineralizations in the Southern Alps: a signal of the Permo-Triassic rifting?

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Keywords: Southern Alps, siderite, ICP-Mass microchemistry.

Siderite mineralizations are distributed along the Southern Alps between Lake Como and Eastern Dolomites, mostly along major faults as Orobic, Val Trompia and Valsugana lineaments. They are dominantly unconformable veins in the Southalpine basement of Lake Como (Dongo, Val Cavargna) and Val Trompia (Torgola and Pineto) and in Late Permian rocks of the Orobic Alps (Lorio and Torsolazzo), or as stratiform conformable ore bodies within Lower Triassic Servino Formation carbonatic rocks (Manina, Fusio, Fura, San Vittore) (Cassinis et al., 1997; Brigo & Venerandi, 2005). Similar setting is described for siderite veins and strata-bound mineralizations in the Eastern Dolomites (Santa Lucia, Transacqua and Valle del Mis). Several publications describe the setting and the characteristics of the siderite, because the mining activity for iron extraction has been active since XV century. This work is aimed to define structural, stratigraphical and geochemical correlations among the siderite mineralizations of the Southern Alps that support a common time and process of genesis.

The composition of the siderite is rather homogeneous but it is enriched in Mn when it forms strata-bound ores in carbonatic rocks, whereas it is enriched in Mg when it forms veins cross-cutting the basement.

The Mn increasing trend in the siderites associated to carbonatic rocks of Early Trias age (Servino) is confirmed by a $\delta^{13}C$ concordant trend. According to Frizzo & Scudeler Bacelle (1983), siderite appears to have invaded the carbonatic rocks and impregnate them more or less extensively.

The origin of Fe and Mg of the siderite remains unclear. Hydrothermal solutions charged of Fe and Mg, at presumed low temperature, traveled across the upper crust in a large portion of the Southern Alps, mostly where extension faults were active since Late Permian and some basin (e.g. Collio) were locally opening. In some places veins cut basement and Permian granodiorite as at Introbio.

A specific time range, spanning from Late Permian to Early Triassic in Lombardy, and to Middle Triassic in the Eastern Dolomites is recorded. The time of siderite impregnation ended with the beginning of the Triassic magmatism in Lombardy and Veneto regions. The siderite mineralizations are a geodynamic indicator in the Southern Alps, possibly related to the Permo-Triassic rifting process.

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Deciphering the tectonometamorphic evolution of the Alboran Domain (Betic-Rif orogen, western Mediterranean): a clue from granite magmatism

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Keywords: Granite magmatism, Structures, U-Pb geochronology, Ar-Ar geochronology, Alpine orogeny, Mediterranean.

The Betic-Rif orogen forms the western termination of the Alpine orogenic system in the Mediterranean region. Still under debate are timing and structures of the high-grade metamorphism (Alpine *vs*. pre-Alpine) in the metamorphic core of the orogen (Alboran Domain). A major source of ambiguity results from interpretation of the metamorphic history of the granulite-facies envelopes surrounding the peridotite bodies exposed within the two arms of the Alboran Domain (Ronda and Beni Bousera). We report occurrence of two distinct generations (hereafter referred as Type-1 and Type-2, respectively) of peraluminous granitic bodies intruded within the Beni Bousera peridotites and their amphibolite-to-granulite facies envelope (northern Morocco). These granitic bodies are central to reconstruction of the high-grade evolution of the Alboran Domain, because they provide first-order structural markers to assess the *P-T-t* history of the high-grade terranes. We document their structural relationships with the host rocks, petrography, geochemistry and timing of granite emplacement is constrained by integrated U-Pb-Th zircon/monazite and $^{40}Ar/^{39}Ar$ dating. Type-1 consists of small (m to dm in size), variably-deformed leucocratic sheets and stocks, which occur exclusively within the granulite envelope, where they locally preserve intrusive relationships with the migmatitic country rocks. Their modal mineralogy consists of Qz (30-50%), K-Fsp (30-35%), Pl (10-25%), and Ky, Grt, Tor, Zrn and Fe-Ti oxides as minor phases (<10%). On the Q'-ANOR classification diagram, they range in composition from granodiorites to syenogranites. Type-2 consists of steeply-dipping dyke arrays discordantly intruded in the Beni Bousera units (including the peridotites) under the control operated by regional strike-slip tectonics. They consists of modally abundant K-Fsp (25-50%), Qz (20-30%), Pl (5-35%) ± Bt ± Mu ± Crd ± And ± Fe-Ti oxides, Zrc and Mnz (<15%). On the Q'-ANOR diagram, they range from alkali-feldspar granites to granodiorites. The Sr and Nd isotope systematics points to melting of fertile metasedimentary sources excluding derivation from the refractory host rocks. The geochronological results indicate granite emplacement occurred during two distinct episodes of crustal melting, in Hercynian (*c*. 290 Ma) and Alpine (*c*. 22 Ma) times for the Type-1 ad Type-2, respectively. These data (i) provide conclusive evidence for preservation of a Hercynian high-grade signature in the Alboran Domain of the Betic-Rif chain, (ii) impose to revise significance of the regional, Early Miocene high-grade and partial melting events in terms of a late-stage thermal pulse that affected a polymetamorphic (Hercynian and Alpine) nappe pile, and (iii) emphasise role of strike-slip tectonics during the Neogene syn-to-post-orogenic Alpine evolution of the western Mediterranean. This study also provides first-order constraints to arrive to a feasible tectono-metamorphic model for the Alpine orogeny in the western Mediterranean.

Occurrence of several explosive eruptions from Marsili seamount: new geochemical data of the Marsili volcanic activity during the last 6.7 ka B.P.

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Keywords: Marsili explosive events, major and trace elements, Y-1.

The Marsili oceanic-like basin (Southern Tyrrhenian Sea, Italy) is an about 2 Ma old back-arc related to the north-westward subduction of the Ionian lithosphere below the Calabrian Arc (Ventura et al., 2013 and reference therein). Several studies focused on the geodynamic interpretation of that area, which is characterized by coexisting active volcanism, compressive and extensional deformations and slab rollback processes. The evolution of the Marsili Seamount (MS), which is located in the central sector the back-arc basin, is still debated. MS is one of the largest volcano of Mediterranean Area and Europe, measuring about 70 km in length and 30 km in width with the top at ~500 m b.s.l.. The about 1 to 0.03 Ma fissural and central MS activity form a complex segmented volcanic structure (Ventura et al., 2013). Effusions of lava flow represent the main eruptive style along with minor explosive eruptions that produced fall and flow deposits in historical time (Iezzi et al., 2014). The composition of the products ranges from medium-K calcalkaline basalts to high-K calcalkaline andesites related to both IAB and OIB-like mantle sources (Trua et al., 2011).

In this contribution, we present new stratigraphic and geochemical data, as well as AMS ^{14}C dating from a 2.35 cm deep-sea gravity core "Marsili1" recovered at 940 m b.s.l. in the MS central area. In particular, major and trace element glass composition (EMPA and LA-ICP-MS) of five tephra layers recovered along the core are reported. The geochemical features of the tephra layers allow in identifying MS and Mt. Etna as source areas. On the base of AMS ^{14}C dating, the MS tephras emplaced between 2 and 7 ka B.P., whereas the Etna distal layer can be correlated with the Y-1 marker layer (ca. 17 ka B.P.). Our results testify, within the recent MS activity, recurrent explosive eruptions in historical time. The occurrence of submarine explosive eruptions in the last 7 ka implies an evaluation of the potential hazards.

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Alpine Tethys closure as revealed by amphibole-rich mafic and ultramafic rocks from the Adamello and the Bergell intrusions (central Alps)

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Keywords: Adamello, Bergell, Zircon, U-Pb, Hf isotopes.

U-Pb ages and Hf isotope data were carried out on zircon from amphibole-rich mafic to ultramafic rocks from the Adamello batholith and the Bergell pluton, the largest Paleogene intrusions of the Alpine orogen. The 206Pb/238U age pattern of U-Pb concordant dates from the Adamello mafic rock shows a major crystallization event at ~41 Ma and older age peaks at ~50 and ~45 Ma. Hornblendite and amphibole gabbro samples of the Adamello batholith have zircon with initial εHf of ~+9.0 and ~+7.0, respectively. Amphibole gabbro and diorite samples of the Bergell pluton yield a younger age of ~31 Ma and have zircon with lower initial εHf (~+4.0).

We propose that the amphibole-rich rocks from the Adamello batholith originated from a depleted mantle source activated by the subduction of the Ligurian-Piedmontese basin. The amphibole-rich rocks from the Bergell pluton formed 10-15 Ma later than the Adamello counterparts by melts derived from a mantle sector metasomatized by the subduction of the Valais Basin. The enriched Hf isotopic signature of the amphibole rich rocks from the Bergell pluton is therefore interpreted to reflect the peculiar lithostratigraphy of the Valais Basin or a primary feature of the newly activated mantle source.

The Periadriatic magmatic province of the Alpine Orogen cannot be considered the magmatic response to a single tectonic event. This study is further evidence that amphibole-rich mafic and ultramafic rocks associated with orogenic granitoids plutons worldwide are a fundamental geochronological and petrological tool to interpret large scale tectonic processes during continental assembly.

The Tertiary dike magmatism in the central Southern Alps: Geochronological data and Geodynamic significance

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Keywords: Southern Alps, dike magmatism, U-Pb ages.

The relationships between tectonics and magmatic activity in the Alps are still debated. Despite an active subduction since the Late Cretaceous, no arc-related magmatism is recorded prior of the Middle Eocene. The emplacement of plutons along the Insubric Fault in a short time span (~ 34-28 Ma) has been generally interpreted in terms of the slab break-off model. The Tertiary magmatism, however, is also characterized by occurrence of widespread calcalkaline dikes not necessarily intruded along the Insubric Fault. The geochemical features of dikes vary from the different areas and are interpreted in terms of mantle source heterogeneity and degree of crustal contamination. U-Pb zircon dating of studied dikes indicates intrusion ages in the 42-34 Ma time interval. These data provide evidence for a pre-Oligocene magmatic activity that was not solely limited to the Adamello batholith. Moreover, dikes roughly rejuvenate from S to N, in an opposite direction with respect to the Alpine subduction polarity. Thus, a more complex geodynamic scenario than the slab break-off model must be envisaged. The absence of arc-magmatism prior to the Middle Eocene can be explained by the low-angle subduction of the Tethyan slab that confined the mantle partial melting zone away from the orogenic wedge. The onset of the Apennines subduction at 55-50 Ma caused the Alpine slab to retreat. The partial melting zone progressively migrated beneath the orogenic wedge and finally reached the axial belt in the Late Eocene, when the Alpine collision was completed. Only at this stage slab break-off occurred and promoted the intrusion of the Periadriatic plutons.

Sources, migration mechanisms and geodynamic environment of K-LILE-Mg-rich melts: Evidence from the Finero Complex (Southern Alps)

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Keywords: Mantle Metasomatism, Southern Alps, Lamproitic Magmatism.

The Finero Complex is located in the northern sector of the Ivrea-Verbano Zone (IVZ, Southern Alps). It outcrops with an antiformal structure showing a mantle unit at the core and a layered mafic-ultramafic intrusion on the flanks, i.e. the Finero Mafic Complex. The youngest unit of the latter (i.e. the External Gabbro) emplaced at the bottom of the continental basement at 232±3 Ma (Zanetti et al., 2013).

The Finero Complex records the unique worldwide example of subcontinental lithospheric mantle column in off-craton setting extensively metasomatised with segregation of phlogopite-bearing mineral assemblages.

Presently, there is a large consensus in considering that the mantle unit experienced a multi-stage melt migration in a supra-subduction environment (Zanetti et al., 1999).

However, the sequence of metasomatic stages and the mechanisms of melt migration are poorly constrained. Besides, the nature of the crustal component(s) (oceanic vs. continental crust) occurring in the ascending melts is still controversial, rendering doubtful the geodynamic reconstruction.

This contribution is aimed at providing new data about field relationships, petrographic features, major and trace elements mineral chemistry of the main lithologies of the mantle unit (e.g. phlogopite-amphibole-bearing harzburgites, dunites with chromitite and pyroxenite bands, phlogopite-bearing websterite, orthopyroxenites), as well as about the O isotope mineral composition and in-situ U-Pb and Lu-Hf isotope data for zircons from chromitite layers.

Our investigation points out that the mantle unit experienced a virtually complete metasomatic recrystallization as a results of a discrete number of episodes of pervasive-to-channelled porous flow migration of hydrous melts, alternated with stages of melt migration in open fractures. The latter mechanism formed pyroxenites usually containing Opx, Cpx, Amph and Phl. Both peridotites and pyroxenites display a similar geochemical signature, characterized by low contents in Al, Ti, Nb, Ta, HREE and Y, associated to large content in Mg, K, Th, U, Sr, Pb, Ba and LREE. The finding of $\delta^{18}O_{Opx}$ vs. SMOW‰ up to +8 and of negative εHf in chromitite zircons suggest that large volumes of crustal component were present in the migrating melts. New U-Pb zircon data for the chromitite layers provide Lower Jurassic ages.

The sources of the migrating liquids, the age and the geodynamic environment of the mantle metasomatism, as well as the age of the crustal accretion of the mantle unit will be addressed. In particular, it will be stressed out the possibility that the K-LILE-Mg-enriched melt migration took place in a late-orogenic environment, similarly to the high-MgO ultrapotassic, lamproitic magmatism widespread in different Mediterranean areas from Oligocene to Pleistocene in association with shoshonitic and calk-alkaline rocks.

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Structural level of Tertiary magma emplacement as a tool to unravel the late orogenic tectonics of the Western Alps

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Keywords: Biella and Traversella plutons, Alpine geodynamics, late orogenic magmatism.

The Biella and Traversella plutons (Zanoni et al., 2008; Zanoni, 2010 and refs. therein) are Periadriatic intrusives of the Alps, emplaced in the internal part of the HP continental Sesia Lanzo Zone. During the Alpine subduction and exhumation the Sesia Lanzo Zone records a polyphasic tectonometamorphic evolution. Pluton cooling involved contact metamorphism overprinting eclogitic to greenschist facies assemblages in country rocks. On the basis of the amount and type of contact metamorphic assemblages the aureole extent was mapped and the variation of thermal peak validated by numerical modeling. Relationships of structural record in country and plutonic rocks suggest that generally the intrusion of both plutons postdates the ductile deformations of the country rocks and that the brittle deformation mainly postdates magma emplacement. These structural and metamorphic relationships between plutonic and country rocks are consistent with magma intrusion taking place at shallow crustal levels, as corroborated by thermobarometrical estimates (Zanoni et al., 2010). This emplacement history indicates that the intrusion of Biella and Traversella bodies occurred when the Sesia Lanzo Zone had almost completed its exhumation within the subduction channel under a low thermal state (e.g. Roda et al., 2012 and refs therein). Numerical modeling suggests that Biella and Traversella stocks intruded a crust characterized by a thermal gradient consistent with that induced by a slab breakoff, as already proposed for the Periadriatic magmatism (Von Blankenburg & Davies, 1995). Tertiary plutons of Western Alps emplaced at shallower crustal levels than in Central Alps (Rosenberg, 2004 and refs. therein) suggesting a slower exhumation of the western portion of Alpine axial zone over the last 30 Ma.

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SESSIONE S21

The role of metamorphic petrology in understanding Earth evolution, mass transfer and orogenic processes. A tribute to Bruno Lombardo

CONVENORS

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Isomekes: A chemically-independent method for geobarometry of UHPM rocks

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Keywords: Inclusion, inclusion-host system, isomeke, elasticity, ultra high-pressure metamorphic rocks, quartz.

Conventional thermo-barometric methods are challenged in ultra high-pressure metamorphic (UHPM) terraines as the temperatures of deep subduction often exceed the closure temperature of geothermobarometers and minerals may undergo discontinuous reactions or re-equilibration during both prograde and retrograde paths. Furthermore, some minerals are not suitable for conventional thermobarometry. We therefore need an independent method to determine P and T that does not rely on chemical equilibrium. The elastic behavior of mineral inclusions trapped in host minerals contained in UHPM rocks provides such an alternative.

Minerals trapped as inclusions within other host minerals develop residual stresses on exhumation as a result of the differences between the thermo-elastic properties of the host and inclusion phases. For example, a quartz trapped in a garnet at 1.7 GPa and 600 °C will exhibit a residual pressure of 1.06 GPa at room conditions. The key to interpreting this residual pressure is that when the inclusion was trapped, the host and inclusion had the same P and T, and the inclusion fitted perfectly within the cavity in the host. Measurement of the residual stress in the inclusions can therefore, in combination with the equations of state (EoS) of the two phases, be used to infer the P and T of entrapment. First we calculate the pressure P_{foot} at room-T at which they would have the same pressure, temperature, and volume. Possible entrapment conditions lie on a line in P-T space passing through P_{foot}, along which the fractional volume changes of the host and inclusion are the same. Such a path is known as an 'isomeke' (Adams et al., 1975), a curved line in P-T space that can be calculated directly from the EoS of the host and the inclusion. The intersection of isomekes for two host-inclusion pairs trapped at the same time, or with an independent P or T estimate is sufficient to uniquely define a point in the P-T history of the assemblage.

This approach can also be used to calculate the stress on mineral inclusions during the prograde history of the rock. For the Kulet whiteschist (Parkinson, 2000), calculations performed with EoSFit7c (Angel et al., 2014) show that at peak metamorphic conditions (about 780 °C and 35 kbar) an isolated quartz inclusion deep in the garnet cores would experience a pressure of about 1.7 GPa and would thus remain well within the stability field of quartz.

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Tectonostratigraphy and metamorphic evolution of the northern Monviso Meta-ophiolite Complex (inner Western Alps)

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Keywords: HP meta-ophiolite, Western Alps, Monviso.

The Monviso Meta-Ophiolite Complex is a remnant of the Piedmont-Ligurian oceanic lithosphere that was subducted below the Adria plate and, during continental collision, tectonically juxtaposed on the paleo-European continental margin units. The northern sector of the Monviso Meta-Ophiolite corresponds to a stack of six tectonic units consisting of serpentinite, metagabbros, metabasalt and metesediments, that were affected by three main tectonometamorphic stages. The first subduction-related stage (D1) was characterized by the development of an early syn-eclogitic foliation (S1), overprinting primary surfaces (i.e. S0 sedimentary bedding and magmatic foliation). The occurrence of garnet-, omphacite-, talc- and lawsonite-assemblage in a Fe-Ti metagabbro particularly indicates P-T peak conditions of 2.5-2.7 GPa for 550-570 °C. The subsequent exhumation-related stage (D2), occurred under epidote-blueschist to greenschist-facies transition, extensively overprinted the D1 structures and mineral assemblages. The D2 was characterized by the development of a regional foliation (S2) that is parallel both to the contacts between the different tectonic units and to the axial plane of map-scale West-verging folds. The D1 and D2 were followed by a late-metamorphic stage (D3) which occurred at shallower crustal levels, developing westward extensional shear zones. Restoring deformation, the northern sector of the Monviso Meta-Ophiolite can be referred to an original ocean seafloor where an exhumed mantle was connected to a basalt-rich ridge segment through an articulated transition zone, formed during intra-oceanic faulting and characterized by different sedimentation processes. This portion of oceanic lithosphere was likely subducted as an almost coherent slice and dismembered into different tectonic units during collision- and exhumation-related deformation.

Petrological constraints on the geological history of the Gran Paradiso Massif

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Keywords: petrology, Gran Paradiso, Western Alps.

The Gran Paradiso Massif consists of two main superimposed units, namely the Gran Paradiso Unit and the Money Unit (Compagnoni, Elter and Lombardo, 1974).

Pre-Alpine history - In the Gran Paradiso Unit, a regional metamorphism of amphibolite-facies grade (~650°C – 6 kbar) is recognized in low-strain volumes. Its age is still unknown, possibly associated with the Variscan orogeny. Porphyritic granitoids intruded during the Middle Permian age producing contact metamorphism at ~700°C – 2.5 kbar (Gabudianu Radulescu et al., 2011) implying that the regional metamorphic rocks were already partly exhumed during the Middle Permian.

In the Money Unit, the sequence consists of (i) graphite-bearing, polygenic conglomerates, (ii) alkaline metarhyolites, (iii) paragneisses associated to amphibolites, and (iv) graphite-poor, monogenic, metaconglomerates (Manzotti et al., 2014a). In the meta-conglomerates, detrital garnet grains (with Alpine garnet overgrowths) are found (Manzotti and Ballèvre, 2013). A LaICP-MS study of the detrital zircons has allowed to assess the Late Carboniferous to Early Permian palaeo-topography in the (future) Alpine region. The volcano-sedimentary sequence is lately intruded by the Erfaulet metagranite.

Alpine history - In the Gran Paradiso Unit, an early eclogite-facies event is recognized (Compagnoni and Lombardo, 1974; Dal Piaz and Lombardo, 1986) in the polycyclic rocks, and the Permian metagranites. Estimated P-T conditions for the eclogite-facies event vary substantially from one author to the other. In the Money Unit, peak P conditions of the early stage (garnet-chloritoid assemblages in the pelitic matrix of the meta-conglomerates) are lower than those recorded in the Gran Paradiso Unit. These data allow to refine a geometrical and kinematical model for the Western Alps.

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The role of melt inclusions in understanding crustal melting

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Keywords: crustal melting, nanogranite, peritectic minerals.

The recent recognition of melt inclusions (MI) in peritectic minerals of high-grade, partially melted metasedimentary rocks has opened up new possibilities to constrain petrological and tectonic processes during crustal melting. In slowly-cooled regional rocks MI are crystallized to a cryptocrystalline assemblage of quartz, feldspars and one or two micas named “nanogranite”. More rarely, in some exceptional geological contexts such as anatectic enclaves hosted in lavas, melt can be quenched to glass during eruption of the host volcanic rocks. Unlike inclusions in igneous rocks, formed by magma cooling and crystallization, MI in migmatites and granulites are trapped during incongruent melting, along the up-temperature path of anatexis. Because of such peculiar origin, they can provide key microstructural and chemical information.

Microstructurally, when they appear trapped within potential peritectic minerals (garnet, cordierite, spinel, ilmenite) and display textural features pointing to a primary origin, MI demonstrate the growth of their host in the presence of melt. Therefore MI represent one of the most reliable microstructural criteria for the former presence of melt in a rock, particularly in cases where deformation and/or recrystallisation have erased previously present igneous microstructures. Not only MI indicate that a rock was partially melted, but also they add constraints to the mineral(s) which coexisted with the melt. An unexpected outcome is that garnet can trap the earliest formed, low-T melts, with muscovite still stable or soon after its disappearance.

Chemically, as the composition of anatectic MI is representative of that of the bulk melt in the system during anatexis, these tiny objects (rarely exceeding 15 mm) represent embryos of anatectic granites. With an appropriate characterization and analytical strategy they can provide the missing information on the primary composition of natural crustal melts before they undergo modification processes such as cumulus, fractional crystallization, mixing or entrainment of exotic material. Information on primary compositions includes the concentrations of volatile components, and hence the nature of the fluid regime during anatexis. While glassy inclusions can be analyzed directly, nanogranites need to be rehomogenized and then quenched. Remelting is done in a piston cylinder, to prevent the decrepitation of inclusions and loss of volatiles. Inclusions can then be analyzed for major and trace elements, and also for H_2O: most melts are leucogranitic and peraluminous, but show important variations in normative Qtz-Ab-Or proportions (with some tonalitic compositions), as well as in H_2O contents.

This presentation will summarize some key results from MI occurrences at El Hoyazo and Ronda (Spain), the KKB of India, the Ivrea Zone (Italy) and Kali Gandaki (Nepal).

Petrographic study of xenoliths from deep crustal levels of northern Karakorum (Shaksgam Valley, Xinjiang, China)

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Keywords: Tibetan Plateau, minette, HP dehydration melting.

Xenoliths hosted in post-collisional volcanic and subvolcanic rocks, that sample the lower crust and the upper mantle on their way up to the surface, give direct information on the structure and on the mineral and fluid composition of the deep core of the orogens.

The Tibetan Plateau, the highest and largest topographic feature on Earth, represents the archetypal product of continent-continent collision. It consists of several terranes progressively accreted onto the stable North Asian Siberian–Mongolian craton since the Early Mesozoic. The limited occurrence of exhumed deep crustal rocks hampers the direct characterisation of the deeper crust and upper mantle beneath the orogen. However, post-collisional volcanic rocks are widespread in the whole Tibetan Plateau, and ultrapotassic dykes hosting lower crustal xenoliths have been reported from many terranes (e.g. Hacker et al., 2000). Post-collisional potassic and ultrapotassic dykes have been also found in the Karakoram terrane (Pognante, 1990) but so far, no crustal xenoliths have been reported.

We present preliminary petrographic data on crustal xenoliths hosted by lamprophyric dykes from the Shaksgam valley, northern Karakorum (Xinjiang, China), in order to provide a first characterisation on the deep crust beneath the western segment of the Himalayan-Tibetan collisional belt.

The lamprophyric dykes are mostly porphyritic minettes, consisting of abundant phlogopite fenocrysts set in a fine-grained groundmass consisting of Kfs + Phl ± augitic or aegirinic Cpx ± Amp ± Pl. The lamprophyric dykes host various types of xenoliths sourced at different depths, from deep to intermediate to lower crustal levels, and variably affected by contact metamorphism induced by the dyke intrusion.

In this study, only xenoliths from the deep crustal level are considered. Apatite-bearing clinopyroxenite is mostly composed of clinopyroxene (> 90 vol%), apatite and minor phlogopite. Basic granulite consists of clinopyroxene, garnet, plagioclase and magnetite. Acid granulite contains Qtz and Pl, and is characterised by abundant Kfs (up to 40 vol%) and zoned garnet (up to 30 vol%), by the almost complete lack of hydrous minerals (biotite < 2 vol%), and by the local occurrence of relict kyanite. Rutile and graphite included in Grt are common accessory minerals. Microstructures and mineral-fluid assemblages suggest that these acid granulites may represent the restitic product of a former pelitic protolith that experienced HP dehydration melting. Remnants of the fluid phases present in the system at deep crustal levels are represented by primary inclusions in Grt.

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Tectonic and metamorphic evolution of the Greater Himalayan Sequence in Central Himalaya: the role of the High Himalayan Discontinuity

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Keywords: Himalayas, metamoprhism, tectonics, exhumation, collision tectonics, P-T-t paths.

The Greater Himalayan Sequence (GHS) is the main metamorphic unit of the Himalayas, running for over 2400 km, bounded to the South by the Main Central Thrust (MCT) and to the North by the South Tibetan Detachment (STD) whose contemporanous activity controlled its exhumation between 23 and 17 Ma (Godin et al., 2006). Several shear zones and/or faults have been recognized within the GHS, usually regarded as out of sequence thrusts. Recent investigations in the GHS in Central Himalaya allowed the Authors to identify a tectonic and metamorphic discontinuity, above the MCT, with a top-to-the SW sense of shear (Higher Himalayan Discontinuity: HHD) (Carosi et al., 2010; Montomoli et al., 2013;). U-(Th)-Pb *in situ* monazite ages provide temporal constraint of initiation of the HHD at 27-25 Ma, older than the Main Central Thrust, and continuing up to 17 Ma. Data on the P and T evolution testify that this shear zones affected the tectono-metamorphic evolution of the belt and different P and T conditions have been recorded in the hanging-wall and footwall of the HHD. The correlation of the HHD with several other discontinuities recognized in the GHS led to propose that it is a tectonic feature running for several hundreds kilometers, documented at the regional scale and dividing the GHS in two different portions. In Western and Central Nepal the occurrence of even more structurally higher contractional shear zone in the GHS (above the HHD): the Tyar shear zone in the Mugu –Karnali valley and the Kalopani shear zone in the Kali Gandaki valley, points out to an even more complex deformation pattern within the metamorphic core. The actual proposed models of exhumation of the GHS, based exclusively on the MCT and STD activities, are not able to explain the occurrence of the HHD and other in-sequence shear zones. Any model of the tectonic and metamorphic evolution of the GHS should account for the occurrence of the tectonic and metamorphic discontinuities within the GHS and its consequences on the metamorphic paths and on the assembly of Himalayan belt.

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High-resolution structurally-controlled ELA-ICP-MS zircon and monazite dating

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Keywords: zircon dating, Variscan, Sardinia.

Zircon dating by ICP-MS methods is a robust approach to constrain the age of magmatic or high-grade (T > 0.5 Tm) metamorphic events. Actually, this requires averaging the concordant Th-U-Pb and Pb-Pb ages of a representative population of zircon grains extracted from a 2 – 5 kg sample. Zircon separation involves crushing, grinding and heavy-liquids/magnetic separation processes. Although suitable crystals – i.e. zircons with a clear magmatic habitus - may be selected during hand-picking, there is no way to control the structural site where a given crystal came from. This limitation generally has no consequenceforpoorly evolvedmagmatic mafic to intermediate rocks. The liquidus-solidus temperatures of mafic melts are in fact above the temperature for U and Pb diffusion in zircon and monazite. Therefore, most crystals formed or were likely re-equilibrated during the crystallization of melt, yielding to simple Gaussian or log-normal age distributions. Felsic rocks such as S- and I-type granites, granulites and migmatites, instead, often record complex P-T-t paths involving multiple partial melting or HT events. This results in a large age distribution characterized by several clustersthat may be difficult to link to specific tectonic events. A way around this analytical limit would be dating zircon grains in thin section; however, most rocks contain less than 2 – 5 suitable zircon grains per thin section, making this method incredibly time-consuming and unworkable.

In this report, it is presented an optimization scheme that allow for efficient structurally-controlled zircon and monazite dating ofrocks using conventional ELA-ICP-MS apparatus. The procedure is based on micro-drilling of crystals from polished 120 mm-thick thin sections. For the purposes of demonstration, several zircon and monazite grains were selected by SEM-EDX and C-L analysis from three different microstructural sites of a Variscan migmatitic orthogneiss (northern Sardinia). The first population of zirconsdrilled from the unmelted domain of the orthogneiss retain only lower Ordovician ages (480.7 ± 2.9 Ma) that can be readily interpreted as the protolith age (Oggiano et al., 2010). The second population drilled from thin (0.1 – 1.5 cm) pseudotachylites that cut across the Late Devonian– Early Carboniferous orthogneiss fabric (Ferrara et al., 1978; Giacomini et al., 2005) gave an upper Mississippian age (324.5 ± 7.6 Ma).Monazite grains sampled from the younger leucosomes show slightly younger ages (313.3 ± 3.3 Ma), in perfect agreement with the field relationships.

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Bruno Lombardo (1944 – 2014)

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Bruno Lombardo, for 35 years Research Fellow at C.N.R., the Italian Research Council, has been an outstanding representative of a generation of earth scientists to whom we are indebted for a consistent synthesis of field observations coupled with a deep petrologic knowledge. Born in Cuneo, in the very core of his beloved Alps, he graduated at the University of Torino in 1970 with a thesis on the Gran Paradiso Massif under Ezio Callegari and Roberto Compagnoni. After a two-year fellowships at the Institute of Petrography of Torino, in 1972 he moved to the C.N.R. “Centro di Studio sui Problemi dell'Orogeno delle Alpi Occidentali” (later part of the C.N.R. “Istituto di Geoscienze e Georisorse”), a position which he held until he retired in 2007. As petrologist and Alpine field geologist who devoted his research to orogenic belts, Bruno Lombardo leaves a significant body of work on the Alps, the Himalaya and Antarctica. Pursuing his first studies on the Gran Paradiso, the crystalline rocks of Western Alps have been an ever-present subject within his whole scientific carreer, with fundamental studies on the origin and metamorphic evolution of Gran Paradiso – Monte Rosa – Dora-Maira Massifs, the Argentera Massif, the Sesia Zone, and the Piedmont ophiolite basin. A major turning point of his research interests can be traced back to 1975 when Bruno joined the Italian C.A.I.-C.N.R. Lhotse Expedition to study the Higher Himalaya and the Tibetan Series of Eastern Nepal. The outstanding mountain scenery and the geology of the Everest-Makalu region lured him to come back to Himalaya some sixteen times between 1975 and 2006, to investigate the geology and metamorphic evolution of High Himalayan Cristallines in the same Everest-Makalu region and Southern Tibet (Everest region and Kharta Valley) and, to the East, in Sikkim and Bhutan Himalaya. During his expeditions, he also studied the basement nappes of NW Himalaya (Zanskar and Nanga Parbat-Haramosh Massif) and Karakorum (Chogo Lungma Glacier, Deosai Plateau and Hunza Valley). In 1985, the invitation to join the first Italian Antarctic Expedition to Northern Victoria Land was another capstone of his scientific activity. He also participated to the 2nd and 4th expeditions and, thanks to his great skills and experience, gave significant contributions in modelling the metamorphic evolution of Wilson Terrane and its relationships with the East Antarctic craton. During this pioneering time of the Italian research activity in Antarctica, he was also appointed project leader of the basement rocks Petrology, Geochemistry and Geochronology division, the P.N.R.A. - National Antarctic Research Program, and member of the C.N.R. Polar Board. Through all his research work, Bruno Lombardo has been able to develop a vast network of scientific collaborations and relationships. All colleagues and friends will miss such a good, intelligent, tenacious, learned, calm and curious research companion.

Partial to complete deprotonation of staurolite during crustal anatexis: nanoSIMS analysis and experimental constraints

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Keywords: Anatexis, Hydrogen, Staurolite.

Staurolite is a common mineral in amphibolite-facies metapelites, but owing to the multiple substitutions allowed by its complex crystal chemistry, it may be stable also in mafic systems at high pressure, or in partially melted Al-rich compositions. In the latter, experiments have so far demonstrated the supersolidus stability of staurolite in the range 700-825°C and 6-12 kbar. Throughout its wide P-T stability field, staurolite also displays huge variations of the H content (from 2.7 to 6.0 atoms per 48 oxygens) that appear to be positively correlated with P and negatively with T. However, direct analysis of H has been performed only in a limited number of studies, and never in staurolite stable at supersolidus conditions.

We report the preliminary results of NanoSIMS analysis of H in staurolite coexisting with melt from two experimental run series. The first sample results from the melting of fine-grained powder of a graphitic metapelite at 893°C and 8 kbar. The staurolite from the starting material has an X_{Fe} of 0.83, and an average H_2O content of 2.2 wt.% (inferred from EMP total closure), that would correspond to 4 atoms H per 48 oxygens. During the experiment the assemblage melt-Qtz-Grt-Sil-Ilm-Crn-Her-St is produced, and St is partially to completely rimmed by hercynitic spinel. The staurolite is much more magnesian (X_{Fe} 0.67-0.72) and contains only 1300 ppm (0.13 wt.%) H_2O, with a 1s error of 0.06 wt.%. These values correspond to 0.24 atoms H per 48 oxygens. Along with the dramatic deprotonation demonstrated by NanoSIMS, the experimental staurolite shows higher total contents of Al and (Fe+Mg), in agreement with previously proposed exchange vectors for deprotonation.

The second sample consists of fragments of garnet with *nanogranite* inclusions from the migmatites around the Ronda Peridotite (Spain), which were brought to 850°C and 15 kbar in order to remelt the polycrystalline inclusions in garnet. In the remelted inclusions, the formation of thin (Fe of 0.57, and H_2O contents of 1.3 wt.%, that correspond to 2.35 atoms H per 48 oxygens. Also this staurolite is richer in Al (>18.5 atoms) with respect to common compositions.

These results suggest that, similarly to other hydroxylated minerals like biotite, also staurolite undergoes a progressive T-dependent deprotonation, and that this process may reach completion with the occurrence of H-free terms at (U)HT supersolidus conditions.

Microstructures in granulitized kyanite-eclogite from NE Sardinia, Italy: insights into the reconstruction of metamorphic evolution

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Keywords: kyanite-eclogite, P-T path, Variscan orogeny.

The studied kyanite-eclogites are massive to poorly foliated rocks cropping out a few kilometers north of Olbia, NE Sardinia. They consist of garnet, kyanite, clino/orthopyroxene + plagioclase sympectites and amphibole. Other minerals identified are sapphirine, spinel, corundum, epidote, biotite, ilmenite, titanite and chlorite. Garnet occurs as millimeter-sized zoned porphyroblasts (core: Grs_{27-26}, Pyr_{23}; rim: Grs_{18}, Pyr_{37}). The garnet crystals preserve armoured relics of kyanite and omphacite as well as several inclusions of quartz, epidote, amphibole, apatite, and rutile. Kyanite is also found in rounded to elongated crystals in the matrix. The kyanite-eclogites are characterized by the occurrence of amazing microstructures rarely observed in other eclogitic samples from Variscan Sardinia (Cruciani et al., 2012). These striking microstructures include: (i) spinel, sapphirine and corundum coronitic assemblages around kyanite, and (ii) double layered-coronas of amphibole and plagioclase around garnet. In the first ones a variable degree of kyanite replacement can be observed in different microdomains. When kyanite is still preserved, the corona around kyanite consists of a thin layer of spinel+plagioclase (Ab_{5-10}) symplectite, in turn surrounded by sapphirine + plagioclase ($Ab_{\sim20}$) symplectite. When kyanite is no more present, in the nucleus of the corona an intergrowth of acicular corundum crystals and Ca-rich plagioclase ($Ab_{\sim13}$) is observed. All these microstructures are surrounded by a continuous thin layer of Na-rich plagioclase ($Ab_{\sim60}$). The double layer-coronitic microstructures around garnet consist of an inner corona of Ca-rich plagioclase (bytownite) and Al-rich amphibole (Al-pargasite, tschermakite or Mg-hornblende, X_{Mg}: 0.7-0.8) adjacent to the garnet, in turn surrounded by an outer corona made up of Ca-Na plagioclase (andesine) and amphibole of the same composition. Preliminary P-T conditions estimated by thermodynamic modelling (method of Cruciani et al., 2008) indicate that garnet core and omphacite formed at P-T conditions of 1.8-2.0 GPa and ~ 650°C. The occurrence of orthopyroxene and sapphirine indicates a temperature of 700-800°C and $P < 1.5$ GPa for the symplectitic assemblages. The composition of coronitic amphibole and plagioclase points to P-T conditions of 0.9-1.1 GPa and 630-730°C for the development of coronas in contact with garnet.

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Carbonatites, silicate melt and fluid produced during anatexis in the middle crust: a case study from Oberpfalz (Bohemian Massif)

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Keywords: Nanogranites, Carbonatite, Anatexis.

In the last decades our understanding of partial melting processes in the lower crust profited from the investigation of fluid inclusions (Touret et al., 2009) and more recently of anatectic melt inclusions (Cesare et al., 2011) within enclaves and high-grade terranes. The latter finding allowed us to directly analyse the original anatectic melt (Ferrero et al., 2012; Bartoli et al., 2013) preserved within peritectic phases, before fractionation, mixing and contamination processes took place. Furthermore, the occurrence of primary fluid inclusions (FI) and anatectic melt inclusions (MI) within enclaves allowed the characterization of the COH fluid present during anatexis under fluid+melt immiscibility conditions (Ferrero et al., 2014).

Primary crystallized MI, or “nanogranites”, and FI have been identified to occur as clusters in garnet from stromatic migmatites (Zeilengneise) from Oberpfalz, Eastern Bavaria (Moldanubian Zone). During the late Carboniferous, these Grt+Bt+Sill+Crd+Spl metapelitic gneisses underwent HT/MP metamorphism, followed by a HT/LP event (Tanner & Behrmann, 1995). Nanogranites, ≤20 µm in size, consist of Qtz+Bt+Wm+Ab±Ap, and show abundant nanoporosity, localized in the quartz. Fluid inclusions are smaller, generally ≤10 µm, and contain CO_2+N_2+CH_4 plus siderite, pyrophillite and cristobalite, mineral phases not observed in the surrounding rock or as mineral inclusion in garnet. Polycrystalline inclusions containing Cc+Wm+Chl±Qz, commonly ≤10 µm in diameter, occur in the same cluster with MI and FI. Microstructural features, negative-crystal shape and the well-developed crystalline faces of calcite within inclusions suggest that they may result from the crystallization of a carbonate-rich melt. The lack of arrays of carbonate-bearing MI, verified by cathodoluminiscence investigation, supports their primary nature, i.e. they formed during garnet growth. This would suggest the occurrence of a silicate melt and a carbonate-rich melt during anatexis at relatively shallow crustal levels, but this hypothesis needs to be further tested through re-homogenization experiments by piston cylinder means.

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REE distribution among zircon, amphibole and garnet in Variscan granulites from southern Calabria (Italy)

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Keywords: REE, amphibole, garnet, zircon.

Two samples of mafic and intermediate granulites with porphyroblastic garnet were investigated for REE distribution among the mineral phases. The granulites underwent Variscan metamorphism experiencing compressive events ~350 Ma ago and decompressional stages up to 280 Ma (Fornelli et al. 2012). The studied samples having comparable REE contents, differ for the presence (sample Tur76A) or absence (sample GRT3) of amphibole. In the amphibole-bearing sample garnet is REE-rich (∑REE= 206 ppm at core and 756 ppm at rim) but distinctly poorer than in the amphibole-free sample (∑HREE=2463 ppm at core and 14784 ppm at rim). Both garnets show a continuous symplectitic corona formed by plagioclase and biotite with or without amphibole. They have a rim rich in REE with engulfments characterized by REE distribution comparable with that of core. The abundance and distribution of REE in the coeval zircons dated around 300 Ma from the two samples, are different: (1) in the amphibole-free sample, ∑REE's range from 1180 to 439 ppm and define steep patterns with low LREE and high HREE contents; (2) in the amphibole-bearing sample, REE contents are lower ranging from 207 ppm to 361 ppm. Amphibole, present only in the sample Tur76A, shows different composition in the diverse sites: 1) in garnet, amphibole displays on average REE=464 ppm, Yb_N/Gd_N=0.26 and Eu/Eu*=0.56; 2) in matrix it contains slightly lower REE (420 ppm) but higher values of Yb_N/Gd_N (1.17) and lower Eu/Eu* (0.43); 3) two types are present in symplectite around garnet showing similar patterns at different level of abundance of MREE-HREE (REE= 493 ppm, Eu/Eu*=0.43, Yb_N/Gd_N=0.49 and REE= 680 ppm, Eu/Eu*=0.38 Yb_N/Gd_N=0.7).

Summing up it appears that: 1) amphibole under granulite facies conditions is rich in REE and, when present, it causes a decrease of REE in garnet and zircon; 2) the outer rim of garnet is affected, due to dissolution, by intracrystalline REE diffusion with increase of REE during the first stage of decompression (~300 Ma); 3) subsequently towards the end of decompression (280 Ma), dissolution was more effective and more rapid than diffusion and produced engulfments depleted in REE; 4) in the corona firstly formed amphibole poorer in REE and, finally, when dissolution of garnet was more rapid then REE diffusion, amphibole taken more REE; 5) amphibole tends to be richer than garnet for MREE's; 6) the elemental ratios between zircon dated 305-303 Ma in the inner rim of garnet and in corona probably indicate the initial stage of decompression; 7) the two kinds of amphiboles from corona having different distribution coefficient with garnet, seem to indicate that expecially MREE's tend to increase with increasing geothermal gradient during post-peak decompression.

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The stability of Cr-chlorite and other hydrates in subduction mélanges: and experimental study in the system Cr_2O_3-MgO-Al_2O_3-SiO_2-H_2O

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Keywords: Subduction mélanges, Earth Mantle, Cr-Chlorite.

The stability of chlorite in the model system MASH is critical in the modelling of the hydration/dehydration sequence in a variable range of lithologies at the slab–mantle interface, where mass transfer in mélange zones generates hybrid rocks. In hydrated ultramafic systems, chlorite (containing 13 wt% of H_2O) is a good candidate for transferring water beyond the stability field of antigorite, being stable up to 4–6 GPa, 700–800 °C. Although chromium is a minor constituent of the Earth mantle, it is incorporated in almost all major mantle phases, i.e., spinels, garnets, and pyroxenes, and it is expected to substantially modify phase equilibria in both mafic and ultramafic rocks. Chromium solubility in chlorite may further extend its stability and likely influence phase relations.

The solubility of chromium in chlorite as a function of pressure, temperature, and bulk composition was investigated in the system Cr_2O_3–MgO–Al_2O_3–SiO_2–H_2O, and its effect on phase relations evaluated. Three different compositions with X_{Cr} = Cr/(Cr + Al) = 0.075, 0.25, and 0.5 respectively, were investigated at 1.5–6.5 GPa, 650–900 °C. Cr-chlorite only occurs in the bulk composition with X_{Cr} = 0.075; otherwise, spinel and garnet are the major aluminous phases. In the experiments, Cr-chlorite coexists with enstatite up to 3.5 GPa, 800–850 °C,and with forsterite, pyrope, and spinel at higher pressure. At P=5 GPa other hydrates occur: a Cr-bearing phase-HAPY ($Mg_{2.2}Al_{1.5}Cr_{0.1}Si_{1.1}O_6(OH)_2$) is stable in assemblage with pyrope, forsterite, and spinel; Mg-sursassite coexists at 6.0 GPa, 650 °C with forsterite and spinel and a new Cr-bearing phase, named 11.5 Å phase (Mg:Al:Si = 6.3:1.2:2.4) after the first diffraction peak observed in high resolution X-ray diffraction pattern.

Cr affects the stability of chlorite by shifting its breakdown reactions toward higher temperature, but Cr solubility at high pressure is reduced compared with the solubility observed in low pressure occurrences in hydrothermal environments. Chromium partitions generally according to $X_{Cr}^{spinel} >> X_{Cr}^{opx} > X_{Cr}^{chlorite} \geq$XCrHAPY > XCrgarnet. At 5 GPa, 750 °C (bulk with XCr = 0.075) equilibrium values are XCrspinel = 0.27, XCrchlorite = 0.08, XCrgarnet = 0.05; at 5.4 GPa, 720°C $X_{Cr}^{spinel} = 0.33$, $X_{Cr}^{HAPY} = 0.06$, and $X_{Cr}^{garnet} = 0.04$; and at 3.5 GPa, 850 °C $X_{Cr}^{opx} = 0.12$ and $X_{Cr}^{chlorite} = 0.07$. Results on Cr–Al partitioning between spinel and garnet suggest that at low temperature the spinel- to garnet-peridotite transition has a negative slope of 0.5 GPa/100 °C. The formation of phase-HAPY, in assemblage with garnet and spinel, at pressures above chlorite breakdown, provides a viable mechanism to promote H_2O transport in metasomatized ultramafic mélanges of subduction channels.

The Carboniferous - Permian evolution of the Sardinia Variscan branch: tracing the geodynamic change trough U-Pb geochronology and geochemistry

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Keywords: Permian volcanism, Sardinia, U-Pb geochronology, calc-alkaline series.

A distinctive feature of the Late Variscan geodynamic reorganization in Southern Europe can be found in the progressive collapse of the southern Variscides and the occurrence of a widespread related magmatism (Cortesogno et al., 1998; Buzzi et al., 2008). Prevalent transpressive/transtensional tectonic movements drove the build up of continental deposits, infilling a great number of intramontane subsiding basins. In this scenario, the volcanism interbedded within the Late Carboniferous-Early Permian succession of Sardinia basins, is represented by K-normal and high-K calc-alkaline andesites and rhyolites followed by large volumes of rhyolites, and dacites.

Whole rock geochemistry and U-Pb geochronological analysis have been performed from samples collected in the NW Nurra basin and central - SE Perdasdefogu, Escalaplano, Seui-Seulo basins. Thus, trace elements and REE together with major elements have been analysed for 17 selected samples. Consequently, LA-ICP-MS U-Pb zircon dating was carried out. The most likely ages of crystallization have been obtained focusing measurements in outer zircon domains showing well preserved igneous textures. As a preliminary result, the calc-alkaline volcanism occurred at 299±1 Ma lasting up to 297±1 Ma in the Nurra basin.

Accordingly, the timing of the post Variscan volcanism, records the active tectonics between latest Carboniferous and Permian, constraining the collapse of the Southern Variscides and post-dating the unroofing and erosion of nappes in the External Zone of the belt. Thus, the lower crust results exposed at 297±1 Ma in Nurra. In the external zone, the intermediate andesite volcanic rocks emplaced at 294±2, in good agreement with the latest felsic volcanism, as old as 292±2 Ma. In this regards, the overlap between the calc-alkaline events and the volcanic/sub-volcanic alkalic one, is not exclusive to Sardinia and Corsica but to Pyrenees.The integration of detailed geochemical analyses (from recent literature) with new radiometric dating, constitutes a consistent dataset for different, though subsequent, volcanic events and provides a robust nail to unravel the plate reorganization between Laurussia and Gondwana during the late Palaeozoic evolution of the Variscan chain.

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Olivine fabric as tool to constrain paleopiezometry and crystallization temperature in orogenic peridotites: an example from the Friningen Garnet Peridotite (Central Scandinavian Caledonides)

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Keywords: Mantle wedge garnet peridotite, Olivine microstructures and fabrics, Scandinavian Caledonides.

The Friningen garnet peridotite (FGP; Seve Nappe Complex, Central Scandinavian Caledonides) is a mantle-wedge garnet peridotite (Van Roermund, 2009) incorporated into the continental crust in a plate interface environment during deep Scandian subduction (Van Roermund, 1989; Gilio and Van Roermund, 2013).

Here we combine 'classic' geothermobarometry and thermodynamic modelling to olivine fabric analysis in order to investigate paleopiezometry and crystallization temperature. These independent methods provide us with new tools to determine P-T histories of much more complex rocks and gain information on tectonic processes and provenance of peridotitic bodies from HP environments.

The FGP shows a complex history of multi-stage crystallization of ol+grt parageneses (Gilio and Van Roermund, 2013). Pre-Caledonian HP-HT metamorphic conditions of 1150±50°C and 2.6±1.0 GPa are determined for the early M1a assemblage (ol+opx+cpx+grt). These physical conditions are followed by an inferred early-Caledonian exhumation event down to 850-950°C and 1.5 GPa (M1b). During Scandian times, the FGP was incorporated into the down-going continental crust and dragged down to UHPM condition (M2; T=800°C and P=3.0 GPa; Janák et al., 2014). Afterwards, it followed the continental crust into eduction (M3; T=800°C and P=1.0 GPa; Janák et al., 2014) and subsequent nappe stacking.

Three olivine microstructures are developed in the FGP in response to three deformation events under different PT and stress conditions.

1) Coarse grained (10-15 mm) olivine M1 porphyroclasts formed around 1000-1100°C under a very low differential stress (1-2 MPa).

2) Medium size (200-1000 µm) M2 olivine 'foam' microstructure, pervasive throughout the entire body formed around 780-880°C under a differential stress of about 10-40 MPa.

3) A fine grained (20-100 µm) M3 olivine 'foam' microstructure, localised along metric-sized, localized shear zones within sub-crustal levels 650-700°C and under a high differential stress (70-100 MPa).

These olivine microstructures are a common feature of several dunitic/harzburgitic bodies in the Scandinavian Caledonides (Clos et al., 2014). Olivine fabric analysis is therefore a very powerful tool to gain insight on crystallization conditions and provenance of ultra-depleted orogenic peridotites, where 'classic' geothermobarometry is useless.

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Gilio M. & van Roermund H.L. 2013. The Friningen Garnet Peridotite (central Sweden): a good example of the characteristic PTt path of a cold mantle wedge garnet peridotite. In 10th International Eclogite Conference, 41.

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From mega- to microscopic and back: The P-T-t-D history of HP rocks from the Sesia Zone

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Keywords: Microstructural, geochronology, Sesia Zone.

Dating individual stages of the metamorphic evolution has become a key point to understand metamorphic terranes. The critical aspect remains how to link age data derived from in situ geochronology of accessory minerals (here allanite) with the mineral assemblages and the P-T conditions derived from these.

This field-based study investigates the Sesia Zone, a continental terrane derived from the NW-Adriatic margin and polydeformed at eclogite-facies conditions during Alpine convergence. The samples studied in detail belong to the central part of the Eclogitic Micaschist Complex. Assemblages comprise multiple generations of phengite, garnet, quartz, epidote, chlorite, allanite and rutile, locally with glaucophane and/or jadeite, or chloritoid.

X-ray maps of garnet show complex zoning, with a late Paleozoic porphyroclastic core surrounded by three Alpine overgrowth zones. Inclusions are abundant: Between the core and the first Alpine rim they are quartz only, but rutile crystals are frequent within the second Alpine rim, and glaucophane + phengite locally occur within rim2 or between rim2 and rim3.

These overgrowth zones can be linked to individual HP stages, if the bulk rock composition (based on XRF analyses) is corrected for the effects of the pre-Alpine cores. Rim1 and rim3 are found to have formed during very similar conditions (~600°C and 1.6.-1.8 GPa), but rim1 is prograde and rim3 is retrograde. Rim2 may reflect the pressure peak (~600°C and 1.8-2.0 GPa). The Si isopleths of phengites and the glaucophane composition are in line with these HP stages.

The allanite crystals show a core rich in LREE, up to three rim generations with lower LREE contents, and a final rim of clinozoisite. The allanite core includes rutile and HP phengite (Si~3.3 a.p.f.u.). This inclusion suggests a correlation between the 2 alpine rims of the garnet; however work is in progress (e.g. REE pattern in garnet and phengite).

Preliminary Th-Pb ages of allanite cores (in situ LA-ICP-MS analysis) span between 75-60 Ma. These ages compare well with the two HP stages (HP1: ~75 Ma; HP2: ~65 Ma) found in several samples of the Fondo slice of the Sesia Zone (Regis et al., 2014).

Ongoing work aims to integrate these data for individual samples at the regional scale, using the spatial and structural relations mapped in this project. The diversity of the results obtained clearly shows that the Sesia terrain comprises several slices and is not as uniform as previously thought.

Regis D., Rubatto D., Darling J., Cenki-Tok B., Zucali M. & Engi M. 2014. U-Th/Pb petrochronology: Deciphering the metamorphic dynamics in an eclogite facies terrane (Sesia Zone, Western Alps). Journal of Petrology (in press).

Structural, metamorphic and geochronological constraints of the Himalayan metamorphic core (HMC) in Western Nepal (Central Himalaya)

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Keywords: Himalaya, monazite textural geochronology, metamorphism.

The Himalayan belt is often regarded as the premier example of continent-continent collisional tectonics and is seen as a proxy for understanding the evolution of ancient orogenic belts (*e.g.* Jamieson & Beaumont 2013). Several important geodynamic processes, currently among the major topics of geosciences, like syn-compressional extension, feedback relations between climate and tectonics, rheological implications and exhumation consequences in response to crustal melting, have been developed starting from studies of the Himalayas (*e.g.* Jamieson & Beaumont 2013). In this contribution we describe the tectono-metamorphic evolution of the Himalayan metamorphic core (HMC) in the Mugu Karnali area in Western Nepal (Montomoli et al., 2013), where a complete and well-exposed cross section of the belt, starting from the Lesser Himalaya up to the Tethyan Sedimentary Sequence (TSS), has been studied. Moreover, in this area, a huge leucogranitic body, the Mugu granite, intrudes the migmatitic portion (in the core of HMC) and probably the base of the TSS.

Combining meso-microstructural observations, pseudosection modeling (as well as MET approach), trace element thermometry (*e.g.* Zr-in-rutile thermometry, Tomkins et al., 2007) and textural geochronology, we present pressure-temperature-deformation-time (P-T-D-t) paths for representative samples along the whole section, ranging from structurally lower chlorite-garnet-bearing rocks (>500°C, 0.8 GPa) up to kyanite-sillimanite-bearing migmatites (>720°C, 1.1-0.7 GPa) and cordierite-bearing gneiss (c. 650-700°C, 0.6 GPa).

Pseudosection modeling coupled with textural and chemical characterization of monazite grains provides a framework for the rigorously interpretion of the timing of monazite growth along the P-T-D path (*e.g.* Foster & Parrish, 2003, Spear & Pyle 2010). In this way, time costrained P-T-D paths from different structural positions within the HMC could be compared with particle paths obtained from numerical modeling in order to quantify geodynamic processes at the collisional front of large-hot orogenic belts.

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Jamieson R.A. & Beaumont C. 2013. On the origin of orogens. Geological Society of America Bulletin, 125, 1671-1702.

Montomoli C., Iaccarino S., Carosi R., Langone A. & Visonà D. 2013. Tectonometamorphic discontinuities within the Greater Himalayan Sequence in Western Nepal (Central Himalaya): Insights on the exhumation of crystalline rocks. Tectonophysiscs, 608, 1349–1370.

Spear F.S. & Pyle J.M., 2010. Theoretical modeling of monazite growth in a low-Ca metapelite. Chemical Geology, 273, 111–119.

Tomkins H.S., Powell R. & Ellis D.J. 2007. The pressure dependence of the zirconium-in-rutile thermometer. Journal of Metamorphic Geology, 25, 703-713.

Metamorphic evolution of the Cerro del Almirez ultramafic rocks (Betic Cordillera, South Spain) as a proxy to dehydration processes taking place during subduction

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Keywords: Serpentinites, subduction, metamorphism, dehydration, fluids release.

Serpentinites are the main carriers of water in subduction zones. The dehydration reaction of antigorite (releasing up to ~ 9 wt % H_2O) affects the composition and rheology of the plates, induces intermediate-depth earthquakes in the slab and plays a fundamental role in the production of arc lavas and in the transference of elements between different domains. The Cerro del Almirez ultramafic massif is the only known locality where the arrested dehydration front due to antigorite breakdown at high pressure conditions has been preserved (Padrón-Navarta et al., 2010). Since the work by Trommsdorff et al. (1998) these outcrops have revealed as a unique setting to investigate the prograde metamorphic evolution from antigorite serpentinite to chlorite harzburgite and its various implications. Atg-serpentinite preserves both prograde mineral assemblages and subduction-related structures. Prior to breakdown, antigorite is Al-rich and exceptionally ordered from a microstructural point of view. Transitional lithologies occur as well preserved layers in between Atg-serpentinite and Chl-harburgite all along the devolatilization front. The gradual disappearance of antigorite leads to the final prograde assemblage in Chl-harzburgite with two contrasting textures: granofelsic (with coarse, round olivine) and spinifex-like (dentritic-like, cm-sized olivine and orthopyroxene) that occur as interspersed, m-sized boudins. We ascribe these textures to shifts of the growth rate ultimately controlled by variations of the excess fluid pressure and the hydrodynamics of fluid expulsion. Fluids chanelling is evidenced by the occurrence of grain-size reduction zones, a few mm to meters wide, with roughly planar conjugate structures. We interpret them as brittle structures generated by hydrofracturing by overpressure fluids in a compressional setting in an otherwise almost impermeable peridotite. This might be an essential mechanism in the first stages of fluid flow through the coldest parts of top-slab mantle in subduction zones. The main geochemical effects of dehydration are, on the one hand, the loss of LREE–MREE, water, and sulfur, which can contribute to ^{18}O, D, and ^{34}S enrichments and oxidation of the sub-arc mantle wedge. On the other hand, Chl-harzburgite is enriched in Ti and the most compatible HREEs (Tm, Yb and Lu) as well as in Th, U, Nb, Ta, Pb, Sr due to fluid circulation in an open system, and thus contributing to their recycling in deep regions of the mantle.

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Padrón-Navarta J.A., Tommasi A., Garrido C.J., López Sánchez-Vizcaíno V., Gómez-Pugnaire M.T., Jabaloy A., Vauchez A. 2010. Fluid transfer into the wedge controlled by high-pressure hydrofracturing in the cold top-slab mantle. Earth Planet. Sci. Lett., 297, 271-286.

Is the Ivrea-Verbano Zone subdivided in two sectors? New insights from the Kinzigite Formation exposed in the Val Cannobina (northern Italy)

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Keywords: Ivrea-Verbano Zone, Val Cannobina, P-T-t reconstructions.

The Ivrea-Verbano Zone (IVZ, Southern Alps), in northern Italy, is part of the pre-Alpine basement characterized by the exposure of a well-preserved lower crustal section. The middle-lower crustal rocks of the IVZ have commonly been subdivided in three major units, from bottom to top: i) different ultramafic mantle bodies; ii) the Mafic Complex (MC), which represents an intrusive complex (gabbros, norites and diorites); iii) the Kinzigite Formation (KF), consisting of amphibolite- to granulite-facies metapelites with subordinate metabasites, marbles and calc-silicate gneisses.

U-Pb zircon data on the MC indicate an emplacement at 295-280 Ma in the central sector of the IVZ (Peressini et al., 2007, and references therein) and at about 232 Ma in the north-eastern sector (External Gabbro, Finero Complex; Zanetti et al., 2013). The Permian intrusion was coeval with granite intrusions in the middle-upper crust and rhyolitic volcanism, while the Triassic intrusion was concurrent with the activity of (low-/high-temperature) shear zones.

In order to shed light on the observed diachronism of the MC and to provide useful insights on the tectonic evolution, new P-T-t data from the KF exposed in the Val Cannobina (Cursolo-Orasso area) were carried out. Here, the KF shows the narrowest thickness and is partially affected by mylonitic deformation. It mainly consists of micaschists and migmatitic paragneisses, dominant at the higher structural levels (SE), and amphibolites, prevailing at the contact with the MC (lower structural levels; NW; Boriani & Burlini, 1995). Septa, both mafic and metapelitic in composition, occur within the MC and show granulite-facies metamorphism. Metapelites are mainly composed of Pl, Qtz, Bt, Grt and Sil. With increasing the metamorphic grade (towards NW), the abundance of Bt decreases, that of Grt increases and fibrolitic Sil is progressively replaced by prismatic Sil. Preliminary P-T estimates on metapelites indicate P of about 0.4 GPa and T ranging from 620 to 700°C. The septa show T higher than 800°C. Preliminary U-Pb dates on monazite from the migmatitic paragneisses zone indicate that an HT metamorphic event occurred at about 277 Ma, coherently with other areas of the IVZ. A single age at 225±7 Ma obtained from a narrow rim suggests a later perturbation of the U-Pb system.

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Peressini G., Quick J.E., Sinigoi S., Hofmann A.W. & Fanning M. 2007. Duration of a large mafic intrusion and heat transfer in the lower crust: a SHRIMP U/Pb zircon study in the Ivrea-Verbano Zone. J. Petrol. 48, 1185-1218.

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Linking the formation of coronitic microstructures around monazite to the growth of garnet in the Pontremoli well metapelites (Northern Apennines, Italy)

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Keywords: REE-minerals, garnet zoning,thermodynamic modelling.

The linkage of textural and petrological information, and mineral dating is central to understand the evolution of orogenic belts. In this regard, the relation between zoned metamorphic minerals, that define *P*-*T* paths, and accessory minerals, that provide geochronological information, is a source of uncertainties, which in turn will affect the quality of the reconstruction of lithospheric processes. In this contribution, a complex polymetamorphic history of a rock is deciphered on the basis of replacement microstructures of monazite, chemical variations in garnet porphyroblasts, and a detailed study of the garnet inclusion mineralogy combined with investigations of element partitioning between garnet and accessory minerals such as REE-rich minerals.

Garnet-bearing metapelites of the Micaschist Complex drilled in the Pontremoli 1 well belong to the Variscan basement of the Northern Apennines (Italy). Samples of these rocks contain coronitic microstructures around monazite grains, consisting of an apatite ring, allanite shell and epidote rim. Garnet porphyroblasts, which show a typical prograde growth zoning, enclose xenotime, allanite and epidote in their inner core, outer core and rim, respectively. Discontinuous variation of Y may be attributed to garnet growth during xenotime breakdown. Moreover, the Ca and P chemical profiles in garnet indicate a simultaneous crystallization of the inner core of garnet and apatite. The garnet composition can thus record modifications in the accessory mineral assemblage. The microstructure and chemistry of the monazite grains suggest that the monazite was an early mineral and underwent partial to total decomposition at peak metamorphic conditions. The chemical age of 296 ± 6 Ma should be older than the garnet-forming metamorphic stage.

Thermodynamic modelling permitted also to obtain a counterclockwise *P*-*T* path for the studied sample: the prograde evolution developed to a metamorphic peak close to 600°C and 7 kbar, and was followed by the peak pressure stage at 520°C and 8 kbar during which Mg-rich muscovite and chlorite with decussate structure crystallize. The replacement of early monazite by apatite, allanite and epidote, inferred through a correlation with the garnet isopleth *P*-*T* constraints, occurred during the prograde evolution at 500-600°C and 5-7 kbar. A nearly isobaric cooling is responsible for the late observed stage at 500°C and 2 kbar.

The obtained *P*-*T* path is different from the previously proposed trajectories for the Variscan basement of the Northern Apennines. The tectonic implications of this polymetamorphic evolution will be discussed.

Geobarometry for host-inclusion systems: the role of elastic relaxation

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Keywords: Inclusion, Relaxation, Equations of State.

Conventional thermo-barometric methods can be challenged in UHPM terraines as the temperatures of deep subduction often exceed the closure temperature of geothermobarometers, and they are also afflicted by the effects of further reactions and re-equilibration on exhumation. The elastic behavior of mineral inclusions trapped in host mineral phases contained in UHPM rocks provides an alternative method that is independent of chemistry and chemical equilibria. Minerals trapped as inclusions within other host minerals will develop residual stresses on exhumation as a result of the differences between the thermo-elastic properties of the host and inclusion phases. Measurement of the residual stress in the inclusions in combination with the equations of state (EoS) of the two phases, can be used to infer the pressures of entrapment. However, until now, even the simplest elastic system of a single inclusion embedded in an isotropic host has not been properly addressed for geological systems. Previous analyses (i.e. Zhang, 1998) have relied on the assumption of linear elasticity and invariant elastic properties of the minerals with P and T, or assume that the host material is completely rigid. These assumptions are not physically correct.

We will present a solution to the single-inclusion problem that incorporates non-linear elasticity and can be applied to determine the stress distribution in the host and inclusion that arises from any change in P and T. Our solution shows that the previous calculations of residual inclusion pressures are incorrect in the relaxation term. The relaxation arises from the difference in stress at the host/inclusion interface that will force the interface outwards thus increasing the radial stress in the host adjacent to the inclusion, and decreasing the P inside the inclusion. The errors from linear elasticity theory are greater with softer hosts, and when the final conditions are not at ambient P and T.

The general form of our solution relies on the concept of the isomeke, a line in P-T space along which the fractional volume changes of the host and inclusion are the same. This allows our solution to be used in combination with any form of equation of state and/or thermal expansion, and is not restricted to linear elasticity or just invertible EoS. Calculations can be performed with Eosfit7c (Angel et al. 2014).

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Exhumation of the crystalline core of the Himalaya: relations between the South Tibetan Detachment and leucogranite emplacement in Western Nepal

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Keywords: Himalaya, STDS, exhumation.

The architecture of the South Tibetan Detachment System, separating the lower medium to high-grade metamorphic rocks of the Greater Himalayan Sequence (GHS) from the overlying Tethyan Himalayan Sequence (THS) is complex. It is characterized by a lower ductile shear zone, affecting the upper part of the GHS (Carosi et al., 1998) and the amphibolites facies rocks at the bottom of the THS (lower THS) and by an upper brittle fault, above which the very-low-grade to non metamorphic rocks of the THS (upper THS) crop out. According to most workers the High Himalayan granites (HHG), located in the upper part of the GHS, intrude and are deformed by the lower ductile shear zone of the STDS.

We report new data from a geological transect located in Western Nepal where the STDS shows a peculiar structural setting.

In the study area the upper portion of the Greater Himalayan Sequence is made by gneiss, migmatites and calcsilicates.

The THS is characterized by a lower portion made by garnet and cordierite bearing gneisses. P-T pseudosection modelling, reveal as the observed assemblage is stable in the range of 0.53-0.65 GPa and 610-720°C.

The upper portion the THS is made by biotite-bearing quartzites, impure limestone, metarenites and subordinate metapelites with a metamorphic assemblage of calcite, quartz, muscovite, biotite ± chlorite and scapolite, indicating greenschist facies conditions. Detrital zircon ages indicate a depositional age from upper Jurassic to lower Cretaceous.

The boundary between the GHS and the THS is intruded by a large leucogranitic body showing a crystallization age at 23-24 Ma (Carosi et al. 2013), constraining the time of youngest shearing event between the two tectonic units.

Dykes from the upper portion of the granite intrude the low-grade metamorphic rocks of the THS causing contact metamorphism within few meters from the granite contact. The low grade foliation is overgrown by biotite and muscovite. The intrusion closest samples show static crystallization of amphibole, clinopiroxene and annealing of calcite-plagioclase-quartz (± kfeldspar) matrix. On the previous samples, in order to quantify the depth of pluton emplacement, a set of geothermobarometric methods have been applied. A broad consistency of all the methods points out a T of equilibration around 600-640°C and a P of nearly 0.5 GPa.

Structural relations and time of emplacement of the leucogranite cast doubts on the exhumation models widely adopted till now for the Himalayan belt.

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Petrological and structural studies in the eastern Nepal Himalaya: data for a geological map and constraints for tectonic models

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Keywords: Himalaya, metamorphism, geological map, tectonic models.

The Himalayan orogen comprises few lithotectonic units extending throughout the length of the chain and separated by major north-dipping tectonic contacts. From lower to upper structural levels (and from south to north) these are the sub-Himalaya, the metamorphic Lesser Himalayan Sequence (LHS) and Greater Himalaya sequence (GHS, subdivided into a lower GHS and upper GHS or Higher Himalayan Crystallines-HHC), and the Tibetan Sedimentary Series.

This contribution discusses petrological and structural data collected from metamorphic units outcropping along several geotraverses in the eastern Nepal Himalaya (e.g. Khimti Khola, Likhu Khola, Dudh Khosi, Arun and Tamur tectonic windows), with the aim of: i) interpreting the geological setting and presenting an original geological map of the eastern Nepal, ii) discussing the P-T metamorphic evolution of the different exposed units, and iii) compare their P-T evolutions with tectonic models proposed for the development of the Himalaya.

At a regional-scale, the investigated area shows a structural setting dominated by a dip to the north of major faults and composite foliations, and the units recorded polyphase ductile to brittle-ductile deformations. The metamorphic grade increases toward higher structural levels, passing from the low- to medium-grade LHS to the high-grade HHC across the lower GHS. The lower GHS is roughly coincident with the Main Central Thrust Zone (MCTZ), a several km-thick shear zone extending along strike all along the Himalayas and driving the southwards extrusion of the high grade rocks over the low grade rocks.

More in detail, along the investigated geotraverses, the metamorphic assemblages range from the low–grade chlorite and garnet zones (LHS), to the medium–grade garnet-biotite, staurolite and kyanite zones (lower part of the MCTZ), up to the sillimanite zone and a further zone of incipient partial melting with breakdown of muscovite and formation of K-feldspar (upper part of the MCTZ). Structurally above the MCTZ, anatexis is widespread in the HHC and is recorded by granulite-facies kyanite-bearing metapelite, in turn followed up section by cordierite-bearing, kyanite-free gneiss.

Structural observations integrated with petrography, mineral chemistry, and petrologic modeling revealed the juxtaposition of rock packages characterized by different P-T evolution and T/depth gradients across the MCTZ and its adjacent domains. A similar setting reveals an imbricate nature of the MCTZ itself, thus emphasizing the complexity of tectonic processes operating during the exhumation of the metamorphic units in the Himalaya.

Evidence of rodingitization process within Ophiolite Units (Liguride Units, Southern Apennines - Italy)

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Keywords: Rodingites, ophiolites, southern Apennines.

New petrological data of the ophiolitic sequences from the Liguride Units (Southern Apennine Chain) are here presented in order to investigate some rodingite dykes preserved within un-sheared low strain domains. Liguride Units shows indeed pervasive shear deformations, developed during subduction process reaching HP/LT conditions typical of blueschist facies (Cirrincione & Monaco, 1996). Nevertheless, local low strain domains are preserved and within these, rodingite dikes occur. The rodingite dikes is composed of garnet, prehnite, chlorite, pumpellyite, and quartz. Hydrogrossularite, prehnite, epidote, calcite, and titanite replace plagioclase and produce Ca-rich basic rocks during hydrothermal alteration of sub-greenshist to greenschist facies metabasalts (Sansone et al., 2011).

The process usually is initialized during the early stage of ocean crust evolution and can continue at later stages of the oceanic crust history (Charlou et al., 1998). It is catalyzed by metasomatism, triggered by injection of Ca^{2+} ions from high alkaline content fluids, probably released during the ocean-floor metamorphism.

In order to extrapolate new quantitative petrological data from this process, after propaedeutic optical and electron-microprobe analytical sessions, a multivariate statistical data handling of X-ray maps, representative for some garnet-replacing plagioclase microdomains have been carried out by means of X-Ray Micro Analyzer software (Ortolano et al., in press). Obtained results were then used for the computation of useful phase diagrams, able to reconstruct the sequence of the metamorphic reactions evolved during the rodingitization process as a tracer of the original ocean floor metamorphic conditions of the Liguride ocean, today merged into the southern sector of the Apennine chain, evaluating at the same time the potential metamorphic effects operating during the following tectonic staking activity of the Frido Unit (Sansone et al., 2011).

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Sequential atoll-shaped garnets formation from the Aspromonte Peloritani unit (northeastern Sicily-Italy): Petrogenetic and Geothermobarometric implications

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Keywords: atoll garnets, image analysis, pseudosections.

Micaschist from Santa Lucia del Mela zone, (Peloritani Mountains), were studied by integrating information obtained from petrographic analysis, image assisted analysis on mineral phases compositions using X-Ray maps and thermodynamic modeling. These rocks are characterized by the presence of atoll garnets, and preserve a continuous array of textures from pristine garnets, to atoll textures, to completely substituted garnets. These textures are linked to the metamorphic evolution of the rocks, consisting of three main stages of metamorphic recrystallization and related deformation are recognized.

The sequence of mineral parageneses recognised to successive deformation events is as follow: D1 is characterised by the assemblage wm1 + chl1 + bt1 + pl1 + grt1 (Inner Core) + qtz + ilm + ap; D2 by grt2 (a and b Relic Outer Core and Relic Rim) + wm2 + chl2+ bt2 + pl2 + qtz + ilm + ap + hem; D3 (associated to garnet core transformation) by grt3 (New Rim) + bt3 + pl3 + wm3 + qtz + chl3 + ilm.

On the basis of textural observations and mineral parageneses, the atoll formation is related to the substitution of garnet cores during the D3 stage, with the consumption of garnet cores (grt1) and production of new garnet rim grt3 with wm, bi, qtz and pl. The recognition of the different stages of garnet growth and associated parageneses has been obtained using image analysis coupled with compositional maps, performed with a dedicated software (Ortolano et al., in press).

Following the textural and minerochemical analyses, PT conditions associated to the three recrystallization phases have been determined from pseudosections. In order to determine the equilibrium volumes during the different stages of the metamorphic evolution, bulk compositions were determined by XRF and by modal determinations assisted by image analysis. Results indicate that in the Mela rocks is recorded a prograde evolution to amphibolite facies conditions in garnet cores, followed by decompression associated to the heating to lower amphibolite facies, and finally by a temperature increase, probably associated to the intrusion of late Variscan granitoids that are widespread in this unit.

Ortolano G., Zappalà L., Mazzoleni P. (in press). X-Ray Map Analyzer: a new ArcGIS® based tool for the quantitative statistical data handling of X-ray maps (Geo- and Material-science applications).

Preliminary study on polymorphs of serpentine of the Koniambo Massif (New Caledonia)

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Keywords: New Caledonia, harzburgite, dunite, serpentine, Raman spectroscopy.

The Koniambo Massif is part of a mountain chain located along the west coast of Grande Terre island, the main island of New Caledonia archipelago. It is composed of three major lithological assemblages of mantle and crustal origin: a strongly serpentinized harzburgite-dunite sequence at the base, followed by a spinel dunite sequence and at the top a succession of layers of harzburgite and minor dunite, which changes to harzburgite on the summit. These associations overlap the Poya Unit, a portion of the upper part of the oceanic crust containing basalts, gabbros and dolerites. The basal unit harzburgite-dunite is totally serpentinised and strongly silicified. The overlying dunites show an homogeneous fine texture: olivine grains altered into serpentine (about 30%) are associated to smaller quantities (less than 1%) of orthopyroxene and spinel. The proportion of orthopyroxene increases from the bottom to the top of the sequence. The upper sequence is mainly composed by harzburgite with alternating layers of dunite, where clinopyroxene is an accessory phase. Rare layers of dunite form thin (< 1 m) and discontinuous horizons. All these sequences represent portions of obducted oceanic plate as a result of compressive tectonics (Ulrich *et al.*, 2010). There are many studies in the literature about the characterization of the minerals of the serpentine family, but a complete methodology, able to distinguish the different polymorphs of the group, is still lacking. This work introduces an innovative analytical strategy that allows to recognize these polymorphs, involving Raman spectroscopy. Samples, coming from the basal and middle sequences of the massif, were studied by means of optical microscopy, SEM-EDS and micro-Raman spectroscopy. Optical microscopy and SEM allow the observation of textural relationships and morphological features of the phases, Raman spectroscopy is essential in the identification of the polymorphs of serpentine group. Raman peaks observed in the high-wavenumber spectral range 3550-3850 cm^{-1} associated with OH stretching vibrations, allow the identification of chrysotile, lizardite, antigorite and polygonal serpentine varieties (Auzende *at al.*, 2004). However, whereas spot analyses alone are not fully adequate to investigate the relationship between the different varieties of serpentine in complex samples, two-dimensional Raman maps are very useful. The main advantage is to recognize the serpentine polymorphs directly on the sample, within their textural environment at the micrometer scale.

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Ulrich M., Picard C., Guillot S., Chauvel C., Cluzel D. & Meffre S. 2010. Multiple melting stages and refertilization as indicators for ridge to subduction formation: The New Caledonia ophiolite. Lithos, 115, 223-236.

Fluid rock interactions as recorded by Cl-rich amphiboles from continental and oceanic crust of Italian orogenic belts

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Keywords: Cl-Amphibole, fluids, metamorphism.

A series of Cl-rich amphiboles coming from oceanic and sub-continental gabbro bodies has been studied in order to compare their microstructural and compositional peculiarities and investigate the fluid-rock interactions in different geodynamic contexts. The first group of amphiboles is within gabbros from the Northern Apennines, and developed subsequently to an hydration event ascribed to oceanic metamorphism (Riccardi, 1994). The second group is found in a slice of continental crust subducted during Alpine collision, within a subcontinental metagabbro from the Sesia-Lanzo Zone of Western Italian Alps. The development of these amphiboles has been ascribed to a hydrothermal event that took place after the exhumation of the metagabbro during pre-Alpine lithospheric extension (Rebay & Spalla, 2001).

The Cl-amphiboles are either found in veins or as rims of zoned amphiboles, where brown-amphibole cores (sometimes Ti-rich), and green amphibole rims, are rimmed by the Cl-rich amphibole. All amphiboles show edembergite to pargasite compositions, with a direct correlation between Fe and Na_A vs. Cl content, and inverse correlation of Mg and Na_{M4} vs. Cl.

A comparison with other Cl-amphiboles that have been observed both in oceanic and continental settings, allow to determine the role played by Cl-rich fluids infiltration in oceanic and continental crust, during lithospheric extension.

The large variations in Si, Al^{IV}, Al^{VI}, Fe, Mg, K and Cl may be related to the $a_{HCl/fluid}/a_{H2O/fluid}$ ratio of the fluid in equilibrium with the amphiboles at various stages of the metamorphic evolution. Amphiboles that locally contain extremely high Cl contents (up to 4% wt) could have been in equilibrium with a locally enriched Cl-fluid. As suggested by the fact that the Cl content of amphibole into the veins is generally lower than in amphibole rims, far from the veins, these equilibrium conditions probably were reached at places where the system resulted locally closed. In addition hydration reaction consumed the H_2O component of the fluid, leaving a Cl-enriched fluid, that then re-equilibrated with the crystallising amphibole. Equilibration temperatures are up to 350°C for the amphiboles from the Apennines, and up to 550°C for those from the Sesia-Lanzo Zone.

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Probing deep CO_2 production in a collisional orogen with petrology

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Keywords: Metamorphic CO2, Calc-silicate rocks, Himalaya.

Active collisional orogens may have strong impact on the global carbon cycle through metamorphic degassing, which would supply a significant fraction of the global solid-Earth derived CO_2 to the atmosphere. The Himalayan belt, a major active "hot" collisional orogen, is a likely candidate for the production of significant amounts of metamorphic CO_2. Large metamorphic CO_2 fluxes may be triggered by prograde metamorphism of big volumes of impure carbonate rocks. So far, the incomplete knowledge of the nature, magnitude and distribution of the CO_2-producing processes hampered a reliable quantitative modeling of metamorphic CO_2 fluxes from any collisional orogen.

We focus on the metamorphic decarbonation processes occurring during the Himalayan orogeny and discuss the distribution of metacarbonate rocks, their petrography and petrological data about the nature of the CO_2-producing reactions.

In the eastern Himalaya, calc-silicate rocks are widespread at different structural levels of the Greater Himalayan Sequence and are intercalated within strongly deformed anatectic metapelites. The studied lithologies are medium- to fine-grained calc-silicate granofels consisting of cm-thick alternated layers differing in mineral modes and compositions; the common equilibrium assemblage consists of Pl + Cpx + Qtz + Grt.

Phase equilibria involving Grt (Grs-Alm s.s.), Zo, Cpx, An, Qtz and Cc in the CFAS–CO_2–H_2O system have been investigated using activity-corrected P–T phase diagrams at fixed fluid composition, isobaric T–X(CO_2) phase diagram sections and phase diagram projections in which fluid composition is not explicitly constrained. The relevance of the Grt-bearing equilibria during metamorphic evolution of calc-silicate rocks is discussed in the light of the observed microstructures and measured mineral compositions.

Petrologic data show that these Grt- bearing calc-silicate rocks may act as CO_2-source during prograde heating and/or early decompression, releasing internally-derived CO_2-rich fluids through Grt forming reactions. For suitable bulk rock compositions, the amount of CO_2 released during Grt growth increases with the increase in Grs component. However, in the studied lithologies, coarse-grained graphite is abundant and it has been interpreted as precipitated from the H_2O-CO_2 fluid released through prograde decarbonation reactions.

The complex interplay between two contrasting processes - i.e. the production of CO_2-rich fluids versus carbon sequestration through graphite precipitation - must thus be considered when dealing with a global estimate of the role exerted by decarbonation processes on the orogenic CO_2 cycle. Even if calc-silicate rocks may act as a significant CO_2 source during prograde heating, if the system remains closed, fluid–rock interactions may induce hydration of the calc-silicate assemblages and the "in situ" precipitation of graphite, thereby removing carbon from the fluids.

Petrology and geochemistry of Alpine peridotites indicate mass transfer during subduction of serpentinized mantle (Cima di Gagnone, Switzerland)

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Keywords: Subduction Mass Transfer Fluids High-pressure Peridotite Serpentinite Trace element.

At Cima di Gagnone, garnet peridotite and chlorite harzburgite lenses within pelitic schists correspond to eclogite-facies breakdown products of hydrated peridotites and are suitable for studying dehydration of serpentinized mantle.Thermobarometry and pseudosection modelling yield peak temperatures of 750-850 C and pressures below GPa.The minimum temperature recorded by the garnet peridotite corresponds to the maximum conditions experienced by the chlorite harzburgite, suggesting that these rocks recrystallized cofacially at 800 C. Alternatively, they might have decoupled during subduction, as achieved in tectonically active plate interface boundaries. The major and rare earth element (REE) variability of the peridotites was mostly acquired during pre-subduction mantle evolution as a result of partial melting and reactive melt flow.The ultramafic suite is also characterized by fluid-mobile element enrichments (B, Pb, As, Sb, Cs, Li, U, Be). Similarity in the U, Pb, B, Li and Sr contents of the Gagnone peridotites to present-day oceanic serpentinites suggests that these elements were partly taken up during initial serpentinization by seawater-derived fluids. Positive Be, As and Sb anomalies and enrichment in radiogenic Sr and Pb of peridotites suggest involvement of fluids equilibrated with crustal (metasedimentary) host rocks during subsequent subduction metamorphism and peridotite entrainment in (meta)sediments. Fluid-mobile element enrichment characterizes all peak eclogitic minerals, implying that multiple hydration events and element influx pre-dated the eclogite-facies dehydration. Peak anhydrous minerals retain B, Li, As and Sb concentrations exceeding primitive mantle values and may introduce geochemical anomalies into the Earth's mantle.The relatively low contents of large ion lithophile elements and light REE in the Gagnone peridotites with respect to much higher enrichments shown by metasomatized garnet peridotite pods hosted in migmatites (Ulten Zone, Eastern Alps) suggest that the crustal rocks at Gagnone did not experience partial melting. The Gagnone garnet peridotite, despite showing evidence for chlorite dehydration, retains significant amounts of fluid-mobile elements documenting that no partial melting occurred upon chlorite breakdown. We propose that the Gagnone ultramafic rocks represent a prime example of multi-stage peridotite hydration and subsequent dehydration in a plate interface setting.

Mantle wedge and COH fluids: themodynamic modelling, experiments and natural cases

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Keywords: experimental petrology, subduction, COH fluids.

Thermodynamic calculations and experiments predict that high-pressure fluids are dominated by water. Nevertheless, the importance of carbon species has been highlighted in the last years because of the relevant CO_2 content of arc magmas and the observation of carbon-bearing phases in mantle-wedge peridotites (e.g., Ulten zone). In C-free, H_2O-bearing systems, experiments have shown that the release of volatiles extends over several tens of km depths and result from a succession of continuous and discontinuous reactions involving hydrous phases in the subducted lithosphere, such as antigorite and chlorite in ultramafics; amphibole, lawsonite, zoisite, and chloritoid in mafic rocks. Phengite and biotite are involved in melting reactions of a variety of bulk compositions whenever K is available. In COH-bearing systems, the framework of phase relationships is more complex. COH fluids interact with the mantle-wedge rocks, prompting the growth of carbonates, hydrous minerals and C polymorphs. However, carbonates once formed are refractory and stable at very high pressures. Therefore, is has been proposed that the transport of carbon in the mantle wedge occurs via solute species in aqueous fluids or via advecting rock masses in buoyant “cold plumes” (e.g., Tumiati et al., 2013), but the problem remains still largely unresolved.

Phase relationships in systems bearing COH fluids are strictly dependent on the composition of the fluid itself, i.e., on the speciation of the volatile components of the fluid (H_2O, CO_2, CH_4…) and the presence of solutes deriving from the dissolution of rock-forming minerals. In the scientific literature, the speciation of COH fluids has been generally assessed through thermodynamic calculations using equations of state of simple H_2O+non-polar gas systems (es. H_2O-CO_2-CH_4), equations that do not consider the complexity related to dissolution processes, which are substantially unexplored in COH fluids. In the pure C-O-H system, C-saturated fluid speciation is a function of the oxygen chemical potential (and therefore oxygen fugacity). Therefore, in natural systems, the fluid speciation can be imposed by the redox state of the rock-forming phases. Alternatively, COH fluids may control the bulk oxidation state of the rock system by redox reactions with the mineral phases. We investigate experimentally the speciation and the dissolution of mantle minerals in COH fluids at buffered fO_2 conditions in equilibrium with graphite. Results highlight the importance of fluids for the transport of carbon and other elements in subduction zones. Experimental data, thermodynamic calculations and natural cases will be shown and compared.

Tumiati S., Fumagalli P., Tiraboschi C. & Poli, S. 2013. An experimental study on COH-bearing peridotite up to 3.2 GPa and implications for crust-mantle recycling. J. Petrol., 54, 453-479.

Lawsonite metasomatism: a new route for volatiles and trace elements in subduction zones

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Keywords: HP metasomatism, Lawsonite, Volatile recycling

Hybrid rocks formed by fluid-rock interactions at high-pressure (HP) metamorphic conditions are active players in the recycling of volatiles and trace elements in subduction zones. Such rocks include chlorite-talc-amphibole-rich (± carbonate) rocks formed by chemical and mechanical mixing of mafic, ultramafic and sedimentary protoliths. The recent discovery of widespread formation of lawsonite-rich hybrid rocks (Corsica, Guatemala, Urals, Turkey) extends the geological and compositional range of these rocks and their significance for volatile transfer to the deep Earth. We present the geological occurrence of these rocks in the HP units of Alpine Corsica, and their main geochemical features for whole rock and in-situ analyses of zoned lawsonite crystals. Field observations at the belt scale permit to define a metamorphic isograd for lawsonite metasomatism, which was found from a minimum of ca. 360 °C and 1.6 GPa to the maximum P-T conditions of Alpine Corsica, i.e. ca. 530 °C and 2.3 GPa, within a continuous metamorphic gradient. From a geochemical point of view, the whole rock experienced a dramatic chemical modification dominated by Ca gain. Significant mass gain also occurred for a large variety of trace elements, including REE, HFSE and some LILE. Lawsonite may have notable major element zoning, including Fe (up to ca 1.5 wt.%) and Ti (ca. 1 wt.%); some lawsonite crystals in vein also display a marked Cr oscillatory zoning (up to ca. 8 wt.%). In some cases, this variation may be correlated with increasing metamorphic conditions. Moreover, lawsonite compositional zoning permitted to define successive stages of mass transfer during metasomatism. As an example, the trace element composition of different lawsonite zones has remarkable variations, comprising LILE and HFSE. Altogether, these data point to mixed fluid sources including serpentinite-, mafic- and sediment-derived fluids, along channelized fluid pathways. The chemical compositions of the final metasomatic product, which in many cases approach the CASH system, favor (i) the precipitation of lawsonite and the unexpected reincorporation of free water at HP conditions, and (ii) the stability of lawsonite at higher temperature and at greater depth compared to the MORB+H_2O system. By means of a thermodynamic approach, we quantified the drastic water enrichment across a metasomatic aureole characterized by intense chemical resetting and massive lawsonite precipitation, and its implication for water transfer at depth. We conclude that these hybrid rocks testify for intense geochemical recycling and water transfer to great depth in subduction, with implications for water cycling to the mantle. Moreover, the dramatic water expulsion and fluid overpressure caused by these lawsonite-rich rocks at lawsonite breakdown may cause localized deformation and seismicity at the subduction interface.

UHT metamorphism of HP rocks? A case study from the Adula nappe complex (Central Alps, N Italy)

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Keywords: Garnet peridotite, UHT metamorphism, Adula nappe.

The Adula-Cima Lunga nappe complex represents the highest of the Lower Penninic units of the Central Alps. Garnet lherzolite bodies crop out at three localities, from west to east: Cima di Gagnone, Alpe Arami and Mt. Duria. This study concerns an outcrop close to Monte Duria, where retrogressed garnet lherzolites occur as m-to hm-sized boudins hosted within amphibole-bearing gneisses that contain also some dm-to-m-sized boudins of more or less preserved eclogites. This rock association is in turn embedded within the migmatitic gneisses that form most of the southern sector of the Adula nappe. Petrographic and chemical analyses indicate that garnet peridotite is composed of olivine (XMg=0.88), orthopyroxene, clinopyroxene and garnet (Py 68; Cr_2O_3 up to 1.45 wt%) with inclusions of Cr-rich spinel (up to Cr/(Al+Cr)=0.55) surrounded by kelyphitic symplectites of opx + cpx/amph + spl. These reaction produced double coronas, one composed of opx (former ol) and one composed of cpx + opx+ spl. In one kelyphite, we observed the uncommon occurrence of ZrO_2 (baddeleyite) and $ZrTi_2O_6$ (srilankite). Tiny crystals of these two Zr-bearing phases (~1 μm) are invariably located in the opx corona after ol. The cpx + opx + spl corona (after grt) contains, instead, zircon. Baddeleyite should have formed through a reaction of the type $Mg_2SiO_4 + ZrSiO_4 = MgSiO_3 + ZrO_2$. ZrO_2 and $ZrTi_2O_6$ display a low amount of solid solution. These compositions are consistent with T below 1200°C, but an improvement of the thermodynamic model is needed in order to better constrain the T of the granulitic overprint on the basis of these Zr-bearing phases.

In eclogites, the HP association consists of garnet (Py40Alm37Sp20), omphacite (preserved as inclusion, containing Jd30 and XMg 0.87), kyanite, K-feldspar, zoisite and minor quartz. Omphacite is almost always replaced by cpx (Jd5) + plag (An55) symplectites. Garnet is surrounded by plag (An33) + opx (En70) symplectites, more often by amphibole+plagioclase. Kyanite is replaced by plag (An84) + spinel ± sapphirine ± corundum. The spinel-sapphirine Fe-Mg thermometer suggests T of about 850°C for this granulite-facies overprint. Corundum-bearing symplectites after kyanite are common at the contact between eclogites and the host amphibole-bearing gneiss. In this contact, cm-sized emerald green zoisite has been found, replaced by anorthitic plagioclase ± clinopyroxene ± spinel ± calcite.

The observed assemblages point to a diffuse static granulitization of both peridotites and eclogite of Mt. Duria, suggesting a nearly isothermal decompression from peak-pressure conditions. The surrounding migmatitic gneiss do not display evidence of such granulitic event, recording T<700°C.

The mechanism and timing of emplacement of the garnet peridotite and associated HP-HT rocks in the country migmatites, and whether or not the subduction event is related to the Alpine or to an older orogenic cycle are still a matter of debate.

SESSIONE S22

Volcano laboratories: where geology, geophysics and geochemistry gather together

CONVENORS

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Magma system conditions and ascent time during the Monte Nuovo eruption (Campi Flegrei, Southern Italy): an experimental and CSD study

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Keywords: Campi Flegrei, experiments, phono-trachyte, alkali-feldspars, CSD.

Processes of unrest, ascent dynamics and eruption of magmas govern the transition from quiescent to active volcanic systems. The knowledge of these processes is fundamental for understanding geochemical and geophysical signals that are observed at high risk volcanoes.

Here we present results from petrological and experimental studies on the phono-trachytic products, representative of those commonly erupted at the Campi Flegrei. In particular, we focus on the Monte Nuovo eruption for which robust background information exists in the literature, including historical chronicles, stratigraphical, textural and petrological studies. This low intensity and magnitude eruption is particularly interesting because it occurred after 3000 years of volcanic quiescence and the reported ground level movements and seismicity have characteristics comparable to the present bradyseisms.

Cooling and decompression experiments on a phono-trachytic composition reproduce the melt evolution in response to an instantaneously applied thermodynamic driving force (undercooling – ΔT). Natural and synthetic products have been characterized by B-SEM investigations, image analysis, Crystal Size Distribution study, X-ray diffractometry, and mineral and glass geochemistry.

Experimental and natural samples are texturally and chemically comparable allowing us to estimate the pre-eruptive conditions of the magma and the timescales of the eruptive process during the Monte Nuovo event in agreement with historical chronicles. Magma crystallization time was estimated from size distribution of feldspar microlites quenched in the matrix of juvenile fragments, by experimentally knowing the relation between population density, sizes and growth rates of alkali feldspar. As a whole, the experimental conditions reproduce the later evolution state of the phono-trachytic magmas, particularly, shortly before and during eruptions. Thus, this study offers a set of pressure (water saturated), temperature and undercooling (ΔT) conditions, useful to constrain the timescale and to better understand the behaviour of Phlegraean magma, starting from the texture of their eruptive products.

Melting of Plume Residue beneath the Afar: Implications for Axial Basalts Geochemistry

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Keywords: Afar, Ethiopia, Erta Ale.

The Afar is the place to investigate both the evolution of the lithosphere from continental break up to incipient seafloor spreading and the interaction between rifting processes and a mantle plume.

The plume has been evoked as one of the main factors involved in the development of the Afar, but its persistence beneath the depression is still a matter of debate. Recent studies have shown the lack of a well developed plume structure beneath the Afar (Hammond et al., 2013), thus suggesting its partial exhaustion. Geophysical investigations hint at an uppermost mantle dominated by broad asthenospheric upwelling (Rychert et al., 2012; Hammond et al., 2013) affected by decompression melting, feeding the magma chambers stored within both the crust and mantle, and the Afar plume magmatism. However, modern basalts erupted along the northern Afar show a strong enrichment in incompatible and trace elements that partially disagree with a shallow depleted mantle reservoir.

Recent geochemical analyses indicate that part of the mantle melting process, still occurs at greater depths (> 80 km) (Ferguson et al., 2013) and several authors suggest the presence of focused diapiric upwelling (Hammond et al., 2013), which probably enhances the melting at greater depths.

EMPA and LA-ICP-MS were used to investigate the composition of modern lavas sampled from the Erta Ale Chain and the Asal region in 2011 and 2013. The plume markers are recognizable but with less intensity compared to the Oligocene High Ti lavas, according to the lower activity of the Afar hot spot. Our results suggest a hybrid source characterized by two main reservoirs: an enriched mantle melting in the grt field and a shallow depleted mantle. We elaborated a numerical model that predicts the composition of the axial basalts through the mixing of melts obtained by melting of these theoretical reservoirs.

We propose for the Afar region the presence of isolated volumes of enriched material genetically related to the remains of the plume. These bodies generate enriched melts that pollute the liquids obtained by the surrounding asthenosphere before they reach the surface. Isotopic investigations are in progress and will help to better define the involvement of each reservoir.

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Unravelling the hidden origin and migration of plagioclase phenocrysts by in-situ Sr isotopes: the case of final dome activity at Nisyros volcano, Greece

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Keywords: In situ Sr isotopes, crystal migration, dusty sieved plagioclase.

In-situ Sr isotope analyses, along with textural and compositional characteristics, of plagioclase phenocrysts occurring in the rhyodacite dome-lavas and associated mafic enclaves, erupted during the last magmatic activity at Nisyros volcano (Greece) have been studied in detail.

Dome-lavas and enclaves have a paragenesis dominated by plagioclase. We recognize five different types of plagioclase based on their specific textures and composition. Dome-lava plagioclases (Type-1) are mainly large (1-5mm), subhedral, clear and poorly zoned crystals with low-An content (An_{25-35}), whereas the plagioclase phenocrysts (Type-4 and Type-5) and groundmass plagioclase microlites occurring in the enclaves have high-An content (An_{75-95}). In both dome-lavas and enclaves two other types of plagioclase do also occur: (i) plagioclase phenocrysts with size and core composition similar to those of Type-1 having a dusty sieve zone (DSZ) at the rims (Type-2); (ii) plagioclases with a DSZ affecting the entire crystal but a thin rim (Type-3). The drilled plagioclases have $^{87}Sr/^{86}Sr$ negatively correlated with their An content. Low-An cores of Type-1 and Type-2 have quite homogeneous $^{87}Sr/^{86}Sr$ (0.7044-0.7046), whose values are more radiogenic than their host magmas (0.70403-0.70408) and similar to those of the previous Upper Pumice (UP) rhyolite magma (0.70438-0.70456). The DSZs of Type-2 and Type-3 show lower and scattered $^{87}Sr/^{86}Sr$ (0.70397-0.70426) with intermediate and variable An content. High-An cores of Type-4 and Type-5 have the least radiogenic Sr isotope composition (0.70379) in equilibrium with that measured in the enclaves (0.70384-0.70389). We demonstrate that Type-1 plagioclase crystallizes in the previous Upper Pumice (UP) rhyolitic magmas, and Type-2 plagioclase derives from entrainment of Type-1 into the still molten enclave magma. The DSZs originated in response to the interaction between the low-An plagioclase and the enclave mafic melt in which dissolution, and re-crystallization acted together as function of the interaction time.

Type-1 and Type-2 plagioclases record, therefore, a long-lived timescale of events starting from their crystallization in the UP rhyolite, representing the original silica-rich magma from which the dome-lava melts derived by open system evolutionary processes (e.g. mixing, mingling and crystal migration), caused by successive refilling of mafic enclave-forming magma. It is noteworthy that the occurrence of DSZs with different width (Type-2 and Type-3) could indicate different interaction timescales between the single crystals and the enclave melt (from few hours to some 40 days).

These micro-analytical data contribute to the understanding of the origin of the rhyodacitic dome-lavas at Nisyros volcano and to set robust constraints on the dynamics of mingling/mixing processes in terms of crystal exchange pathways and enclave disaggregation.

The CFDDP 506 m drilling mud and cores at Campi Flegrei (Italy): volcanological and environmental clues on the eastern sector of the caldera

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Keywords: Campi Flegrei, CFDDP, mud drilling, cores, volcanism, paleoenvironments.

The Campi Flegrei caldera, inhabited by more than 350.000 people, is one of the most studied volcanic areas in the world. Nonetheless, several aspects about the tectonics, the nature of the deformation (net uplift of c.a 4 m between 1950 and 2013) and the volcanic system are still matter of debate.

This contribution presents the results of a 506m deep pilot well drilled in the Bagnoli Plain, in the Campi Flegrei caldera, c.a 1.6 km away from its eastern border. The drilling was conducted in the frame of the Campi Flegrei Deep Drilling Project (CFDDP), which is funded and supported by the INGV and the ICDP.

The obtained results are derived from analysis of cuttings, cores and geophysical logs. Stratigraphic, volcanological and geo-environmental information have been constrained from mineralogy, paleontology, Sr-isotope geochemistry and ^{40}Ar/^{39}Ar geochronology. Measurements of gasses within the drilling mud and geophysical data collected with the down hole logging also provide information on the geothermal system. Furthermore, 4 seismic stations were installed around the drilling site, in addition to the monitoring permanent network. No induced seismicity occurred during the drilling activity. Power Spectral Density of the recorded signal evidences sea waves (below 1 Hz) and anthropic (around 8 Hz) seismic noise. The network detection threshold, as a function of the earthquake magnitude and hypocentral distance, was computed to understand the limits of the instrumentation used.

The CFDDP drilling penetrated essentially pyroclastic rocks younger than 47.8 ka. The clast type, characteristis, texture, mineralogy, and log-derived compositional contents are similar to those documented in the literature for the Phlegraean area. Based on lithological and log data, the general sequence is as follows: i) a basal gray pumice-bearing tuff at the base; ii) a greenish tuff between 470 and 270 m, progressively less altered; iii) a ~60 m-thick monotonous level of brown dense to vesicular glass fragments; iv) unit with an abundance of microfossils in association with dominantly sub-rounded or rounded vesicular to dense heterogeneous grains in the 255-36 m depth range, and carbon, wood fragments and peat in the shallowest portion; and v) superficial products that differ for the relative abundance of variably angular vesicular –to- dense and porphyritic fragments.

Characterization of sediments indicates sub-aerial conditions or aggressive environments between 245 and 506 m of depth, while the shallowest 245-36 m bgl interval shows a succession of subaerial and subaqueous paleoenvironments. The reconstructed stratigraphic sequence allows us to highlight some important features about the evolution of the eastern sector of the caldera. The results have implications on the origin and structure of the caldera, on the pre-caldera volcanic history, on the recent caldera dynamics and on the hazard assessment.

The Punta Chiarito Tephra (Ischia, Italy): eruption dynamics and emplacement mechanism inferred from stratigraphic, sedimentologic and petrological data

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Keywords: Ischia, eruption dynamics, resurgent calderas.

Volcanism in resurgent calderas is a common feature, in which areal distribution of vents, style of volcanism and chemical composition of the erupted magmas, can be strongly influenced by the local stress field induced by resurgence mechanism and dynamics. In the Ischia resurgent caldera almost all the volcanic vents of the past 5 ky are located in the lowland bordering eastward the resurgent block. The Punta Chiarito Tephra (ChT) is the sole pyroclastic deposit of this period exposed in the western sector of the island, over an area of at least 5 km^2. The ChT has been archeologically dated at the end of the 8th century b.C. as it buried a human settlement of this age.

Here we present the results of an integrated stratigraphical, sedimentological, petrological and volcanological study, carried out on this tephra.

The ChT has been subdivided in Eruption units and sub-units according to the observed sedimentological features. Clasts morphology, degree of vesiculation and sedimentary structures, analyzed both in the field and laboratory through grainsize and SEM analyses, allowed the reconstruction of the eruption dynamics, type of fragmentation, transport mechanisms and depositional processes. The variations of geometrical and sedimentological characteristics (shape, thickness, grainsize, sedimentary structures) of each unit, together with direction of provenance of ballistic clasts, were used to constrain the position of the eruption vent, presently buried under landslides.

Mineralogical, geochemical and isotopic determinations allowed the characterization of both the juvenile products and the composition of the erupted magma in the frame of the evolution of the magmatic system of Ischia in the past 5 ky.

The ChT sequence was generated by a sequence of magmatic and phreatomagmatic explosions that extruded a homogeneous alkali-trachytic, well-vesicular and porphiritic magma. The eruption began with a phreatomagmatic phase, which generated the basal surge of Member A. A violent strombolian-to-subplinian eruption column formed soon after and produced the fallout deposit of Member B. In the following water entered the conduit leading to a new phreatomagmatic phase, with the emplacement of the dilute pyroclastic density currents of Members C to E. The eruption ended with the formation of a pulsanting sub-plinian magmatic column generating the fallout deposit of Member F. Lithic clasts and SEM investigations indicate a progressive increase of water-magma interaction during the course of deposition of member C and its decrease from member D to F. Sr-isotopic ratio for crystals and whole-rocks indicates that the magma batch was isotopically homogeneous and deviated its composition during the eruption, towards more radiogenic values in response to magma-water interaction.

Natural gadolinium discharged from volcanic sources

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Keywords: Gadolinium anomaly, REE distributions, geochemistry.

Although a large fraction of chemicals is provided from volcanic fluids to the environment (Oppenheimer et al., 2014) only a scarce literature was focused on the Rare Earth elements (REE) release from high temperature fumaroles (Möller et al., 2003; Gilbert & Williams-Jones, 2008; Zelenski et al., 2013). In order to fill this gap, this research was carried out mainly taking in account the REE partitioning during the emissions of fumarolic fluid between newly-forming sublimates and the remaining gas phase. The latter was collected as alkaline condensates according to Sortino et al. (2006). The investigated high temperature fumaroles (95-450°C) occur in several volcanic systems at Vulcano, Aeolian Islands and Phlegrean Fields (Italy), Santorini, Cyclades Islands (Greece), Canary Islands (Spain) and Cape Verde where strong passive emission of fluids occur.

Fumarolic sublimates show higher lanthanide contents, whereas alkaline condensates represent the most volatile fractions of these fluids. The analysis of geochemical behaviour of these elements was investigated studying the features observed in shale-normalised REE patterns (vs. PAAS, Taylor and McLennan, 1995). This analysis indicates that Gd is preferentially partitioned in the vapour phase during the sublimation of less volatile fluid fractions. Consequently, positive Gd anomalies occur in alkaline condensates with respect to coexisting solid sublimates where this effect is less evident. Their amplitudes can be assessed according to the equation:

$$\frac{Gd_n}{Gd^*} = \frac{Gd_n\sqrt{\mathrm{Ho}_n}}{\sqrt[3]{Tb_n^2}}$$

(Moller et al., 2007) where n-suffix indicates normalised lanthanide concentrations and Gd* is the expected normalised Gd concentration according to Tb and Ho contents. Comparing the amplitudes of these anomalies with the temperatures of investigated fumaroles larger Gd/Gd* values are mainly found in higher temperature fumaroles (450-250°C) in Vulcano ($1.5 \leq Gd/Gd^* \leq 6.8$) and less in lower temperature fumaroles (285-82°C) studied in Phlegrean Fields, Canary and Cape Verde islands ($1.1 \leq Gd/Gd^* \leq 2.7$).

Moreover, comparing the amplitudes of Gd/Gd* and related HCl/HF ratio values of alkaline condensates a significant positive relationship is observed only in alkaline condensates collected from higher temperature fumaroles ($T > 200$ °C). This evidence is consistent with a preferential REE complexation via Cl-complexes in vapour phase and can be considered a consequence of nephelauxetic effect. According to this suggestion the growth of positive Gd anomalies is a consequence of changes of the first Gd hydration sphere during the formation of Gd-chloride complexes at higher temperature and does not occur if complexes are formed at temperatures up to 200 °C (Mayanovic et al., 2007).

Being REE-chloride complexes highly soluble species quickly removed from the atmosphere by water droplets, Gd coming from volcanic gas phase could represent a significant component of the geochemical Gd cycle in aqueous media.

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Compositional changes of erupted lavas and styles of volcanic activity at Mt. Etna during the 2011-2013 period

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Keywords: Etna, magma recharge, paroxysmal activity.

A comprehensive characterization of volcanic rocks related to paroxysmal events developed between January 2011 and April 2013 at Mt. Etna, was here performed through in situ analysis of mineral phases and whole rock geochemistry. The collected dataset provide evidences that magmas feeding the 2011-13 activity preserve a geochemical signature comparable to that of the 2007 erupted products , though with minor differences due to a different evolutionary pattern.

Analysis performed on the main mineralogical phases such as clinopyroxene, plagioclase and olivine showed fluctuations through time of Mg#, An and Fo. Whole rock major and trace elements also display similar compositional changes, which could be accounted for by a transient, pulsating recharge by more basic magma. In order to support this hypothesis, several simulations of magma evolutionary processes were performed by means of MELTS at fixed chemical-physical parameters.

Results point to the superimposition of crystal fractionation and recharge by a more basic magma as the main differentiation processes controlling the composition of the 2011-2013 volcanic products. Composition of the recharging end-member is compatible with that of the most basic magma emitted during the 2007 and the first-emitted products of 2012. Analysis of the erupted volumes of magma, together with petrologic evidences, support the idea that large volumes of non-erupted magma are stored in the intermediate feeding system (2-6 km b.s.l.) after a phase of major magma recharge from the deep portions of the plumbing system (>6 km b.s.l.). The transient recharges from the intermediate level toward the shallow reservoir could be able to trigger paroxysmal activity at the surface.

Experimental constraints on phase relations in a multilevel magmatic system: the Phlegraean Volcanic District (South Italy) case study

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Keywords: Phlegraean Volcanic District, Experimental Petrology, Phase Relations.

The Phlegraean Volcanic District (PVD) is an active area that hosts about 1,5 million people within its surroundings. This makes the area one of the most dangerous on the Earth. The activity of the PVD (including Campi Flegrei and the islands of Ischia and Procida) produced dramatic explosive events in the Mediterranean area during the last 200 ky, and many studies have been performed to investigate the magmatic differentiation processes responsible of the largely compositionally variable products emitted during PVD activity. However, these studies have mostly followed a petrological and geochemical approach, whereas very few experimental studies have been carried out to understand and constrain origin and evolution of PVD magmas, and only limited to differentiated compositions.Here we present an experimental study conducted on a rock of primitive composition, probably representing the mantle derived parental magmas feeding the PVD, outcropping in the area, a K-basalt from the Solchiaro eruption. This rock has been used as starting material for an experimental study addressed to unravel the differentiation mechanisms acting in the PVD plumbing system. The experiments were performed in a piston–cylinder apparatus at three different pressures, 200, 400 and 800 MPa based on the current knowledge of the PVD plumbing system structure. The ranges of temperature and water concentration investigated were 1050 - 1300 °C and 1-7 wt%, respectively. These experiments allows us to reconstruct the phase relations of Solchiaro K-basalt in the P-T-H_2O space. At 200 MPa and H_2O content lower than 4 wt%, olivine is the liquidus phase followed by chromium spinel, clinopyroxene, and finally plagioclase. At 400 MPa and H_2O lower than 3 wt%, olivine is still the liquidus phase but chromium spinel also occurs; then, clinopyroxene and plagioclase crystallize. Interestingly, at 800 MPa and water content below 1.5 wt%, chromium spinel and clinopyroxene replace olivine as liquidus phases; whereas for water content above 1.5 wt% all the three phases occur on the liquidus. This suggests the equilibrium of primary PVD magmas with a wehrlitic source at pressure corresponding to the crust-mantle boundary. Moreover, our 800 MPa experiments corroborate results from a recent study on melt inclusions constraining the amount of water in the PVD primary magma at values up to 2 wt%. The high pressure experiments, showing olivine on the liquidus only for H_2O content in the melt above 1.5 wt% suggest that in a magmatic system characterized by water content below 1.5 wt%, the occurrence of olivine as liquidus phase can possibly occur by the increase of XCO_2 in the magma. Experiments to investigate the role of XCO_2 on the phase relations of PVD primitive magmas are in progress.

Sulfur in alkaline melts: An experimental study

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Keywords: sulphur solubility, phonolite, basanite, erebus.

We present preliminary results of experiments to establish the solubility of sulfur (sulfate and sulfide) in natural alkaline melts (basanite, KI-04; and phonolite, ERE-97018) from Erebus volcano, Antarctica. Melt composition is known to strongly influence S solubility in natural melts, particularly with respect to FeOtot and SiO2 [Ducea et al.]. Although melt polymerization is thought to have a significant effect on sulfur solubility and speciation, it is likely that a number of other factors, including melt alkali and iron content, also play a role in controlling sulfur behavior in melts. This experimental study examines the interplay between alkalis, oxygen fugacity, pressure, Fe and S oxidation state, and Fe and S coordination geometries and their effects on S^{6+} and S^{2-} solubility. Sulfur saturated and undersaturated experiments have been carried out at a range of oxygen fugacities (log $fO2 = -12$ to -6) and pressures (1 bar to 1 kb) at superliquidus temperatures (1030 and 1200 °C for phonolite and basanite, respectively). This range of experimental conditions and analyses of the S contents via EPMA and sulfur and iron speciation via XAS will allow S solubility and partitioning to be evaluated with respect to experimental conditions.

Preliminary results indicate a marked increase in total S solubility in evolved phonolite melt relative to primitive basanite at similar T- fO2 conditions. Experimental data indicate a steep increase in S solubility at highly oxidizing conditions (fO2 = NNO+1.53; ~1000 ppm dissolved S) and minimum solubility at moderately oxidizing conditions (fO2 = QFM+0.23; ~200 ppm dissolved S). The strongly non-linear relationship between S solubility and fO2 has implications for sulfur degassing at Erebus volcano, whose erupted products indicate a distinct decrease in oxygen fugacity during fluid-magma ascent.

Future experiments at higher pressure and analyses of all experimental products via XAS will elucidate the roles of oxygen fugacity, pressure, Fe and S speciation, in controlling S solubility in basanites and phonolites. Comparisons of our results to data from more polymerized (low-alkali) melts and incorporation of data from an unpublished experimental study of S in phonolite at sub liquidus conditions [D. Moncreiff et al.] will further our understanding of the relation between melt polymerization and S solubility and allow us to characterize the behavior of S in lower temperature systems.

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On the relationships between tectonics and volcanism in the offshore Capo Vaticano, SE Tyrrhenian Sea, during the Plio-Pleistocene

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Keywords: sub-marine volcano, normal faults, Calabria.

High-resolution bathymetry and a grid of single-channel reflection seismic profiles (Sparker and Chirp) were recently recorded in a sector of the upper slope of Capo Vaticano (CV) promontory (Tyrrhenian coast, W Calabria) where forward and inverse modeling of previously acquired aeromagnetic data highlight the presence of a WNW©\ESE elongated, 20 km long and 3¨C5 km wide, magnetized body extending from sea floor to about 3 km below sea level. Magnetic properties of this body are consistent with those of the medium to highly evolved volcanic rocks of the Aeolian Arc (De Ritis et al., 2010).

Forthwith offshore promontory, the bathymetry highlights a complex-shape seamount that develops along a WNW direction, orthogonally interrupted by NE-trending ridges (Loreto et al., 2013), the largest of which shows major- and minor-axes of ca. 11 and 2 km, respectively. Summit elevation is ca. 70 m. Several vented fluids points were imaged on top of the seamount by chirp profiles. The largest of which rises from seafloor up to 6/7 m within water column, assuming the acoustic water velocity of 1500 m/s.

Two faults systems associated with extensional faults are mainly observed on seismic profiles. High-angle NW-trending normal faults, SW-dipping, formed along the continental slope connecting the south-west continental shelf of the CV promontory to the Gioia Tauro basin (Pepe et al., 2013). These faults generally have small displacements, up to 40 m, and are sealed by Pleistocene deposits. A NE-trending normal fault, SE-dipping, is also observed on both chirp and sparker profiles. Its length is estimate to be more than 30 km, partially borders the NE-trending ridge intersecting the NW-trending fault. Landward, another NE-trending normal fault affects Pliocene and lower Pleistocene, and is sealed by upper Pleistocene.

The described new geophysical data lead to a re-examination of the magnetic anomaly field interpretation. In fact, the revealed NE-trending ridge encounters the CV NW-SE ridge just where the peak value of the Reduced-to-the-Pole magnetic anomaly lies. Therefore, the inherent source body is emplaced where the maximum fracturing occurs. This suggests highly magnetized material crystallized in a vertical conduit that fed a volcanic system, likely fault-controlled, surrounded by the almost not magnetized rocks of the Gioia and the Paola sedimentary basins and of the Arco Calabro Peloritano units.

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Magma storage and ascent dynamics of early volcanic manifestations at Salina (Aeolian Islands)

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Keywords: volcanological evolution, volcano feeding system, salina island.

The Rivi and Capo volcanoes represent the early (240-87 ka; De Rosa et al., 2003; Leocat, 2011) sub-aerial volcanic manifestations at Salina, in the central portion of the Aeolian archipelago. Their lava flows and pyroclastic deposits from strombolian fall-out activity have been here investigated through a multidisciplinary geological-petrological approach. Our geological field survey confirmed that Rivi and Capo volcanoes are part of a unique N50°E aligned volcanic complex, here named Rivi-Capo Volcanic Complex (RCVC). The Capo volcano, which is the most ancient center on the island (from 240 ka; Leocat, 2011), is constituted by three different volcano-stratigraphic Formations. During the deposition of Lower and Middle Capo Formations activity was mainly tectonically-controlled along a NE-SW direction. The last products of Capo volcano (the here-named Upper Capo Formation) are related to a late-stage resumption of volcanic activity at 87 ka (De Rosa et al., 2003). Rivi volcano developed between 160 and 131 ka (Leocat, 2011) and has been divided into two major Formations (Lower and Upper Rivi Formations), separated by a northward-directed sector collapse of the volcanic edifice.

Rock sampling has been stratigraphically constrained and led to reconstruction of the magma feeding system processes through time. Whole rock compositions exhibit a general trend of evolution toward more basic terms within the Capo and the Rivi volcanoes. MELTS simulations and mass balance modeling suggest that the RCVC rocks are the result of fractional crystallization of plagioclase, clinopyroxene and olivine (ca. 45 vol.% of solid removed) from a primary magma. Continuous recharge and mixing by more basic magma coming from the deep portions of the magmatic plumbing system contribute to the final volcanic rock composition. Our textural and microanalytical data on plagioclase and clinopyroxene crystals lead to redrawing of the plumbing system configuration for the RCVC with respect to previous hypotheses. These data allow the definition of a multi-level magmatic storage system with reservoirs at ~20 km and ~4 km of depth below the sea level. When processes of magma differentiation, ascent and storage are considered together with the stratigraphic position of each sample, a history of continuous modification of the RCVC plumbing system can be advanced. Specifically, volcanism could have been characterized by fissure-type eruptions during the early stages and gradually changed later to central-type volcanism.

De Rosa R., Guillou H., Mazzuoli R. & Ventura G. 2003. New unspiked K-Ar ages of volcanic rocks of the central and western sector of the Aeolian Islands: reconstruction of the volcanic ages. J. Volcanol. Geotherm. Res., 120, 161-178.

Leocat E. 2011. Histoire eruptive des volcans du secteur occidental des Iles Eoliennes (Sud de la Mer Tyrrhénienne, Italie) et evolution temporelle du magmatisme. Unpublished PhD thesis, University of Paris 11 Orsay, France.

Seismic expression of the shallow structure of The Neapolitan Yellow Tuff (NYT) caldera offshore the Campi Flegrei

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Keywords: Campi Flegrei, Neapolitan Yellow Tuff, Collapse caldera.

In this study we integrate high-resolution swath bathymetry, single-channel reflection seismic data and gravity core data, to provide new insights into the shallow structure and latest Quaternary to Holocene evolution of the submerged sector of the Neapolitan Yellow Tuff (NYT) caldera (Campi Flegrei) in the Pozzuoli Bay. The new data allow for a reconstruction of the offshore geometry of the NYT caldera collapse – ring fault system, along with the style and timing of deformation of the inner caldera resurgence.

Our interpretation shows that the NYT eruption (~15 ka BP) was associated with a caldera collapse bounded by an inward-dipping ring fault system. The ring fault system consists in a 1-2 km wide fault zone that encircles an inner caldera region ~ 5 km in diameter and is often marked by the occurrence of pore fluids ascending through the fault zone, up to the seafloor, particularly in the western sector of the bay. A shallow magmatic intrusion along the ring fault zone was also detected offshore Bagnoli in the eastern part of the Pozzuoli Bay (Sacchi et al., 2014).

Following the NYT eruption, the inner caldera region underwent significant deformation and resurgence with a maximum cumulative uplift of the offshore structure in the order of 180 m. The net uplift rate of the caldera resurgent dome was ~ 9 - 12 mm/year during the period 15.0 – 6.6 ka BP. The style of deformation of the resurgent structure can be described in terms of a broad doming, accompanied by subordinate brittle deformation, mostly concentrated in a small apical graben at the summit of the resurgent dome (Cole et al., 2005).

Chronostratigraphic calibration of seismic profiles obtained by three tephra layers cored in the Pozzuoli Bay indicates 5 to 25 m of post-Roman differential subsidence and tilting towards ESE of the inner caldera resurgence, as recorded by the drowning of the infralittoral prograding wedge below the present-day storm wave base.

Cole J.W., Milner D.M., Spinks, K.D. 2005. Calderas and caldera structures: a review. Earth-Science Review, 69, 1-26.

Sacchi M., Pepe F., Corradino, M. Insinga D.D., Molisso F. Lubritto C. 2014. The Neapolitan Yellow Tuff caldera offshore the Campi Flegrei: Stratal architecture and kinematic reconstruction during the last 15 ky. Marine Geology, 354, 15-33.

Magmatic underplating and inremental growth of a granite pluton in the Sesia Magmatic System

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Keywords: Caldera, Ivrea Verbano, supereruzione.

A virtually complete crustal section in the Sesia Valley of northwest Italy provides a unique opportunity to directly constrain the igneous evolution beneath a continental volcanic field. Capping the section, a bimodal, though mainly rhyolitic, volcanic complex containing a >15-km-diameter caldera is intruded by a granitic cupola segregated from a 7- to 8-km-thick granitic pluton that is rooted in migmatitic paragneiss at mid-crustal levels. At deeper levels, an 8-km-thick gabbroic body, "magmatically underplated" between 17 and 25 Km, intrudes amphibolite- to granulite-facies crustal rocks. Consistent with a cause-and-effect relationship between magmatic underplating in the deep crust and silicic plutonism and volcanism at high crustal levels, SHRIMP U/Pb zircon ages for volcanic, granitic and underplated gabbroic rocks are constrained to a relatively narrow time window of ~290 to ~280 Ma. A Concordia age of 282 + 0.75 Ma on zircons from the caldera-fill ignimbrite indicates that caldera collapse occurred late in the evolution of this magmatic system. Field relations and geochemistry constrain the thermal history of the Sesia section and the processes of magmatic underplating, crustal anatexis and assimilation, and hybridization during its magmatic evolution. Underplating was accommodated by crustal extension, which is recorded by structures produced by the flow of gabbroic cumulates downward and away from a small magma chamber perched near the top of the intrusion. Heat from the underplated gabbro induced anatexis in country-rock paragneiss, producing granitic melts that migrated higher in the crust. Eu and Ba enrichments, εNd < -2.5, $^{87}Sr/^{86}Sr > 0.7075$, indicate that the parental melt of the underplated gabbro ingested significant amounts of paragneiss previously stripped of a granitic component. The peraluminous composition of granitic and volcanic rocks indicate that melting of metapelitic paragneiss was a contributing source, but $^{87}Sr/^{86}Sr$ values (~ 0.710) are intermediate between the compositions of the paragneiss and the underplated gabbro, indicating that late-stage, residual melts produced by fractional crystallization of the underplated gabbro also contributed to the formation of granite and silicic volcanic rocks. Mass balance computations are consistent with assembly of the granite pluton by mixing of a relatively constant ratio of anatectic and AFC-derived granitic components modulated by thermal buffering in the deep crust by anatexic and AFC processes. Petrographic observations suggest that remelting of the granite pluton contributed to formation of a granitic crystal mush, which may have set the stage for caldera collapse.

Timescales of magma storage and ascent at Mt. Etna volcano from plagioclase trace element zoning

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Keywords: Volcano-tectonics, trace elements, magmatic processes.

How long magma takes to ascend to Earth's surface after storage and how the transfer mechanisms influence the eruptive behaviour are major questions for volcanologists. The use of plagioclase crystals at Mt. Etna volcano, chiefly because it is stable over a wide range of physical-chemical conditions and is sensitive to changes in thermodynamic parameters during its growth in magma storage and transport zones, has recently shown the efficiency of this tool to reconstruct a number of volcanic processes during storage, degassing, and ascent (Viccaro et al., 2010). In this work, textural data and trace element zoning in plagioclase phenocrysts for products of historic (pre-1971 AD) and recent (post-1971 AD) activity of Mt. Etna volcano contributed to addressing these questions for the complex storage and transport system of this volcano. The observed textural characteristics of crystals include near-equilibrium textures (i.e., oscillatory zoning) and textures with variable extent of disequilibrium (patchy zoning, coarse sieve textures and dissolved cores). One of the main differences between crystals of the historic and recent activity is the higher average anorthite content for the post-1971 AD plagioclases, which agrees with the more basic character of the hosting lava. Among the most noticeable variations, recent plagioclases also exhibit higher K, Rb, LREEs and lower Ba abundances than the historic ones, with the largest differences more evident at high anorthite (An) contents. Variations in anorthite content along core-to-rim profiles obtained on crystals with different types of textures for both the historic and recent eruptive periods were evaluated particularly versus Sr/Ba. At comparable average An contents, crystals characterized by oscillatory zoning, which are representative of near-equilibrium crystallization from the magma, display distinct Sr/Ba ratios (~6 in historic and ~17 in recent lavas). We suggest these features are primarily related to recharge of a new, geochemically-distinct magma into the storage and transport system of the volcano since 1971 AD. In addition to distinct trace element and textural characteristics of plagioclase, Sr diffusion calculations for plagioclase suggest that magma residence times are generally shorter for magmas erupted in recent times (i.e., post-1971 AD) compared to those erupted during the historic period. These estimations match well with the enhanced extension rate within the upper 10 km of the crust observed during the last decades, and are also in accordance with the increased eruptive frequency after the 1971 AD eruption.

Viccaro M., Giacomoni P.P., Ferlito C., Cristofolini R. 2010. Dynamics of magma supply at Mt. Etna volcano (Southern Italy) as revealed by textural and compositional features of plagioclase phenocrysts. Lithos, 116, 77-91.

Hydrothermal alteration, fluid entrapment, and paroxysm (Colli Albani Volcano, Italy)

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Keywords: hydrothermalism, metasomatism, Colli Albani.

Colli Albani is a quiescent volcano belonging to the Roman Magmatic Province. Several recent and historical hydrothermal manifestations in the Colli Albani area have been connected with CO_2 and other gases accumulation and release during tectonic activity (Funiciello & Giordano, 2010; Carapezza & Tarchini, 2007; Chiodini et al., 2012).

A multidisciplinary approach (including outcrop mapping, in situ permeability measurements, minero-petrographic and geochemical analyses) has been applied for understanding what are the main factors controlling gas entrapment and release in the west-southwestern sector of the Colli Albani area, where sulfur and sulfide mineralizations and strongly altered ignimbrites are exposed. The alteration acme corresponds to a narrow sector of active degassing at the top of a buried normal fault that acted as main conduit for magmatic fluid rising. Rock alteration fades away in 2-3 km from the fault and this is typified by the occurrence of localized and selective alteration structures within the ignimbrite succession. Based on the mineralogical assemblage, the steam-heated advanced argillic alteration facies can be attributed both to the fault-proximal and fault-distal domains. Geochemical signature of unaltered/altered rock pairs indicates that element accumulation/depletion is variable within the ignimbrite succession and within the same lithotype, accomplishing for a drastic change in rock petrography and permeability. The progress of the hydrothermal alteration can be framed in a spatio-temporal cyclic process in which mineral precipitation and fracture healing contribute to hydrothermal fluid entrapment and overpressure. The sudden release of hydrothermal fluids may be at the origin of the paroxysmal manifestations that characterized the final phase of the Colli Albani Volcano.

Carapezza M.L. & Tarchini L. 2007. Accidental gas emission from shallow pressurized aquifers at Alban Hills volcano (Rome, Italy): Geochemical evidence of magmatic degassing? J. Volcanol. Geotherm. Res., 165, 5-16.
Chiodini G., Tassi F., Caliro S., Chiarabba C., Vaselli O., Rouwet D. 2012. Time-dependent CO_2 variations in Lake Albano associated with seismic activity. Bull. Volcanol. 74, 861-871.
Funiciello R. & Giordano G. (Eds.) 2010. The Colli Albani Volcano. Special Publication of IAVCEI, 3. Geol. Soc., London, pp. 400.

SESSIONE S23

Tracing isotopes for tracking processes: advances in radiogenic and stable isotope geochemistry

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The *Ursus spelaeus* lifestyle and feeding behaviour: a tale from Sr isotope studies

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Keywords: In situ Sr isotopes, Ursus spelaeus's habitat, fossils bones and teeth

The work presented here is focused on the chemical and isotopic characterization of some fossil remains of *Ursus spelaeus* founded in the Grotta all'Onda cave, at Camaiore (Tuscany, Italy). The principal aim of this study is the reconstruction of the lifestyle and feeding behavior of one of the major mammals living in the region during last interglacial phase. To pursue our purposes we follow a new analytical approach based on the application of *in situ* Sr isotopes on tooth and bones collected by the *Ursus spelaeus*'s skeleton. The idea is to possibly trace and determine the relationship between the animal and the territory in which he lived.

All wet chemical analyses have been carried out using ICP-MS Laser Ablation at the Natural History Museum of London, while microprobe and isotopic analyses have been performed using a Jeol JXA9600 at the Laboratory of Microanalysis of the CNR-IGG in Florence and a Microdrilling device plus Triton Thermal Ionization Mass Spectrometer (TIMS) at the Laboratory of Isotope Geochemistry of the University of Florence, respectively.

Major element analyses establish that bioapatite is more mineralized in enamel than in dentin and bone samples. Trace element analyses show distinct contents between tooth enamel and dentin among all the samples analyzed, with dentin generally enriched in trace elements, such as V, Sr and Ba.

Teeth and bones have variable Sr isotope composition with bones and dentin being less radiogenic than the enamel. The tooth enamel samples (the mineralized portion) can be considered unaffected by diagenetic alteration and, in addition to higher $^{87}Sr/^{86}Sr$, have also lower Sr/Ca than other organic-rich samples (bones and dentin). The latter have indeed an isotopic composition pointing to that of soils in which they were found, testifying, despite the recent age of the fossil specimens (40 ka), the occurrence of *post mortem* exchange process. The tooth enamel samples can instead be feasibly used to trace the living habitat of the *Ursus spelaeus*, and their Sr isotope signature is consistent with the Triassic carbonate formation (*Calcare Massiccio)* of the Tuscan nappe outcropping in the surrounding of the Grotta all'Onda cave.

Considering major and trace element composition of enamel samples, the only samples not affected by *post mortem* exchange processes, we can gain information on the dietary habits of the studied *Ursus spelaeus*. Given the well-known Ca biopurification process along the trophic chain (soil ® plants ® herbivores ® carnivores), the Sr/Ca and Ba/Ca of enamel samples indicate that the Grotta dell'Onda *Ursus spelaeus* was probably herbivore. This interpretation, however, should be considered carefully and would need to be corroborated by further investigation, by comparing paleontological with geochemical data, taking also into account the soil composition (both trace and isotopes) in which the *Ursus spelaeus* have been found.

Multiple isotope approach to unravel the sequence of water-rock interaction and hydromagnesite precipitation at Montecastelli (Tuscany)

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Keywords: serpentinite, brucite, CO_2 mineral sequestration.

Atmospheric carbon dioxide is spontaneously sequestered through the weathering and subsequent carbonation of serpentinite outcrops at Montecastelli (Tuscany, Italy). The three selected studied areas consist of: i) serpentinite escarpment close to a spring water; ii) gangue materials dumped in front of the entrance of a serpentinite-hosted copper mine; and iii) the main tunnel of the serpentinite-hosted copper mine. The three sites are characterized by high humidity and the serpentinite rocks appear whitish in color, completely coated by a thin carbonate crust. XRD analyses indicated that precipitated minerals of the carbonate crust are, in different proportion, hydromagnesite, nesquehonite, manasseite, pyroaurite, brugnatellite, very often in association with aragonite. No silica (quartz, opal, chalcedony) has been detected. Serpentinite host rocks do not evidence any pervasive alteration and/or dissolution, with the exception of localized carbonate late veins. In addition, these rocks contain significant amount of brucite, not often recovered in oceanic serpentinites. The emerging waters, sampled in the three areas, have high pH, relatively high TDS (Total Dissolved Solids) and high Mg/Ca molar ratio with respect to the meteoric water, indicating that the chemical compositions are controlled by interaction of rainwater with serpentinite host rocks. Isotopic analyses ($\delta^{18}O$, $\delta^{2}H$, $^{87/86}Sr$) of rainwaters, emerging waters, serpentinites and carbonates highlighted that the carbonates have been precipitated from superficial waters circulating into the serpentinite bodies. Overall, our data point to an on-going rapid uptake of atmospheric CO_2, triggered by high humidity and presence of magnesium oxide (brucite) into the rocks. At low temperature, brucite dissolves easier then serpentine minerals, as already reported in some occurrences of weathered serpentinites. This natural process introduces new application on the carbon mineralogical sequestration and its study could open new solutions for the environmental sustainability and GHG reduction.

Dating the lithospheric mantle: A comparison of Re-Os ages in single sulfides and whole-rock in cratonic mantle xenoliths from Somerset Island (Canada)

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Keywords: lithospheric mantle, Somerset Island, platinum group elements, Os isotopes.

Dating mantle rocks aims at constraining ages of partial melting as well as the possible crust-mantle genetic relationships. The Re-Os isotopic system, based on the radioactive decay of ^{187}Re into ^{187}Os, is the chronometer of choice to undertake mantle samples dating. Nevertheless, mantle xenoliths have generally experienced a complex petrological history often consisting in partial melting and later metasomatic overprinting events. However, meaningful chronological constraints on these petrological processes can still be obtained by Re-Os dating of single sulfide grains, the main host-phases of Os in mantle lithologies, whose origin might be related to discrete processes (i.e. metasomatism or mantle melting). Mantle xenoliths from Somerset Island show a large range in Re-Os model ages (2.7-1.3 Ga) correlating with increasingly metasomatism-overprinted HSE signatures. Four mantle peridotites showing representative whole-rock Re-Os model ages and HSE signatures of the full Somerset Island suite were selected to unravel the complex petrological history of the lithospheric mantle root under Somerset. Individual sulfides (down to 20 micron across) were micro-sampled from thick sections, with Os extracted via μ-distillation and analyzed by N-TIMS. In three xenoliths, sulfides have preserved Archean Re-Os model ages (T_{RD}) of 2.8 Ga, likely corresponding to the timing of sub continental lithospheric formation. The 2.8 Ga age is not recorded in the whole rock suggesting that sulfides have the ability of preserving the original Os isotopic composition inherited during mantle melting. These 2.8 Ga Re-Os model ages are recorded in primary inclusions in olivine or in inner portion of altered sulfides. The second group of sulfides is characterised by extremely radiogenic Os isotopic composition corresponding to future model ages. Those sulfides are clearly related to later metasomatic processes (e.g. kimberlitic infiltration). The third group of sulfides shows intermediate ^{187}Os isotopic composition, yielding Re-Os T_{RD} ages of 2.0-2.2 Ga and 1.7-1.9. Both age ranges correlate with crustal events having been recorded in Somerset Island as the 2.0 Ga Thelon Orogeny, which marks the collision of the Slave and Rae cratons, and the 1.7 Ga magmatic events characterised by plutonic intrusions. Our findings highlight that mineralogical and textural investigations along with Os isotopic measurements of sulfides provide robust chronological constrains able to unravel the complex petrological evolution of lithospheric mantle roots.

Cross-study of different isotopic systems in high-pressure ultramafic rocks reveals mass transfer at subduction zones (Cima di Gagnone, Central Alps)

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Keywords: boron isotopes, mass transfer, ultramafic rocks.

The use of isotopes for tracing processes occurring at plate boundaries led to important advancements in understanding the geochemical evolution of the Earth. In particular, across-arc boron (B) isotope variation enabled to define fluid-mediated mass transfer in subduction zones and the genesis of arc lavas. Subsequently, isotopic studies of high-pressure terrains allowed to examine the possible sources of fluids triggering mantle metasomatism and partial melting. Recently, many studies indicate the plate interface as primary site for fluid/rock interaction and element exchange between different subduction reservoirs, with major global implications. To understand interaction between these reservoirs, we examined the lithospheric mélange from Cima di Gagnone (Central Alps; Trommsdorff, 1990). Here, de-serpentinized chlorite harzburgite and garnet peridotite bodies are embedded in metasediments, same as occurs in top-slab melanges (Scambelluri et al., 2014). An original oceanic setting has been established for some chlorite harzburgite lenses enclosing MORB-type eclogite and metarodingiite. The whole rock-suite (peridotite, eclogite, metarodingite, paraschist) shows low δ^{11}B (-3 to -12 ‰). In a d^{11}B vs. B/Nb plot, ultramafic rocks fall on a trend between high-pressure serpentinites (with high B and d^{11}B up to 20 ‰) and host metasediments. Coherently with the mélange concept, this points out interaction between the above rock systems that reset the isotopic signature of the ultramafic rocks. This is clearly recorded by the Sr and Pb isotopic composition of ultramafic rocks, whose enrichment in radiogenic Sr and Pb (^{87}Sr/^{86}Sr=0,7124; ^{206}Pb/^{204}Pb=18,837) indicates fluid-mediated exchange with metasediments. Moreover, metaperidotite enrichment in fluid-mobile elements removed at low-temperature, like As and Sb, suggests that exchange took place since the early stages of subduction. These features provide clues to understand accretion of peridotite and sedimentary materials in plate-interface subduction channels, and related mass transfer from slab-to wedge.

Scambelluri M., Pettke T., Rampone E., Godard M. & Reusser E. 2014. Petrology and Trace Element Budgets of High-pressure Peridotites Indicate Subduction Dehydration of Serpentinized Mantle (Cima di Gagnone, Central Alps, Switzerland). Journal of Petrology, 55, 459-498.

Trommsdorff, V. (1990). Metamorphism and tectonics in the Central Alps: The Alpine lithospheric mélange of Cima Lunga and Adula. Mem. Soc Geol It., 45, 39-49.

Effects of sulphur degassing in komatiite-hosted Ni-PGE ores at Wannaway, Yilgarn Craton, Western Australia

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Keywords: komatiite ore, degassing, in-situ sulfur isotopes.

Drillcores of a complete mineralized sequence involving a komatiite-hosted metallic sulfide layer give a unique opportunity for studying the mechanisms of Archean Ni-Fe-PGE metallogeny. The Wannaway Ni-PGE sulfide deposit is located in the Ni-rich Kambalda Domain, Western Australia. The drilled sequence includes a sulfide-rich orebody occurring at the base of a komatiite flow overlying sulfidic black shales and metabasalts with remarkably well preserved, pristine features in spite of low- to mid-metamorphic imprint. In the orebody a basal massive sulfide layer grades to matrix-disseminated facies upwards where sulphides are intergrown with silicates. The ore consists of FeS (pyrrhotite-troilite)-pentlandite assemblage with minor sphalerite, Cr-Fe spinels, and accessory PGE-bearing Ni-Co-Bi-As/Te sulfosalts, chalcopyrite and alabandite. Sulfidic black shales host Fe-Zn-Cu-Pb-Ni sulfides and PGE-rich Ni-Co-Bi-As/Te sulfosalts with distinct chemistry. Significant changes are observed in the primary ore assemblage and phase chemistry with stratigraphy. Such features may correlate with factors involved in the ore genesis: role of wallrocks in S saturation of magma, role of coexisting immiscible S, As and Te liquids in PGE enrichment, and, especially, mechanisms of degassing of volatile components (S, O) during the crystallization of the metallic magma layer. S degassing is recorded in progressive changes in the ore chemistry culminating in the crystallization of a primary, S-poor troilite-sphalerite-pentlandite-alabandite-magnetite assemblage in the degassed upper part of the ore sequence. This study was also the basis for in-situ, ion probe multiple S isotope analyses on dominant Fe-Ni sulfide phases across the whole ore sequence. Plots of $\delta^{34}S$ vs. $\Delta^{33}S$ compare the effects of mass-dependent ($\delta^{34}S$) to the mass-independent fractionation index $\Delta^{33}S$, the latter fingerprinting Archean crustal S reservoirs characterized by intense photochemical reactions between S-bearing gases and unshielded cosmic UV rays (Jamieson et al. 2006). Both ore and black shale clusters plot at positive non-zero values of $\Delta^{33}S$, coping with S saturation of magma via assimilation of S-rich sediments. A remarkable feature is the flat $\Delta^{33}S$ arrays for both ore Fe sulfide and pentlandite, which are in textural, chemical and isotopic equilibrium. Both phases display shifts in $\delta^{34}S$ values related to stratigraphy and chemistry, and testify progressive lowering of $\delta^{34}S$ signatures from basal massive ore upwards. Such a trend may correlate with intense isotopically heavy SO_2 outgassing of the lava (Marini et al. 2011).

Jamieson J.W., Wing B.A., Hannington M.D. 2006. Evaluating isotopic equilibrium among sulfide mineral pairs in Archean ore deposits: case history from the Kidd Creek VMS deposit, Ontario, Canada. Econ. Geol., 101, 1055–1061.
Marini L., Moretti R., Accornero M. 2011. Sulfur Isotopes in Magmatic-Hydrothermal Systems, Melts, and Magmas. Rev. Mineralogy & Geochemistry, 73, 423-492.

Mo and stable U isotopes as tracers for subduction components in the Quaternary West-Mediterrean potassic and ultrapotassic magmatism

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Keywords: Mo and U stable-isotopes, geochemical tracers, Italian potassic magmatism.

The central-western Mediterranean is one of the most important areas on Earth for studying subduction-related potassic and ultrapotassic magmatism. In a very restricted area, leucite-free (lamproite) and leucite-bearing (kamafugite, leucitite, and plagioleucitite) ultrapotassic rocks have been emplaced and are associated with shoshonites and high-K calc-alkaline volcanic rocks.

Despite their alkaline characteristics, the least evolved Italian ultrapotassic rocks associated with destructive plate margins invariably show a strong depletion of Nb and Ta along with the highest levels of incompatible trace elements ever seen in any volcanic arc. These characteristics are thought to be derived through the recycling of sediments via subduction within the mantle wedge, and their extreme trace element enrichments make them unique for understanding the roles of different subduction-related metasomatic agents (e.g. silico-clastic vs carbonate). In fact, the variable compositions of the sedimentary materials, subducted along the Adriatic slab and transported into the overlying mantle forming a vein network, could explain the distinct geochemical signature of each Italian magmatic region (Avanzinelli et al., 2009).

We propose to investigate this issue considering two stable isotopic systematics that are perceptive to redox condition-related isotopic fractionation. We measured Mo and stable U isotopes with the high-resolution MC-ICP-MS (Neptune), using a double-spike technique, on selected volcanic rocks from three Italian magmatic provinces and representative samples of subducting sediments.

Molybdenum has seven stable isotopes, which have been shown to fractionate during the incorporation into oceanic sediments. Under oxic conditions, Mo adsorbs to particles into the sediment, particularly when Fe-Mn oxides are present, producing lighter isotopic composition ($\delta^{98}Mo/^{95}Mo$), whilst is quantitatively removed in anoxic conditions, leaving sediments with a heavier isotopic signature. The recently observed variability in natural $^{238}U/^{235}U$ values (different from the widely used "consensus" value of 137.88) due to isotopic fractionation during the redox transition between the U(IV) and U(VI) oxidation states, produces as well as Mo isotopes, a lighter isotopic composition ($\delta^{238}U/^{235}U$) in oxic sediments compared to a heavier composition in anoxic sediments. We interpret those results in order to recognize the U and Mo isotopic signature of sediments, with different lithology and chemical composition, recorded into the selected volcanic rocks, and to set new constraints on the metasomatic agents responsible for the transition from silica oversaturated lamproite-like to strongly silica undersaturated HKS magmas.

Avanzinelli R., Lustrino M., Mattei M., Melluso L., Conticelli S. 2009. Potassic and ultrapotassic magmatism in the circum-Tyrrhenian region: Significance of carbonated pelitic vs. pelitic sediment recycling at destructive plate margins. Lithos, 113, 213–227.

Chromium isotopic signature of naturally Cr (VI) contaminated spring waters from Western Tuscany

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Keywords: chromium isotopes, serpentinites, spring waters.

Weathering of serpentinites produces soils and sediments with high Cr concentrations. High Cr (VI) contents (up to 50 µg/l) have also been found in some spring waters spilling out from serpentinite bodies that outcrop in Cecina Valley (Western Tuscany). Petrographic and minero-chemical analyses of both rocks and soil samples highlight the occurrence of minerals able to release Cr (III) but the scarce presence of Mn-oxides, able to rapid oxidise Cr(III), implies that local presence of Cr (VI) in waters have to be ascribed to other processes.

With the aim of enhance the understanding of serpentinite rocks weathering processes, and Cr mobility, radiogenic (Sr-Pb) and Cr isotope composition of serpentinites, soils and spring waters coming from Western Tuscany selected sites have been performed.

Sr-Pb isotopes of serpentinites evidence a significant interaction with recent, low-T, waters; all spring waters display Mg-HCO3 chemical composition but a Sr-Pb isotopic signature isuggest low interaction with serpentinite bedrocks. Cr isotopes are generally used to investigate Cr(VI) reduction occurred in contaminated ground waters, during biotic and abiotic processes, which produces a strong positive fractionation of residual unreduced Cr(VI) as well as a powerful tool for to reconstruct the redox state of ancient sea water. Nevertheless, little is know about fractionation effects accompanying Cr (III) oxidation although small positive fractionation has been experimentally demonstrated. The spring waters preliminary investigated for Cr isotopes are strongly positively fractionated (δ^{53}Cr values between +0.5 and +2.6‰) as observed in other naturally Cr (VI) contaminated ground waters (Izbicki et al., 2008). The observed strong positive fractionation can be the result of both Cr oxidation and partial back reduction of soluble Cr (VI). Differently the investigated serpentinite bedrocks display very low δ^{53}Cr values (-0.2 and -0.3‰) compared to those reported in literature for this type of rocks (Farkaš et al., 2013).

Izbicki J.A., Ball J.W., Bullen T.D. & Sutley S.J. 2008. Chromium, chromium isotopes and selected trace elements, western Mojave Desert, USA. Appl. Geochem. 23, 1325–1352.

Farkasˇ J., Chrastný V., Novák M., Čadkova E., Pašava J., Chakrabarti R., Jacobsen S.B., Ackerman L. & Bullen T.D. 2013. Chromium isotope variations (δ^{53} Cr) in mantle-derived sources and their weathering products: Implications for environmental studies and the evolution of δ^{53} Cr in the Earth's mantle over geologic time. Geochimica et Cosmochimica Acta, 123, 74–92.

The hare as a climatic proxy for south-eastern Turkey

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Keywords: Stable isotopes, climate change, Holocene, hare, Turkey.

The study of fossil skeletal remains by stable isotope analysis can give information related to environmental and climatic conditions that may integrate different archeological surveys.

The archeological site of Arsalantepe (Malatya, Turkey) represents a very interesting case study. The systematic excavation has been carried out through a stratigraphic approach since the sixties, by University Roma La Sapienza. This allowed analyzing skeletal samples from a time interval between 6000 and 1500 B.P., that was characterized by regional and global climatic changes (Frangipane, 2012).

In the site many faunistic species were found, both domestic and wild. Hare (*Lepus capensis*) is present in every stratigraphic interval. Data in literature show that hares are characterized by an inverse relationship between the relative humidity and the $\delta^{18}O$ values of the skeletal phosphate, suggesting the use of hare fossil bones as a record of relative umidity conditions (Delgado Huertas et al.,1995).

Considering the existence of a relation between carbonate $\delta^{18}O$ and phosphate $\delta^{18}O$ (Iacumin et al., 1996), and the greater easiness in sample preparation, the analyses were performed on the bone carbonate fraction ($\delta^{18}O_{carb}$). The $\delta^{13}C$ on the carbonate and collagen fraction and the $\delta^{15}N$ on collagen were also measured. A significant variation of $\delta^{13}C_{carb}$ and $\delta^{15}N_{coll}$ between different levels was found: a clear positive peak was recorded in level VIA (5300-4950 B.P.), which is in good agreement with the heavy drought that happened in the Mediterranean areas in 5200 B.P.(e.g., Staubwasser & Weiss, 2006).

The obtained results prove that isotopic signals of this species are a good proxy for the reconstruction of the relative variation of humidity in the history of Arslantepe.

Delgado Huertas A., Iacumin P., Stenni B., Sanchez Chillon B. & Longinelli A. 1995. Oxygen isotope variations of phosphate in mammalian bone and tooth enamel. Geochimica et Cosmochimica Acta, 59, 4299-4305.

Frangipane M. 2012. Proceedings of the conference "Fifty years of excavations and researches at Arslantepe-Malatya (Turkey). The contribution of La Sapienza University to the study of the earliest centralized societies". Rome, December 5-7, 2011.

Iacumin P., Bocherens H., Mariotti A. & Longinelli A. 1996. Oxygen isotope analyses of coexisting carbonate and phosphate in biogenic apatite: a way to monitor diagenetic alteration of bone phosphate?. Earth and Planetary Science Letters, 142, 1-6.

Staubwasser M. & Weiss H. 2006. Holocene climate and cultural evolution in late prehistoric-early historic West Asia. Quaternary Research, 66, 372-387.

The evolution of stable S-isotopes in poly-metamorphosed sulfide deposits from the Italian Western Alps

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Keywords: sulfur isotopes, high pressure metamorphism, fluid-rock interaction.

Devolatilization reactions in subducting slabs produce H_2O- and CO_2- dominated fluids which take part in metamorphic reactions and enhance element mobility. Although sulfur is a minor component of subduction-related fluids, it can play an important role in mobilizing normally un-reactive calcophile and siderophile elements (potentially to be released into mantle wedge) and in taking part in oxidation-reduction reactions.

Evidence of fluid-rock interaction, mineral replacements and/or re-crystallization during metamorphism can be recorded by sulfides and give insights on the mobilization of sulfur and metals in subduction related processes.

On this basis, mineralized samples from two ocean floor-related sulfide deposits (Servette and Beth-Ghinivert in the Italian Western Alps), with different HP to greenschists facies poly-metamorphic evolutions, were investigated with a detailed micro-textural and isotopic study by means of in situ analyses of S-isotopes ratios.

In situ $\delta^{34}S$ values within individual pyrite and chalcopyrite grains were interpreted combining micro-textural, mineralogical and geochemical analyses which allowed to assess the effectiveness of metamorphism in modifying the isotopic record. Evidence of fractionation of stable sulfur isotopes between sulfides and fluids was utilized as a tool to identify fluid-rock interaction processes and mobilization of sulfur during metamorphism.

Ocean-floor related features are well preserved at Beth-Ghinivert even at the micro-scale and very little metamorphic overprint is recorded by the sulfides mineralization. At Servette evidence of metamorphic textures is widespread and sub-millimeter scale modifications of $\delta^{34}S$ values occur, indicating interactions with an infiltrating hydrothermal fluid. However, none of the deposits record diffusive metamorphic re-equilibration at the deposit scale and largely preserve isotopic records and mineralogical features ascribable to ocean-floor metasomatism.

The preservation of pre-Alpine isotopic features is here interpreted as a consequence of negligible fluid/rock interaction (i.e. limited fluid release) and negligible sulfur release during subduction-exhumation metamorphism. As a consequence, the contribution of sulfur to the mobility of chalcophile and siderophile elements is minimized to the conditions experienced by the two deposits.

This study evidences the key-role of the amount of circulating fluids and of deformation in determining the isotopic evolution of subducted sulfide deposits and in favoring sulfur release during metamorphism.

The mantle isotopic printer

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Keywords: isotope geochemistry, mantle, petrology, mantle plumes.

Computer printers can reproduce all the range of colours using a limited number of colours (black, magenta, yellow, cyan). Similarly, the isotopic composition of oceanic basalts and nearly all the continental counterparts can be expressed in terms of very few mantle end-members (the equivalents of the colour reservoirs). The four most important (actually, "most extreme" since some of these are extraordinarily rare) mantle end-members identified by isotope geochemists nearly thirty years ago are DMM or DUM (Depleted MORB Mantle or Depleted Upper Mantle), HiMu (High-Mu, where Mu = 238U/204Pb), EM-I and EM-II (Enriched Mantle type I and type II). Other mantle end-members, or components, have been proposed (PHeM, FoZo, LVC, PreMa, EM-III, CMR, LoMu, C, and so on) but these can be considered as less extreme components or mixtures in the geochemical mantle zoo, to mix metaphors.

Various petrogenetic models have been proposed to explain the presence, the abundance, the physical state and the origin of the four principal mantle end-members. Models differ from thermodynamic engines in that the latter must be constrained by thermodynamics, in particular the 2nd Law. All the basic mantle "colours" are present in a relatively restricted area concentrated E of Australia, in the Polynesia-Melanesia-Micronesia region. With the exception of DMM/DUM all the other mantle end-members require the involvement of olivine-poor lithologies. These lithologies have been attributed to recycled upper/lower continental crust rocks, recycled oceanic crust, terrigenous and/or pelagic sediments, kimberlites, carbonatites, sulphides, oxides or simply frozen basaltic melts crystallized at depths. Thermal anomalies are not associated with or required to explain these end-members. A small degree of melting is sometimes invoked to explain absolute trace element contents or the trace element fractionation recorded in submarine to subaerial lavas. Shallow degassing and contamination is implied in noble gas systematics.

It is the shallow anomalies that are responsible for intraplate volcanism. Mantle plumes and a fully convecting mantle are based on assumptions that violate physical, mineralogical and cosmological considerations. Physically realistic Earth models have a thick upper thermal boundary layer, characterized by superadiabatic thermal gradient, with a thickness in the order of 200-250 km. This is sufficient to explain three out of the four mantle colours in terms of shallow mantle dynamics, e.g. plate tectonics. Such a thermodynamically self-consistent model eliminates the need for lower mantle involvement in oceanic basalt petrogenesis and in igneous activity in general. All the isotopic colour cartridges can be placed at shallow depths.

Origin and evolution of Po river water (Northern Italy): insights from geochemical and isotopic ($\delta^{18}O$- δD) data

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Keywords: geochemical data, isotopic data, Po river, Northern Italy.

The Po river is the most important fluvial system of Northern Italy and the related basin, the Padanian Plain, is strongly influenced by urban settlements, as well as by industrial, agricultural and zootechnical activities.

In spite of its importance, systematic geochemical and isotopic investigations of its water are rare, difficultly accessible and never reported for the whole basin scale. The present contribution aims to fill this knowledge gap, reporting a comprehensive data-set including oxygen and hydrogen stable isotopes, as well as major and trace element concentration of dissolved species for 54 Po river water samples collected in different seasons at increasing distance from the spring, i.e. from the upper part of the catchment to the terminal (deltaic) part of the river at the confluence with the Adriatic Sea.

The isotopic compositions demonstrate that the predominant part of the runoff derives from the Alpine sector of the catchment through important tributaries such as Dora Baltea, Ticino, Adda and Tanaro rivers, whereas the contribution of the Apennines tributaries is less important. The geochemical and isotopic compositions show that the Po river water attains a homogeneous composition at ca. 100 km from the spring. The average composition is characterized by $\delta^{18}O$ -9.8‰, δD – 66.2‰, TDS (Total Dissolved Solids) 268 mg/L, chloride 17 mg/L and by a general $Ca–HCO_3$ hydrochemical facies, which is maintained for most of the river stream, only varying in the terminal part where the river is diverted in a complex deltaic system affected by more significant evaporation and mixing with saline water evidenced by higher TDS and chloride content (up to 8,198 mg/L and 4,197 mg/L, respectively). A series of geochemical and isotopic maps have been carried out to visualize spatial gradients, which reflect the evolution of the river water composition at progressive distance from the source; more detailed maps were focused on the deltaic part in order to visualize the processes occurring in the transitional zone toward the Adriatic Sea. The data also highlight anthropogenic contributions, mainly represented by significant concentration of nitrate (average 8 mg/L) and possibly arsenic (average 12 µg/L), which have to be monitored to minimize environmental risks. On the whole the data allow the calculation of geochemical fluxes transferred by the river to the sea, and more in general contribute to the definition of a "hydro-archive" which is useful to highlight ongoing variation in the related ecosystems.

Conservation of $^{87}Sr/^{86}Sr$ isotopic ratios in the oenological food chain of "Red" wines to validate their use as geographic tracer

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Keywords: Sr isotopes, geographic traceability, wines.

The use of $^{87}Sr/^{86}Sr$ in tracking wine regional provenance was among the most pioneeristic application of isotope geology to other sciences. In most of the cases, however, the analytical uncertainty observed in Sr isotopes analyses of wines from literature is larger than most of the rock/soil isotopic variability, giving strong difficulties in matching data of wines with those from geological substrata of the vineyards. Recently, high-precision analytical method for determining $^{87}Sr/^{86}Sr$ has been provided enabling then the direct comparison between data on wines with those of the geological substrata. Although the use of high precision Sr isotopic measurement, in some case discrepancies have been observed between the $^{87}Sr/^{86}Sr$ ratios in wine with those of geological material of the substrata of the vineyards. This might be due either to adulteration of the analysed wines or to processes related with the oenological chain from the Sr uptake by the roots of the vine to the winemaking process.

With this contribution we present a detailed study on the distribution of $^{87}Sr/^{86}Sr$ in the complete food-chain of an Italian "Red" wine with the aim of verifying the occurrence of $^{87}Sr/^{86}Sr$ decoupling between the wine and the geological substratum (i.e., rocks). We determined $^{87}Sr/^{86}Sr$ in soil, grape, grape juice (must), and wine on four different farms from the broad "*Cesanese*" wine region. The "*Cesanese*" cultivar is a red Italian grape variety that is grown primarily in the Latium district, Central Italy. The "*Cesanese*" Red wine is produced using 100 % of the homonymous grape and it is regulated and certified through three geographically distinct production areas: the *Cesanese di Affile*, *Cesanese di Olevano* DOC, and *Cesanese del Piglio* DOCG. The selected wineries cover the three distinct DOC areas and they are from a geologically and geochemically well defined region, from which a wide isotopic set of data for volcanic rocks is available.

Our data indicate that all of the wines, musts, and grapes from different vintages have an excellent reproducibility of their Sr isotope composition within each single vineyard, independently from the nature of the substratum, climate, altitude, geomorphology, and water availability. These data also demonstrate that Sr isotopes are not affected by the wine-making process as we obtained the same Sr isotope composition in grape, must, and bottled wine. This evidence indicates a good manifacture practices of the different producers (i.e., without artificially adulterating the wine organoleptic characteristics).

With this study we corroborate and validate the use of $^{87}Sr/^{86}Sr$ as a robust geochemical parameter that, in addition to organoleptic characteristics, is apt to trace the authenticity of the geographic provenance of high-quality red wines of the Consortium of Cesanese, Latium, Italy.

IMS 1280-HR: a versatile ion microprobe for Geosciences

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Keywords: sims, geochronology, geochemistry.

SIMS (Secondary Ion Mass Spectrometry) is applied to a variety of applications in Geosciences, because it provides *in situ* measurement of elemental and isotopic composition in selected µm-size areas of the sample.

The IMS 1280-HR is a large geometry magnetic sector ion microprobe delivering unequalled analytical performance for a wide range of applications: tracking geological processes using stable isotopes, dating minerals, determining the content of trace elements, screening and analyzing large numbers of particles.

High density cesium or oxygen primary ion beam bombardment combined with optimized transmission allow high precision stable isotope studies and analysis of trace elements at high sensitivity (e.g. mandatory for Pb analyses in Zircon). The multicollector system ensures ultimate reproducibility for stable isotope ratio measurements (H, C, O, S, Li, B, Mg...) and significantly increases the throughput of the instrument by reducing the total acquisition time. Thanks to its superior imaging capabilities (both microscope and microprobe), the IMS 1280-HR is capable of mapping the distribution of major, minor and trace elements or isotopes at sub-micron lateral resolution.

Hundreds of scientific papers have been published covering major application fields in geo- and cosmochemistry, geochronology, environmental studies,... A review of recent analytical data obtained with the IMS 1280-HR on different domains will be presented, among which:

Hydrogen / Deuterium analysis in apatite from lunar rocks. The determination of the isotopic signature and amount of lunar water has profound implications for our understanding of the history of the Earth-Moon system.

Oxygen isotope ratio analyses in zircon. O isotopic signatures in zircon are used to infer magmatic and pre-magmatic histories, including the presence of liquid water on the surface of earliest Earth.

Sulfur isotope ratio analyses in olivine-hosted sulphides from ocean island basalts. Basaltic lavas at some oceanic intraplate hotspot volcanoes are thought to sample ancient subducted crustal materials.

Magmatic dating of individual crystals from the Yellowstone supervolcano. U-Pb and U-Th dating measurements combined with oxygen isotope analyses allow to investigate the genesis of voluminous post-caldera rhyolites.

Martian meteorite age using micro-baddeleyite: U–Pb isotopic analyses of resistant micro-baddeleyite (ZrO_2) and host igneous minerals performed in a basaltic Martian meteorite in order to distinguish between the ages of formation and the ages of the impact events (that launched debris towards Earth).

SESSIONE S27

Microstructures: characterization, interpretation and modeling as a key to deformation and reaction mechanisms, and technological processes

CONVENORS

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Natural and laboratory compaction band in porous carbonates: a 3D characterization using synchrotron X-ray microtomography

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Keywords: porous carbonates, compaction bands, porosity, connectivity, X-ray computed microtomography.

Porous carbonates form important reservoirs for water and hydrocarbons. Post-depositional processes (e.g. mechanical) are important to quantify because they may affect the fluid flow properties of reservoirs. Field-based studies (Tondi et al., 2006; Rustichelli et al., 2012) described bed-parallel compaction bands (CBs) within carbonates with a wide range of porosities. These CBs are burial-related structures, which accommodate volumetric strain by grain rotation, grain translation, pore collapse and pressure solution. Cilona et al. (2012) performed triaxial compression experiments, under dry conditions on the porous cretaceous grainstones (the Orfento Formation, in Majella Mountain, Abruzzi), reproducing for the first time CBs in laboratory. In this work, the authors defined the pressure conditions at which natural CBs form and documented the role of Hertzian cracks for grain size and porosity reduction within the CBs.

Here we use a new methodology to characterize the pore networks of natural and laboratory CBs and compare them with the host rock one.

Data were collected using the synchrotron X-ray microtomography technique at the SYRMEP beamline of the Elettra-Sincrotrone Trieste Laboratory (Basovizza (Trieste), Italy). Quantitative analyses of the samples were carried out using the Pore3D software library (Brun et al., 2010). The porosity was calculated from segmented 3D images of deformed and pristine rocks. The process of skeletonization, which provides the number of connected pores within a rock volume, was applied. By analyzing the skeletons we were able to highlight the differences between natural and laboratory CBs, and to investigate how pore connectivity evolves as a function of the deformation.

Preliminary results show that within compaction bands both pore volume and connectivity are reduced in comparison with the undeformed host rock. Natural CB has a lower porosity with respect to the laboratory one. In natural CBs, the contact among granules seem be welded, whereas in the laboratory CBs it shows pores with irregular shape.

Brun F., Mancini L., Kasae P., Favretto S., Dreossi D. & Tromba G. 2010. Pore3D: A software library for quantitative analysis of porous media: Nucl. Instrum. Methods Phys. Res. A, 615, 326-332.

Cilona A., Baud P., Tondi E., Agosta F., Vinciguerra S., Rustichelli A. & Spiers C.J. 2012. Deformation bands in porous carbonate grainstones: field and laboratory observations. J. Struct. Geol., 45, 137-157.

Rustichelli A., Tondi E., Agosta F., Cilona A. & Giorgioni M. 2012. Development and distribution of bed-parallel compaction bands and pressure solution seams in the Bolognano Formation carbonates (Majella Mountain, Italy). J. Struct. Geol., 37, 181-199.

Tondi E., Antonellini M., Aydin A., Marchegiani L. & Cello G. 2006. The role of deformation bands, stylolites and sheared stylolites in fault development in carbonate grainstones of Majella Mountain, Italy. J. Struct. Geol., 28, 376-391.

X-ray computed microtomography in geosciences

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Keywords: X-ray computed microtomography, X-ray phase-contrast imaging, image processing, rock textures.

X-ray computed microtomography (μ-CT) has become an invaluable technique for geologists, with wide applications in various geological disciplines. X-ray μ -CT is a non-destructive technique and it is based on both conventional and synchrotron radiation sources (Baker et al., 2012). This technique produces three-dimensional (3D) images of the internal structure of objects, determined by variations in morphology, mass density and/or chemical composition. It is a powerful tool for 3D investigation of several geological materials with spatial resolution at the micro- and submicron- scale. The possibility to visualize and measure textures in 3D is crucial for understanding the processes responsible for the formation of rocks. Therefore, all kind of rocks can be studied and the morphology of unique and precious samples (such as fossils) can be investigated in a non-destructive way.

This contribution provides an introduction to the principles of X-ray μ-CT and to the image analysis to study several geologic issues. Furthermore, different factors affecting the image quality and several image processing methods will be discussed.

The use of synchrotron radiation X-ray imaging in geosciences allows to dramatically improve the contrast and spatial resolution compared to conventional sources, allowing to perform highly precise quantitative analyses in rocks. X-ray phase-contrast imaging can also improve the visualization of features with small differences in mass density and chemical composition with respect to the rock matrix, so this technique is crucial to analyze geological samples characterized by several phases.

In this seminar several applications of X-ray μ-CT methodologies for the extraction of quantitative information from 3D images of geomaterials will be presented.

Important applications of X-ray μ-CT are e.g. the study of bubbles and crystals in volcanic rocks. Several studies of crystallization kinetics were carried out using two-dimensional images (e.g. Arzilli & Carroll, 2013) but recently these processes have been investigated using volumetric datasets. Another example is in the field of structural geology, where X-ray μ-CT was employed to study the porosity and connectivity of carbonates and how the localized deformation acts on their structure.

Arzilli F. & Carroll M.R. 2013. Crystallization kinetics of alkali feldspars in cooling and decompression-induced crystallization experiments in trachytic melt. Contrib. Mineral. Petr., 166, 1011-1027.

Baker D.R., Mancini L., Polacci M., Higgins M.D., Gualda G.A.R., Hill R.J. & Rivers M.L. 2012. An introduction to the application of X-ray microtomography to the three-dimensional study of igneous rocks. Lithos, 148, 262-276.

Microstructural characterization of raw and fired sanitary-ware vitreous body by Synchrotron Computed Microtomography

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Keywords: sanitary-ware ceramic, synchrotron X-ray microtomography, microstructure.

China whiteware products represent a large part of ceramic materials and cover a wide range of applications like tile, dinnerware and sanitary-ware. They are mainly formed by a vitreous body which comes from heating above 1100 C a mixture of clays, fluxing agents (typically feldspar) and fillers (typically quartz), after previous processing like, for example, aging, drying and body preparation (Carty & Senapati, 1998). Phase composition of vitreous body has been widely studied in past and is characterized by a glassy matrix with some crystalline phases like mullite, which forms upon heating, and residual filler (Martin-Marquez et al., 2009). Additionally, a well developed porosity can be present, with consequent implication on some technological properties of the materials like mechanical strength (Braganca & Bergman, 2003).

In the present investigation, four different industrial sanitary-ware compositions have prepared by fixing the “hard” compound (21 % feldspar, 19 % quartz and 6 % China whiteware waste) and by varying the “plastic” compound with four different industrial clay components (one per sample). After casting procedure, half of each sample was saved to investigate the packing of the green body whilst the other half was fired in a muffle furnace at the peak temperature of 1200 C to investigate the porosity of the fired product, for a total of eight samples.

All these eight samples, after previous XRPD characterization, have been investigated by Synchrotron Computed Microtomography at the SYRMEP beamline (Elettra, Trieste) in phase contrast modality.

Data reconstruction have been performed and the microstructure have been evaluated by processing slices with a Matlab written code. In particular, it was possible to focus on voids but also on zircon crystals that come from the 6 % of China whiteware waste, due to their “transmitted” signals which differ from the one of the other phases (i.e. quartz, mullite and glass).

For each sample, it was possible to characterize the volume of voids and zircon in terms of total volume and size distribution in the 10-1000 μm range; moreover, Higgins sphericity index and Flynn diagrams have been determined.

The results have been also compared with mercury porosimeter measurements.

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Comparison of Total Scattering data from gahnite nanocrystals

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Keywords: PDF, total scattering, nanospinels, synchrotron, in-house diffractometer.

Total scattering technique (X Ray Powder Diffraction) has been used to investigate the structure of nanocrystalline (and possibly disordered) spinel gahnite $ZnAl_2O_4$. This experimental method allows to use both the Bragg scattering (used in traditional crystallography) and the diffuse scattering, caused by anything that does not diffuse exactly following the Bragg law (such as defects, local distortions, etc.). High energy incident wave is required and three different instruments have been employed: (i) ID31 high resolution diffractometer at the ESRF (9 line detectors, all with crystal analyzers, (λ=0.3999Å), (ii) ID15B high energy beamline at the ESRF with 2D image plate detector (t), (λ=0.1421Å) (iii) PANalytical diffractometer with silver anticathode, with an X'Celerator detector (λ=0.5608Å). In order to compare the three diffraction data sets, the related Pair Distribution Functions (PDFs) are presented. PDFs are functions in which peaks represent the correlations between all pairs of atoms and were obtained with PDFgetX3 (Juhas et al., 2013) that allows to scale, correct, and FT the diffraction data. The same procedure was applied to all data sets subtracting the relevant empty capillary scattering, and correcting and normalizing the data. Different functions for each data set have been calculated changing parameters, such as the background scale, to reduce noise in PDF and optimize the function. The PDFs were visually compared, and then were refined by means of PDFgui (Farrow et al., 2007), using the simplest possible model of a spinel (totally direct, with space group symmetry respected). All the refinements were made exactly in the same way, by refining the same parameters, for the sake of a fair comparison. Small differences in the refined structural parameters could be caused by different instrument's characteristics but also by parameters used in PDF calculation, so attention should be paid to the procedure of PDF attainment from total scattering data.

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Characterization, interpretation and modeling of the present day oceanic crust microstructure by using innovative techniques based on neutron diffraction and X-ray microtomograph

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Keywords: oceanic crust. neutron, microtomography.

Our understanding of the emplacement kinematics of submarine lavas and dikes is often limited to plan-view geometries of near-axis lava or tectonic windows exposing disrupted portion of oceanic crust. Instead, drilled cores provide in situ access to the intact internal microstrucure of submarine rocks. Two innovative methodologies revealing significant constraints on the mechanisms and forces involved in microstructure formation of present day drilled oceanic crust are here presented. These include (1) a neutron diffraction-based analysis for studying an off-axis submarine lava flow and (2) a X-ray microtomography-based analysis for studying the lava-dike transition, both achieved from the drilled oceanic crust of the ODP/IODP-Site 1256 (Cocos Plate).

Quantitative insights into submarine lava microstructures and strong evidence for NW-SE lava flow direction that is parallel to the paleo-ridge axis of the East Pacific Rise, are provided. In situ shear within submarine lavas revealed by composite shape and lattice preferred orientations of minerals, accounts for a dominant laminar non-uniform type flow.

Since porosity and porous shape, as well as permeability strongly affect the physical properties of rocks, namely compressional-wave velocities, the porosity shape in basalt from the lava-dike transitionis has been achieved by synchroton X-ray microtomography (micro-CT) without requiring any sample preparation. Micro-CTimages enhance the phase-contrast between primary (igneous) minerals and alteration minerals now filling the pores. Overall, quantitative data of the volume and shape of the pores (at the sample scale) allow to evaluate the "empty" (effective) porosity or paleo-porosity (pores now filled with secondary minerals) in the investigated basalts, as well as the 3D-pattern of micro-cracks.

For the first time on present day oceanic basement and despite the environmental difficulties in the study of the subseafloor under deep water, this work shows that, by using only punctual data deriving from ocean drilling and non-destructive 3D analysis techniques it is possible to obtain detailed microstructural information on distinct stratigraphic basement layers possessing different emplacement mechanisms as well as various post-magmatic evolution.

3D distribution of primary melt inclusions in garnets by X-ray microtomography

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Keywords: Garnet, Melt inclusions, Microtomography, garnet, anatexis, melt inclusions, X-ray computed tomography.

Modeling the spatial distribution density of melt inclusions is important to understand the growth and trapping history of peritectic minerals and coexisting fluids/melts during the partial melting of the crust. X-ray computed microtomography (micro-CT) is well suited for this purpose, owing to its three-dimensional (3D) imaging capabilities and non-invasiveness. X-ray micro-CT has been applied here to investigate the 3D distribution of primary melt inclusions in almandine-rich garnets from El Hoyazo (Neogene Volcanic Province, SE Spain). Glassy inclusions are trapped in nearly all mineral phases in metapelitic enclaves found within El Hoyazo dacites and have been extensively analyzed in previous literature (e.g. Acosta-Vigil, 2007; Cesare, 2009).

X-ray micro-CT experiments based on a conventional microfocus source (Dept. of Geosciences, Univ. of Padova) and a synchrotron radiation source (the SYRMEP beamline, Elettra - Sincrotrone Trieste) were carried out on sub- to euhedral garnet crystals (1-5 mm in diameter). Despite the high X-ray absorption of the largest garnets, the internal features of the samples were successfully imaged, with spatial resolutions down to a few microns for synchrotron-based data. A multi-step image analysis procedure, specifically optimized for the investigated samples, was adopted to accurately segment melt inclusions from other non-relevant features within the garnets (e.g. fractures or muscovite crystals) that could not be adequately separated using simple grey values thresholding of tomographic data. This allowed to accurately measure characteristic size and shape parameters of melt inclusions and to calculate their spatial distribution density as a function of radial distance from the centre of the garnets. The 3D spatial distribution of other trapped mineral phases (e.g. monazite, zircon, apatite) was investigated as well, and compared with the distribution of melt inclusions.

Preliminary data analyses revealed the occurrence of a clear peak of melt inclusions density, ranging approximately from 1/3 to 1/2 radial distance from the centre of the distribution, while mineral phases appeared to be more randomly distributed. No evidence of a sharp boundary between inclusion-rich cores and inclusion-free rims was found. The results obtained so far, together with chemical profiles of the garnet composition obtained using SEM-EDS, suggest that the investigated garnets grew in one single event in the presence of anatectic melt, under a constantly decreasing melt supply.

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Bubble coalescence in magmas: Insights from in-situ high-temperature synchrotron-based X-ray tomographic microscopy

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Keywords: bubbles, volcanoes, synchrotron.

The possibility of removing gas from magma during its rise to the surface decreases the probability of an explosive volcanic eruption to occur. In this respect, bubble coalescence and the achievement of a permeable network play a pivotal role in favouring magma degassing and limiting the explosivity of eruptions. Significant growth and interaction between bubbles occur in natural volcanic systems during ascent of the magma to the surface. Thus, we performed real time, 4D, high-temperature experiments at atmospheric pressure using laser heating and synchrotron-based X-ray tomographic microscopy at the TOMCAT beamline of the Swiss Light Source (SLS). We forced gas exsolution in natural magmas and observed bubble nucleation and growth in situ. The experiments were performed from room temperature up to 1300 K on two different types of crystal-free rhyolitic samples: one vesicle-free obsidian and one obsidian containing pre-existing vesicles. We characterized the main textural variations (bubble volumes, size distributions, shapes, and bulk textures) during the nucleation and growth of bubbles in these highly viscous systems, and tracked the evolution of parameters such as viscosity and overpressure in the foaming samples, which are essential for retrieving information on the processes preceding an eruption from the interpretation of the textures observed in eruptive products. The microstructural features of the starting material, nominally the presence of initial vesicles, strongly influence the dynamics of bubble coalescence. The presence of bubbles in the starting material tends to limit coalescence, therefore increasing the possibility of bubble overpressure. A possible implication of these experiments is that volcanic systems where magma is volatile-saturated already in the subvolcanic reservoir may have a higher tendency to feed explosive volcanic eruptions.

Image processing of crystallized textures using phase-contrast synchrotron X-ray computed microtomography data

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Keywords: X-ray microtomography, image processing, phase-contrast imaging.

X-ray computed microtomography has become a fundamental tool in geosciences to study textures of igneous, metamorphic and sedimentary rocks directly in 3D. This technique is useful to study the vesiculation of pumices (Polacci et al., 2009), but only recently there has been more interest to study the crystallization process using volumetric datasets, where the phases of interest often have similar density. Therefore, image processing for these samples require more sophisticated procedures to separate crystals from silicate glass.

Feldspars are one of the most abundant crystalline phases of igneous rocks, hence their crystallization conditions and abundance are intensely investigated by geologists. Moreover, feldspar is one of the most difficult phases to segment during image analysis, making the separation of feldspars from the silicate glass a challenge.

Here we show that the crystallinity of natural and synthetic rocks could be studied using microtomographic datasets. In this case, a pumice from Stromboli and a synthetic trachyte from the Campi Flegrei were selected in order to separate plagioclases and alkali feldspars from the glass and bubbles.

Data were collected using the propagation-based synchrotron X-ray phase contrast microtomography technique at the SYRMEP beamline of the Elettra-Sincrotrone Trieste Laboratory (Basovizza (Trieste), Italy). Although propagation-based X-ray phase contrast imaging can improve the visualization of weakly absorbing features in a sample, making visible the edge of feldspars, the segmentation of these crystals cannot be directly obtained from the raw phase contrast X-ray images. Phase-retrieval methods are needed for extracting phases of interest (Beltran et al., 2010). A single distance phase-retrieval algorithm (Paganin et al., 2002) was applied to the dataset to improve the contrast between feldspar and glass in the reconstructed images; this allowed us to obtain a better segmentation for microtomographic data where the absorption contrast was too low. Through this technique we are able to isolate feldspars both in natural samples and in synthetic ones, and to perform quantitative analysis of these phases using volumetric datasets. Our preliminary results have demonstrated that phase retrieval processing will be an invaluable tool for geologists to study rock textures.

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The potential information contained in CPOs: modelling granulite facies quartz pole figures

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Keywords: Crystallographic preferred orientation, Modeling CPOs, Granulite facies metamorphism.

The activity of single slip systems during ductile deformation is strongly influenced by the resolved shear stress, the deformation temperature and the strain rate. Pole figures are therefore snap-shots of the deformation conditions of rocks during specific moments of the evolution of orogens and potentially can preserve information on the above mentioned factors. Furthermore, since pole figures vary with changing deformation paths, pure shear and simple shear components of deformation and hence vorticity can be ideally calculated. In order to test which information can be extracted from CPOs, we modelled quartz CPOs using the kinematic model of Kaminski and Ribe (2001, 2002), implemented with quartz slip systems data published by Beata and Ashbee (1969), Lister (1979), Lister and Hobbs (1980). In our contribution we compare numerically modelled CPOs with data measured on granulite facies migmatitic gneisses of Calabria and with published CPOs from the Saxony granulite terrain (Lister and Dornsiepen,1982).

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Submarine lava flow direction revealed by neutron diffraction analysis in mineral lattice orientation

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Keywords: lava flow, microstructures, neutron diffraction.

Submarine lava flows are the main constituent of young oceanic crust. Studying submarine lava flows is important for understanding the lava eruption and transport mechanisms, either at the ridge axis or off-axis. However, since submarine lava flows are often inaccessible, our knowledge of their internal structure is much less complete than that of better studied subaerial lava flows.

In submarine environment, the most well-known mid-ocean ridge off-axis lava flows occur near fast and superfast spreading ridges, such as the North East Pacific Rise (e.g., Alexander and Macdonald, 1996) and the South East Pacific Rise (e.g., White et al., 2002) as well as ultraslow spreading ridges (e.g., Standish and Sims, 2010). Such lava flows may be important constituent of the ocean crust, since their volumes, although highly variable, may be as high as few tens of km3 (e.g., White et al., 2002). Therefore, it is of great importance to understand the internal structure of submarine lava flows by in situ techniques, in order to unravel the emplacement mechanisms. The unique opportunity to examine the interior of an in situ and intact lava flow, which is normally inaccessible to seafloor investigations, is by drilling.

An investigation of a submarine lava flow drilled at ODP/IODP Site 1256 is performed by combining three-dimensional (3-D) Lattice Preferred Orientation (LPO) data, obtained by neutron diffraction, with bidimensional (2-D) Shape Preferred Orientation (SPO) data. The main purpose is twofold, i.e., (i) to unravel the transport direction and mechanism of a submarine lava flow by defining the internal microstructure of a drilled section of upper oceanic crust and (ii) to perform a quantitative LPO and SPO study on several ~cm^3 samples from the 1256D lava field discussing the development of different types of fabrics and therefore the dynamics and direction of the lava flow.

This work greatly benefits from neutron diffraction texture analysis, and indeed, this is the first study to present a microstructural analysis of a submarine drilled volcanic body, thus establishing a consistent method for inferring subaqueous lava flow direction on oriented core samples. In particular, our results contribute to the understanding of submarine lava flows that are emplaced off-axis, i.e., at a certain distance, from mid-ocean ridges that, although not uncommon, are still poorly studied.

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SESSIONE S33

Planetary Geology: frontiers of geological exploration, modeling and understanding

CONVENORS

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Aeolian Activity in Herschel Crater, Mars

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Keywords: Large Dark Dunes; Aeolian Processes; Herschel crater.

In this report, we present a study of a large dark dune field in Herschel Crater, a 300-km-diameter impact basin located close to the martian equator (14.4°S, 130°E).

We quantify the movement of the aeolian bed forms (ripples and dunes) using the High Resolution Imaging Science Experiment (HiRISE) datasets [1]. Dunes are migrating at the rate of ~0.45 meters per Martian year, while ripples are moving at the rate of ~ 1.46 meters per Martian year.

Both ripples and dunes are migrating toward the south, suggesting dominant winds blowing from the north to the south.

Furthermore, with the aid of the Mars Regional Atmospheric Modeling System (MRAMS) [2, 3] we compare the ripples and dunes morphologies and migrations with the modeled wind stresses and directions.

The modeled winds blow from the North and from the East seasonally, the interaction of these two wind regimes within the dune field might explain the complex pattern of the ripples while the modeled winds toward the south are in agreement with the observed ripple and dune migrations toward the south.

These results are congruous with the recent observations of ripple and dune migration in Gale Crater [4], the landing site of the NASA Mars Science Laboratory (MSL) rover, which is about 80 km to the NE. Our results confirm that this region of Mars is particularly active from an aeolian point of view.

McEwen A.S., Eliason E.M., Bergstrom J.W., Bridges N.T., Hansen C.J., Delamere W.A., Grant J.A., Gulick V.C., Herkenhoff K.E., Keszthelyi L., Kirk R.L., Mellon M.T., Squyres S.W., Thomas N. & Weitz C.M. 2007. Mars Reconnaissance Orbiter's High Resolution Imaging Science Experiment (HiRISE), J. Geophys. Res., 112, E05S02, doi: 10.1029/2005JE002605.

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A peculiar spectral unit in the Southern Amazonian Polar Layered Deposits

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Keywords: South Polar Deposits, Spectral classification, Mars.

South Polar regions were geologically mapped by Tanaka and Scott (1987). Several works followed and discussed the evolution of the South Polar Deposits revealing different geological units: i) Noachian crater terrains, ii) Dorsa Argentea Formation, characterized by smooth deposits and large irregular pits of Hesperian age, and iii) Amazonian polar layered deposits and polar ice deposits (Apl and Api, respectively). In particular the Apl deposits are characterized by alternating dark and light lithologies in a smooth, medium albedo material with sparse craters (Milkovich et al., 2002). Recently, thanks to the use of spectral parameters associated to mafic absorption around 1 µm, Carrozzo et al. (2012) highlighted how a portion of these deposits can be clearly differentiated from a spectroscopical point of view. In particular, the 1 µm band integral, the reflectance peak at 0.685 µm and the 0.8/1.0 µm reflectance ratio allowed to consider this area as different in composition from the surrounding Apl terrains, and spectrally similar to some craters dominated by dark dunes. This region was considered as a new spectral unit enriched in pyroxene content (Carrozzo et al., 2013). We have considered the spectral features from this region of interest and preliminary mapped it using the Spectral Angle Mapper (Kruse et al., 1993) supervised classifier to OMEGA mosaic of successive Solar longitude (Ls). The results evidence that this portion of the Apl area is the only region spectrally mapped, confirming that it is peculiar from a spectroscopical point of view compared to the rest of the South Polar region. Here, we'll show morphological and spectroscopical characteristics of this region to better address the characteristic of this smooth region and understand its possible formation and evolution.

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Particle sizes influence on the retrieving optical constant of silicates on planetary regolith in the VNIR by Hapke model

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Keywords: Reflectance spectroscopy, Optical Constants, Hapke model.

Regoliths of inner planets are characterized by silicate materials, rocks and particulates, at different grain sizes. Visible and Near-Infrared (VNIR, ~0.4-2.5 µm) spectroscopy is an important tool to explore their mineralogical composition. Several techniques can be used to identify and quantify the mineral phases, like radiative transfer model. Optical constants can be retrieved from reflectance spectra applying this model (e.g. Hapke model; Hapke, 1993). Moreover, the particle sizes of an individual component and its distribution are important factors which influence the retrieving of the optical constants from Hapke modeling. Several papers (e.g. Lucey, 1998; Warrel and Davidson, 2010) approach the retrieving of silicate optical constants from reflectance spectra applying radiative transfer models considering measurements of a mineralogical component at multiple narrow size range. Otherwise, few papers discussed the application of this method for wider size ranges considering the effective size distribution. Recently, Carli et al. (2014) shows how the particle size distribution strongly affect the retrieved imaginary part (k). Here we present a preliminary systematic application of the Hapke model to different silicates to better constrain the particle size influence. We have measured spectra of different pyroxene, olivine and plagioclase at several narrow particle size ranges (250-224, 224-200, 200-180, 180-150, 150-125, 125-100, 100-75, 75-50, and 50-20 µm) and wider weighed particle size ranges (e.g. delta size ca. 100µm) of which we retrieved the optical constants and fitted the particle size as single average value and as distribution of multiple size components.

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Radioactive decay as a second-order kinetics transformation process. Consequences on radiometric dating

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Keywords: Radioactive decay, Second-order kinetics, Solar activity, Decay constant, Apparent age, True age.

The exponential law with negative exponent which describes the change over time in the number of atomic systems of the radio-active species is derived from the observed change over time in the respective rates of decay, and interpreted in terms of first-order kinetics. However, this law cannot describe the change over time in the number of intrinsically-unstable systems, because after an infinite time-span of observation systems still survive unchanged.

Instead, the exponential law adequately describes the change over time in the number of systems which transform due to interaction with external physical entities. The atomic systems we presently call 'radio-active' are actually 'radio-activated', the observed change in the rate of decay of 'radio-active' nuclides is more adequately interpreted and discussed in terms of second-order kinetics, and the decay constant λ of a 'radio-active' species contains information about the concentration of the activating species. This line of reasoning is supported by recent interpretations of experimental data which suggest the existence of a relationship between solar activity and distance and the rate of decay of beta- and alpha-emitting radio-active nuclides (Jenkins & Fischbach, 2009; Jenkins et al., 2012).

It can be reasonably hypothesized that the sun changed its activity over the geological time. In this case a change in the value of the decay constants of the 'radio-active' nuclides occurred over time. A radio-activated nuclide is not characterized by a 'decay constant' λ, but by a 'decay parameter' λ, and we can calculate the effect of the change in λ over time on the age values of geological systems we calculate by using parent-daughter 'radio-active' nuclide systematics. The age values we calculate using the value of λ we measure nowadays are always apparent ages, and if the value of λ decreased monotonically over the geological time, the deviation of the apparent age from the true age of a geological system increases with the true age of the system.

Moreover, since the apparent age of a geological system we obtain by using a parent-daughter radio-active systematics depends not only on the true age of the system but also on the change in the value of the decay parameter of the parent nuclide over the true age time-span, and since the change in the value of the decay parameter depends on the change in the activity of the respective star, coeval geological systems on planets orbiting around different stars generally have different apparent age, and cannot be correlated.

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Capabilities of the SHARAD instrument to detect subsurface features on Mars: an example of possible buried outflow morphologies in Elysium Planitia

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Keywords: Mars, Outflow Channels, Marte Vallis, Elysium Planitia, SHARAD.

Most part of the channels systems on Mars surface are attributed to the outflow of water, released from the subsurface (e.g. Baker & Milton; Pacifici et al., 2007; Andrews-Hanna & Phillips, 2007). In the present work, we analyze Elysium Planitia region, in which is present a broad and young outflow channel system (Marte Vallis). Recent studies (Morgan et al., 2013) identified also in the subsurface of Marte Vallis several anastomosing channel formed around streamlined islands, later eroded and buried by lava flows (Jaeger et al., 2010; Leverington et al., 2011). Using available radargrams from the SHAllow RADar (SHARAD) (Seu et al., 2004) on board the Mars Reconnaissance Orbiter, we analyzed possible geological structures in the subsurface of Cerberus Tholi, about 500 km East of Marte Vallis. In several of them, we identified reflectors with concave-upward morphology intersecting the surface. We interpret these reflectors as possible facies boundaries. The concave-upward features are up to some hundreds of kilometers wide in section view and have an estimated depth up to one hundred meters. In some cases, the material within the concave-upward morphologies has a diverse response (lower power reflection) to the radar signal than the surrounding terrains. Also, it is possible to observe a "stair-stepped" profile of some reflectors at their two termini. On the basis of their locations, we speculate that these geological features can be part of the Marte Vallis outflow channel system. However, it is not clear if we are observing possible depositional basins (i.e. paleolakes) or fluvial channels. Also, the symmetrical "stair-stepped" profile suggest possible terraces and, thus, more than one erosional episode. Further analysis is still ongoing.

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Landslides in Valles Marineris and other locations of Mars: a new database and examination of morphologies in relation to the deposition environment

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Keywords: Mars, Valles Marineris, Landslides.

In recent years, there has been much interest about landslides on planetary bodies other than the Earth. On Mars, landslides are often extremely well preserved after billions of years, so that they may shed light on ancient times where the hydrologic regime was likely much different from present.

Many Martian landslides punctuate the wallslopes of the 4,000-kilometers long, 8,000 meters high equatorial gorge of Valles Marineris. We have collected data for a large number of these landslides on a database and attempted a classification based not only on similarities with terrestrial events, but also on characteristics that may be informative of the environment of deposition. Landslides on Mars present a series of peculiar features such as the nearly vertical collapse close to the scarp, the extreme thinning, long runout in the distal part. We present some conceptual and numerical approaches to understand the dynamics of these landslides that may help infer the conditions at the moment of flow. It is found that the presence of ice could explain some of the morphologies and run-out of these landslides, but stress that exposed ice like in a modern glacier may be problematic.

Quantitative 2D and 3D modeling of a ancient Gilbert-type fan delta in Shalbatana Vallis, Mars: paleoclimatic and paleohydrologic implications

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Keywords: Quantitative sedimentology, 2D and 3D fan-delta modeling, paleohydrology.

We reconstructed the paleohydrology and sedimentology of a ancient (3.4 Ga) martian Gilbert-type fan delta using a 2D and 3D basin-filling model (Sedflux 2.0, Hutton and Syvitski, 2008). Forward simulations were implemented to reproduce the observational evidence of a ~10 km^3 fluvio-lacustrine deposit having a maximum with of about 12 km and a 7 km mean radius formed within a 450-m-deep lake along Shalbatana Vallis. Using high-resolution imagery and stereo-derived topography from remote sensing datasets we inferred the majority of the model input parameters, bathymetry and morphometric properties of both the sedimentary basin and the deposits (e.g. area, height and especially volume and thickness of the sediments within the deltas). Likewise, average hydrologic and sedimentologic inputs for the simulations were inferred by using the morphometric characteristics of the latest active distributary channels (i.e. width, depth, and slope) as determined from imagery and topographic data. Particularly, paleoflow velocities and water discharges were derived using the Darcy-Weisbach equation, which allows to determine the paleohydrology of the channels from a series of parameters including width, depth, and slope of flow, friction factors and median grain sizes (D_{50}). The latter granulometric sizes and their relative proportions were derived from (a) typical terrestrial ranges and from (b) measurements performed from microscopic images on martian alluvial sediments investigated by the Mars Science Laboratory rover at Gale crater (Williams et al., 2013). Sediment discharges were calculated using terrestrial bedload and suspended sediment transport predictors (e.g. Van Rijn and Ribberink equations) modified for application to martian flows. Finally, model runs were finished when the sediment volume transported and deposited through the simulation would match that of the actual deposits. Assuming continuous water and sediment discharges in stillstand conditions, the minimum formation timescales for the main fan-delta are from 400 to over 1000 years depending on the considered range of input parameters. Although this latter scenario (continuous and constant peak discharges) is rather questionable from a paleoclimatic point of view, it could be compatible with the hypothesis of episodic climatic optima produced by regional factors, like for example impact craters, volcanism, or tectonics and associated persistent hydrological activity. Therefore, our results suggest that martian deltas might have not been exclusively formed during extended epochs of clement climatic conditions and thus that they do not necessarily imply the occurrence of favorable and durable conditions for life.

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Geomorphology and sedimentology of an unnamed ancient fluvial system in the Acidalia region of Mars

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Keywords: Fluvial system, lake, delta, Mars.

Using mainly High Resolution Stereo Camera (HRSC) image and topography mosaics we investigated a nearly 300-km-long valley system located westward of Idaeus Fossae in the Acidalia region of Mars. The valley apparently originates from a subsided area developed on the ejecta of a relatively fresh crater and extends eastwards trending approximately in E-W direction before terminating in one of the depressions of Idaeus Fossae. The valley floor is mainly characterized by the occurrence of well-preserved braided and anabranching channel systems locally forming extensive meandering patterns. After about 80 km from the apparent source area the valley drains into a ~20-km-diameter unnamed crater forming a deltaic deposit whose front lies at about 1800-1820 m below the martian datum. The deltaic deposit is about 8-km-long and morphologically resembles the Jezero delta (Fassett and Head, 2005), showing a well-developed distributary pattern with evidence of channel switching on the delta plain. The floor of the crater-lake is not incised by the main valley, however a breach area along the eastern crater rim consists of two spillover channels at about the same elevation of the crater inlet (-1820 m). These latter channels connect the crater lake to the eastward portion of the valley continuing towards Idaeus Fossae with its anastomosing channels. The HRSC topography of the crater lake shows that the elevation of delta front (an indicator of the lake main water level) is consistent with that of the valley inlet and outlets at B1 (i.e. -1820 m), thus suggesting that the lake reached its equilibrium state at this level acting as a bypass between the western and eastern portions of the main valley. Moreover, the lack of incision on the crater lake floor suggests that (a) the lake was relatively stable with limited water level fluctuations only responsible for the partial delta entrenchement and channel avulsion on the delta plain and that (b) the overall lake retreat was enough fast to prevent the erosion of the crater floor and significant entrenchment of the delta. Finally, after exiting the open crater lake the main valley continues to the east after breaching two N-S oriented ridges through other two breaching-spillover area characterized by the occurrence of deep scours at the base of the breached ridges. The studied system is particularly interesting since it might have been generated by regional mechanisms like for example impact related groundwater ice melting as suggested by the presence of the subsided region (likely due to subsurface volume loss) on the crater ejecta where is located the source region of the valley system. This hypothesis is also supported by the fact that both the latter depression and the valley seem to postdate the crater ejecta based on cross-cutting relationships.

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New augite geothermometer for nakhlites

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Keywords: augite, closure temperature, Martian nakhlite, single crystal X-ray diffraction, thermal history.

Nakhlites, together with shergottites and chassinites constitute the "SNC" group of Martian meteorites. MIL 03346 is a nakhlite, that was found at Miller Range, in Antarctica and is mainly composed of clinopyroxene (79%), with minor olivine (1%), and 20% vitrophyric intercumulus material (McBride et al., 2005; Treiman, 2005). The clinopyroxene is augite with a homogeneous core ($En_{36}Fs_{24}Wo_{40}$) and an iron-enriched rim ($En_{8}Fs_{64}Wo_{28}$).

Since the first modern petrologic studies of Nakhla, the nakhlite group of meteorites has been interpreted as augite-rich cumulate igneous rocks, derived from basaltic magma, that erupted onto the surface of Mars (Bunch and Reid, 1975; Reid and Bunch, 1975). However, the relative low closure temperature (T_c) of ca. 500 (±100)°C calculated for MIL 03346 by Domeneghetti et al (2013) with the available geothermometer (Brizi et al, 2000) would imply a slow cooling rate that is in disagreement with the petrologic evidence for an origin from a fast cooled lava flow.

Ex-situ annealing experiments combined with high-resolution single-crystal X-ray diffraction (HR-SC-XRD) on crystals from MIL 03346 clearly showed that the degree of order remained unchanged at 600°C thus suggesting that the actual T_c is close to this temperature. Therefore, we undertook an *ex situ* annealing experiments combined with HR-SC-XRD at 600, 700, 800 and 900 °C until the equilibrium in the intracrystalline Fe^{2+}-Mg exchange is reached. The experiments have been performed on two crystals from exactly the same fragment of MIL 03346 sample in order to calibrate a new geothermometer for augites from Martian nakhlites:

$$\ln k_D = -4421(\pm 561)/T(\mathrm{K}) + 1.46(\pm 0.52)\ (R^2=0.988),\ \text{where}\ k_D = [(Fe^{2+}_{M1})(Mg_{M2}) / (Fe^{2+}_{M2})(Mg_{M1})].$$

Applying this new equation to MIL 03346 the closure temperature resulted to be 605(84)°C about 100°C higher than that calculated with previously available calibration (i.e. Brizi et al. 2000). However, this closure temperature is still lower than expected based on petrologic evidences and suggests that MIL 03346 clinopyroxene bears record of a thermal event that postdates, or is superimposed on, the natural cooling path of the host lava flow.

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Landslides in Valles Marineris, Mars, and their possible triggering mechanism

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Keywords: Valles Marineris, Landslides, Crater damage zone.

Slope stability and landslide size-frequency analysis on Earth has been at the focus of research of disaster prevention for decades. On Mars, several landslides can be observed in region of sufficient elevation and slope, especially at the rims of craters, along water outflow channels, and especially in correspondence of Valles Marineris, a huge gorge cutting the Martian crust for 4,000 km along the equator. There, landslide span over a large interval of volume and aerial distribution, ranging from 0.15 km2 to a maximum of 12,000 km2 (Crosta et al, 2013). Landslide slope stability methods equivalent to the ones used for the Earth may be adapted to shed light on the nature of deep Martian rock and of the mechanisms of failure.

One of the important point that should be solved concerns the factors controlling the spatial distribution of such failures. Mechanical properties of the heavily cratered Martian upper crust could have been controlled by different factors: lithology, “tectonic” stresses, weathering, water circulation and impact cratering. In this work, we concentrate especially on the role of meteoroid impacts as a predisposing factor for failures in Valles Marineris. Impacts resulted in a fractured crust covered by breccia layers (1 to 3 km thick) and impact ejecta overlain by Aeolian, aqueous and unconsolidated regolith. Numerical models, laboratory impact experiments and seismic data all support the idea that fractured zones exist around craters and extend both radially and at depth below the crater to a distance equal to half the crater diameter. This damage zone presents poor mechanical properties, affecting the hydrology and the slope instabilities along the valley flank on Mars. Considering that the craters are very frequent and evenly distributed on Mars’ surface, we make the hypothesis that the control of shock damage zone on landslide size can regulate the size frequency distribution of Martian landslides (Frattini et al, 2014). Preliminary numerical simulations performed with a 3D Janbu simplified method corroborate this view, but other predisposing factors may have been at work during the history of Mars.

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Geological map of Victoria quadrangle (H-2) of Mercury from MESSENGER images

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Keywords: Mercury (planet), Planetary Geologic Mapping, Geographic Information System.

Identifying geological units and their superposition relationships is fundamental for understanding the evolution of Mercury. Hermean geological units are strictly related to impact processes, whose deposits are often recognised through geomorphological interpretation of remote sensing datasets. The first stratigraphical and geological study of Mercury was released by Spudis & Guest (1980), whose work was based on the images taken by Mariner 10 covering 42% of the total surface of Mercury. The planet has been officially divided into fifteen quadrangles: 2 polar, 5 equatorial and 8 at mid-latitudes. Quadrangle H-2 (= Hermes sheet n. 2), named "Victoria" (20°N – 65°N Lon.; 270°E – 0° Lat.), has been partially mapped by McGill & King (1983), though a wide area (~64%) remained unmapped due to the lack of imagery. Following the terrain units recognised and described by the above authors, we produced a geological map of the entire quadrangle using MESSENGER (MErcury Surface, Space ENvironment, GEochemistry and Ranging) data. The images taken by the Mercury Dual Imaging System (MDIS) Wide Angle Camera (WAC) and Narrow Angle Camera (NAC) allowed us to map geologic and tectonic features in much greater detail than the previously published map. We used the MDIS map projected BDR (Basemap reduced Data Record) at 256 px/deg (~166 m/px) as a reference layer together with the released global mosaics at 500 m/px (Becker et al., 2009) and 250 m/px. Also, we added WAC and NAC images from the released datasets at different resolutions and illumination directions when needed. In addition to that, MLA (Mercury Laser Altimeter) topography and stereo topography from MESSENGER flyby "M2" (Preusker et al., 2011) were used to better constrain unit boundaries. Victoria quadrangle is characterised by a N-S thrust array constituted by Victoria Rupes, Endeavour Rupes and Antoniadi Dorsum. A previous study made on craters cross-cut by these thrusts reveals fault dips of 15-20° and a near dip slip motion (Galluzzi et al., 2014). Completion of the geological map along with the structural analysis of this array enable a complete geological overview of the area, which will lead to a better understanding of the tectonic evolution of Mercury.

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Dating a thrust system on Mercury: implications for the planet's thermal evolution

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Keywords: Mercury, thrust system, dating.

The tectonic evolution of Mercury is dominated at a global scale by contractional features such as lobate scarps that are widely distributed across the planet. These structures are thought to be the consequence of the secular cooling of Mercury. Therefore, dating these features is essential to place constraints upon the timing of planetary cooling, which is important for understanding the thermal evolution of Mercury. The Messenger cameras (MDIS WAC and NAC), acquired images of new regions of the Mercury surface that allowed us to detect several new lobate scarps especially where the illumination geometry is more favorable for structural analysis. Among them a 2000-km long thrust system, located between 80°-100°E and 30°N-15°S, has been detected which consists of several individual lobate scarps exhibiting a north–south orientation and a westwards vergence. We dated this system using several different methods. Traditional stratigraphic analysis was accompanied by buffered crater counting of units that overlap the thrust system, allowing us to determine an absolute model age for the tectonic feature. These complementary methods give consistent results, implying that activity on the thrust ended between 3.5–3.7 Ga, depending on the adopted absolute-age model. These data provide important constraints on thermal evolution models of Mercury.

Ancient Martian lakestands and fluvial processes in Iani Chaos: geology of Light-Toned Layered Deposits and their relationship to Ares Vallis outflow channels

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Keywords: Mars, Iani Chaos, Ares Vallis, Outflow Channels, Light-toned Layered Deposits, Water, Evaporites.

Iani Chaos is a ~30,000 km2 region that lies at the head of the Ares Vallis outflow channel system (Pacifici et al., 2007; Warner et al., 2009). Mapping of Ares Vallis reveals multiple episodes of erosion, likely linked to several discharge events from the Iani Chaos aquifer. We present the first detailed map of the Iani region. Five chaos units have been distinguished with varying severity of modification (primarily by erosion and fracturing), starting from a common terrain (Noachian highlands). We observe a general progressive decrease of their mean elevation from the Mesas, Mesas & Knobs and Hummocky terrains to the Knobs and Knobby morphologies. This trend is consistent with a greater initial collapse of the original surface with an increase of the fracturing and/or of the erosional degree of terrains. Light-toned Layered Deposits (LLD) have been mapped and described in Iani Chaos. These terrains are clearly distinguished by a marked light-toned albedo, high thermal inertia and their pervasively fractured morphology. The LLD deposits both fill the basins made by the collapsed chaotic terrains and are found to be partially modified by the chaos formation. LLD also overlap chaos mounds or are themselves eroded into mounds after deposition. These stratigraphic relationships demonstrate that LLD deposition occurred episodically in the Iani region and throughout the history of the development of the chaos. The composition and morphologies of the LLD are consistent with deposition in an evaporitic lacustrine environment, likely to be the surface manifestation of a subsurface aquifer. For the first time, we have mapped and analyzed potential fluvial features (i.e., channels, streamlined islands, terraces, grooved surfaces) on the surface of the LLD. These landforms mark a fluvial system that can be traced from central Iani, some to all of which is linked northward to Ares Vallis. Using HRSC Digital Elevation Models, we have compared the elevation of the LLD and channel units and find that the altitudes of the chaos units are strictly comparable with the altitude of the floors of the major Ares Vallis channels. This is a decisive evidence of a possible fluvial system within Iani linked to the Ares Vallis outflow system. Also, on the contrary of previous works (Warner et al., 2011) it suggests that LLD are coheval with the Iani Chaos and Ares Vallis formation.

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Possible mud volcanism and astrobiological potential on Mars

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Keywords: Mars, mud volcano, geology, astrobiology, exploration.

Mud intrusion and extrusion on Earth are well-known phenomena whereby fluid-rich, fine-grained sediments ascend within a lithologic succession mainly because of their buoyancy (Kopf, 2002). The buoyancy maybe given because the involved sediments are in overpressured or undercompacted conditions with abnormally high porosities for their depths due to processes such as rapid sedimentation, tectonic loading, gas hydrate dissociation, or diagenesis and mineral dehydration reactions, among others. Mud volcanoes (MVs) on Earth typically exhibit cone- or pie-shaped edifies and flows, which are made of a clay mineral-rich matrix and a range of clasts. Mound features interpreted to be MVs occur at various locations on Mars, including Isidis Planitia, Utopia Planitia, the Utopia/Isidis overlap, Acidalia Planitia, Arabia Terra, and Chryse Planitia (e.g, Ori et al., 2000; Oehler & Allen, 2010; Pondrelli et al., 2011; Komatsu et al., 2011). Confirmation of the MV hypothesis on Mars has not been obtained yet but improved spacecraft data provide further support for the purported MVs. Mud volcanism on Mars would be very important in understanding the processes of sedimentation, water saturation, and fluid and gas movement in the crust.

The surface environment of Mars is considered to be hostile for life or organic materials due to radiation and oxidation. Thus Martian subsurface environment may have been more suitable for biological activity, and astrobiological exploration of subsurface is an approach worth consideration. On Earth, MVs are an important "window" into the underlying strata, because both a low-competence parent bed (clay-rich layer) and some rock fragments are transported to the surface. Similarly, mud volcanism on Mars would provide a window into subsurface crustal materials that were deposited earlier in geologic records. Fluids such as water and methane are relevant to the topic of biology/astrobiology, and fine-grained sedimentary materials have the potential to preserve biosignatures or even result from biological processes (Komatsu & Ori, 2000), making accumulations of subsurface materials transported upward to the surface by mud volcanism potential astrobiological investigation sites.

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Relationship between surface geology and impact cratering: global and local studies from Mars and Mercury

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Keywords: Craters, geology, planets.

Understanding which are the relations between impact crater and geology on a planetary surface is a fundamental step in the comprehension of the geological evolution of the planet. Here we present some examples about impact craters on Mars and Mercury, in particular we will show the modelling of a large impact on Mars and the geological mapping of the Raditladi crater on Mercury using Mars Global Surveyor (MGS) and MESSENGER data respectively. The aim of our work is to highlight relations at different scales, between the impact phenomena and the geological and geophysical consequences that the impact produces on the target body, both on the surface and in the crust.

Geological constraints for carbonate occurrence within Elorza Crater central pit

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Keywords: carbonates, Elorza Crater, central pit, carbonatites.

Elorza Crater is located just North of the Ophir Cavus and is characterized by a prominent and well-preserved central pit. The latter appears to be affected by several fault and fracture systems, although the most noticeable structural lineament cut through its NW sector with a NE-SW trending.

The structural and geological evolutions of Elorza Crater appear to be quite complex. The HiRISE images of the central uplift area allow to identify aeolian deposits and detrital materials, that partially fill the central and nearly flat depression of the pit. Two different types of terrains exposed along the internal and external slopes of the central pit can be observed: highly fractured massive rocks showing light to very-light tones and layered rocks showing darker tones.

CRISM data clearly show the carbonate signature near 2.3 um. Carbonates occur on top of the pit rim, where dust is less abundant. On the base of this preliminary study, we advance different hypotheses to explain the occurrence of carbonates at Elorza Crater.

Models for central pit formation imply the collapse of the central peak, whose formation is related to the impact, as the result of the presence of subsurface volatile phases such as water or ice (Barlow, 2010). As a consequence, the subsurface rocks are uplifted and exposed to surface and the thickness of the stratigraphic uplift is related to the diameter of the impact crater. In this context, the carbonate rocks can be interpreted as part of an older and deeper Martian crust, exhumed during the impact crater formation and relate processes, although the origin remain unknown.

Similarly, Michalski & Niles (2010) explain the formation of carbonate rocks at Leighton Crater as the result of metamorphic processes, which acted on interlayered carbonate-siliciclastic sediments buried under basalts or, alternatively, as metasomatization of the basaltic crust by $CO2$ -rich fluids of unknown origin.

The complex structural and geological setting of Elorza Crater, associated to the analogies of the central bulge with a volcanic morphology, as well as the occurrence of carbonate signature, can also be explained by volcano-tecnonic processes. On Earth, carbonate rock of igneous origin are named carbonatite; they occur as dikes or sills within zoned alkaline igneous complexes, otherwise they occur as lava flows or, more often, pyroclastic deposits. The presence of diagnostic minerals, such as melilite, monticellite, phlogopite is useful to distinguish them from sedimentary carbonates. We compared the CRISM spectra and those acquired on samples of terrestrial carbonatites and the similarities are marked.

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First geological observations of 67P/CHURYUMOV-GERASIMENKO comet nucleus from Rosetta mission

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Keywords: Cometary nuclei, Rosetta-OSIRIS,67P/CHURYUMOV-GERASIMENKO.

Up to date several cometary nuclei have been acquired at different resolutions (9P/Tempel 1 up to 10 m/pixel, 19P/Borrelly up to 47 m/pixel, 103P/Hartley 2 up to 7m/pixel, 81/Wild2 up to 14 m/pixel) revealing that the geomorphology of cometary nuclei is extremely variable but with several recurrent features such as spike/pitted and mottled terrains, flat floored craters, smooth and flat surfaces, mesas, ridges and troughs (e.g. Basilevsky et al. 2006). The great inhomogeneity of cometary surfaces is thought to be mostly due to different degree of repeated sublimation which leads to planation, slope retreats, development of lag deposits of variable thickness, focused ablation on pits, smoothening, widening and degradation of impact craters. Jet activity has been instead seen associated to rough areas and mounds on 103P/Hartley 2 comet (Syal et al. 2013). Finally layered terrains (recognized on 9P/Tempel 1, Thomas et al. 2007), fractures, pits and faults can give important hints on the geological evolution of the body since they might reflect primordial aggregation as well as later thermal and impacting evolution. All these geomorphological features are prone to modifications due to cometary activity, while the comet is approaching the Sun. The Rosetta mission, following the comet along its path towards the Sun will give the unique opportunity of realizing detailed geological maps with the aim of defining primary stratigraphic and structural relationships among geological bodies as well as monitoring surface changes. In particular on August 2nd, 2014, the Rosetta far approach trajectory towards 67P/C-G, will end up reaching a distance from the comet surface of about 720 km. At this time, the 67P/C-G nucleus will be imaged through 288 OSIRIS-Narrow Angle Camera (NAC) pixels covering its diameter with a spatial resolution of 13 m. From August 3rd, up to August 31st, i.e. during the Comet Approach Trajectory (CAT), the fore seen spacecraft distance will be rapidly reduced down to 52 km, giving the unique opportunity to get full frame images (2048 X 2048 px) and a complete coverage of the nucleus with a scale of 90 cm/px. It is worth pointing out that such images will provide the best ever cometary surface characterization to date. We will present the preliminary geological observations from these images.

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Synthesis of Fe^{2+}- bearing plagioclases: a valuable tool for interpreting reflectance spectra from Solar System bodies

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Keywords: plagioclase, VNIR spectra, synthesis.

The acquisition of Visible and Near-infrared reflectance (VNIR) spectra is a tested methodology in order to infer compositional information about the surface of Solar System bodies. Nonetheless, because this methodology is sensitive to Crystal Field absorptions and Vibrational Overtone, different types of uncertainties on the interpretation of the mineralogy can occur using VNIR spectra. In this regard it would be desirable to be able to count on spectroscopic database of minerals (and rocks) to be compared with the acquired spectra of Solar System bodies. The database can be assembled taking into consideration both natural (terrestrial or extra-terrestrial) and synthetic materials. Aim of this study is to synthesize Fe^{2+}- bearing plagioclases and characterize them through the acquisition of VNIR spectra. In fact, this mineral represents a main phase on the surface of many Solar System bodies, like Vesta, as it was found in Howardite - Eucrite - Diogenite (HED) meteorites, and Moon, as it was found in lunar samples and meteorites, as Anorthitic (An) rich phase containing Fe^{2+} as a minor element. Plagioclase is a common phase on the Earth too, but Fe can be present as 3+ and 2+ oxidation state. Thus, a treatment process in a controlled atmosphere was necessary in order to synthesize An90 plagioclases with variable amounts of FeO (up to 1 wt%). Synthesis were performed at 0.1 MPa using a Deltech DT-31 vertical gas mixing quench furnace in which oxygen fugacity is controlled by means of a mixture of CO and CO_2 flowing through the furnace and measured by a $SIRO_2$ oxygen sensor. Starting materials were usually contained on a Pt wire loops and suspended in the hot spot by means of a thin Pt wires. Different synthesis procedures were followed in order to get the best homogeneous composition of products. Indeed the varied parameters were the following: bulk of starting material (Fe^{2+} or Fe^{3+} in oxides and carbonates mixtures), vitrification cycles (0-2), T and duration of vitrification (1550-1580 °C, 15-90 minutes), duration of sintering at 1400 °C and $\log fO_2 = -9$ (18-28 hours). Products were analyzed by XRD and EPMA before VNIR characterization. In general, synthesized plagioclases have a good homogeneity as regards An contents but not for their FeO contents when nominal FeO is > 0.5 wt%. VNIR spectra on both glasses and plagioclases, besides showing the typical Fe absorption bands, proved to be a sensitive approach to test the compositional homogeneity of synthetic products.

Geological-geomorphological map of ExoMars 2016 landing site

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Keywords: ExoMars, landing site, Mars.

Geological mapping is of paramount importance for landing site selection and analysis, and is an essential part of the planning process for a space exploration mission. As part of the ETSA (Environmental Terrain Support Analysis) framework, we realized a geomorphological map of the ExoMars 2016 Entry Descent Landing module (EDL) landing site. ExoMars 2016 represents the first mission of the European Space Agency (ESA) Aurora Exploration Programme, realized in collaboration with Thales Alenia Space Italia (TAS-I) as prime contractor. The target landing of EDL is an ellipse (110x24 km) in the Meridiani Planum area of Mars. The geomorphological map (scale about 1:100K) has two main purposes: i) to characterize the landing area from the geological and geomorphological point of view and ii) to provide useful information for to support the engineering design of the EDL. Data utilized consist of low, high and very high resolution data. In order to mitigate the misalignments of data acquired from different spacecraft, the entire dataset have been manually coregistered, proceeding from lower to higher resolution data. Low and high resolution data consist of MOLA, THEMIS, HRSC and CTX data. Very high resolution data consists of MOC NA and HiRISE images. The landing ellipse of ExoMars 2016 partially overly, but not coincide, to the landing ellipse of NASA mission Mars Exploration Rover Opportunity. As a consequence, part of the ExoMars 2016 landing site is densely and completely covered by very high resolution images (MOC NA and HiRISE), while in the other part high resolution images are discontinuous and sparse. Furthermore, Opportunity data of the Martian surface have been utilized in order to better distinguish and characterize geomorphological units of investigated area. The ExoMars 2016 landing site area is one of the flattest and featureless region of Mars. In the entire landing ellipse the altitude vary only about 300 m, and larger part of the landing site is covered by aeolian features characterized by wavelengths ranging from few meters to few decameters. Larger part of impact craters appears widely reworked or buried. In such condition (sparse high-resolution images and almost featureless surface) the main difficulty of this work consisted in the possibility of distinguish and map different aeolian bedforms and rocky outcrops. The main units have been locally distinguished trough very high resolution images, and then their boundary extended on the base o high and low resolution data. To this purpose, a novel algorithm called Multi Scale Tonal Roughness (MSTR) has been developed in order to enhance and quickly map metric and decametric-scale features in high and very high resolution images. Recognized geomorphological units consist mainly of bedrock units, probably belonging to the so called Bourn Formation, some different aeolian units, and impact crater related units.

The exploration of Galileian satellites by the JANUS camera onboard the ESA JUICE mission

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Keywords: Jupiter satellites, Icy surfaces, remote sensing.

JANUS (Jovis, Amorum ac Natorum Undique Scrutator) is a camera selected for the ESA JUICE (JUpiter ICy moons Explorer) mission, which is the first ESA large-class mission planned for launch in 2022 and arrival at Jupiter in 2030 (Grasset et al., 2013). The mission will be operative for at least three years making detailed observations of the giant gaseous planet Jupiter and three of its largest moons, Ganymede, Callisto and Europa.

The Galilean satellites Io, Europa, Ganymede and Callisto show an increase in geologic activity with decreasing distance to Jupiter (Stephan et al., 2013). Io, nearest to Jupiter, is volcanically active. Europa could still be tectonically and volcanically active today, while Callisto, the outermost Galilean satellite, is geologically inactive but bears witness to past processes in the system through its surface features. Ganymede holds a key position in terms of geologic evolution because it features old, densely-cratered terrain, like most of Callisto, but also widespread resurfaced regions, similar to most of the surface of Europa. Ganymede observations from an orbiter are essential to investigate: (1) its wide range of surface ages which reveals a geologic record of several billions of years; (2) its great variety in geologic units and geomorphical features; (3) its active magnetic dynamo; (4) the possible presence of a subsurface ocean. The three icy Galilean satellites show tremendous diversity of surface features, witnesses of significantly different evolutionary paths. Each of these moons exhibits its own fascinating geologic history – formed by competition and also combination of external and internal processes. Their origins and evolutions are controlled by factors such as density, temperature, composition (volatile compounds), stage of differentiation, volcanism, tectonism, rheological behavior of ice and salts to stress, tidal effects and interactions with the Jovian magnetosphere and the space. These interactions are still recorded in the present surface geology which displays also possible cryovolcanism, widespread tectonism, surface degradation and impact cratering.

JANUS design is tuned to: (i) achieve Ganymede global coverage at pixel scale ranging from about 400 to 3 m/px in 4 colour filters (the mission available data volume being the limiting factor for JANUS coverage vs. resolution capabilities), (ii) observe 1.1% of Europa's surface at ground resolution ≤ 200 m/px and 3.2% at ≤ 400 m/px with maximum resolution of 6.5 m/px for selected targets, (iii) cover 14% of Callisto's surface at ground resolution of ≤ 400 m/px with maximum resolution down to 5-10 m/px for selected targets.

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Magnetic behaviour of the high Ni NWA6259 iron meteorite

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Keywords: iron metorite, permanent magnet, tetrataenite.

Magnetic properties of metallic meteorites are of interest as a model for the effect of textures and cooling history on the planetary magnetism. Among metallic minerals present in meteorites tetrataenite, an ordered FeNi alloy has a special interest as a strong permanent magnet, with an appeal also beyond the Earth Science community: recently tetrataenite structures were proposed as potential for time-resolved records of planetesimal dynamo fields (Bryson et al. 2014), but also as permanent rare-earth free magnets (Lewis et al 2014).

Here we present the results of the characterization of magnetic properties in a tetrataenite from the NWA6259 high Ni metallic meteorite. NWA6259 is the second highest Ni content meteorite (42.6 wt%) and was described as a strong permanent magnet iron meteorite (Mubarok et 2013).

X-ray diffraction and microprobe analysis performed on a 11.3 g slice showed that the microstructure of the NWA6259 meteorite consists almost completely of tetragonal L10 FeNi tetrataenite. The phosphide inclusions found by Mubarok et al. 2013 were instead not found.

Room temperature magnetic characterization was performed by means of Superconducting Quantum Interference Device Magnetometry(SQuID). Hysteresis loops with maximum applied field of 30 kOe were performed along two different directions, as well as Isothermal Remanence Magnetization (IRC) and DC Demagnetization (DCD) curves. The magnetic analysis of the meteorite fragment was completed by measuring room temperature recoil curves.

M(H) curves measured at room temperature give magnetization value of $1.2*10^3$emu/cm^3, in agreement with literature data (Mubarok et al 2013). The presence of the secondary soft phase (bcc FeNi) was investigated measuring recoil curves. In fact, if a soft phase was present, a reversible portion of the recoil curve would be observed, according to what happens in exchange-spring magnets. No clear effect of "exchange-spring" behavior was measured confirming XRD data.

The measured coercive field is Hc≈400 Oe, which is slightly smaller than what generally observed, from 500 Oe up to 4000 Oe, as a function of the sample texture (Lewis et al 2014, Mubarok et al 2013). The lower measured coercive field may indicate the presence of regions of the sample a with different sample texture, as suggested by the lower coercive field, may indicate the presence of a sample structureorientation of the easy magnetic axes, to be investigated by EBSD methods.

The presence of a different sample texture respect to previous investigations, as suggested by the lower coercive field, indicates further textural heterogeneity in magnetic structure, likely related to magnetic domains within a chemically homogeneous structure. A potential as a cooling rate indicator of magnetic behavior is discussed.

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Evolution of the fluvio-lacustrine system of the Eberswalde crater (Mars)

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Keywords: Eberswalde crater, Mars, fluvio-lacustrine environments.

The Eberswalde crater (33° W–24° S) hosts a delta-like landform (Malin & Edgett, 2003), that has been interpreted as fan delta thus entailing that a standing body of water filled the crater (Bhattacharya et al., 2005; Wood et al., 2008; Pondrelli et al., 2008). According to some authors (e.g., Mangold et al., 2012), it lasted over several years to hundreds of years, while others (e.g., Bhattacharya et al., 2005) suggest a duration of a 100.000 years.

The sedimentary deposits of the Eberswalde crater rest nonconformably on top of an older Substratum which include the Holden crater ejecta blanket. They consists of layered to faintly layered and non-layered light-toned deposits (Pondrelli et al., 2011).

According to Malin and Edgett (2003), Moore et al. (2003), Bhattacharya et al. (2005), Wood (2006) and Pondrelli et al. (2008), delta plain, delta front and prodelta can be recognized. Several minor fan deltas debouches in the crater from all the directions.

The Eberswalde fan delta consist of five lobes (four deltaic) which relative stratigraphy can be unraveled through cross-cutting relations. We inferred the approximate water level correspondent to each lobe from where the transition between delta plain and delta front occurs. This water level is different for each deltaic lobe.

Lobes are divided by unconformable surfaces, erosional truncations and flooding surfaces. We tentatively inferred a water level curve in which we distinguish three water level fluctuations to which a higher order regressive trend is superimposed (Pondrelli et al., 2008).

The three lower order cycles appear to reflect water level fluctuations. Most probably, hinterland-related processes controlled part of the deposition, but the cyclic water level fluctuation inferred suggest some form of climatic forcing. The higher order trend records the progressive drying out of the basin.

The progressive drop of the water level inferred from the main deltaic system is consistent with the observation in the contributing basin, where a younger channel incised older lacustrine deposits and in the basin, where fluvial channels prograde on the offshore.

Such an evolution appears not to be consistent with a 10s to 100s years long geological history nor with a localized controls. We favor instead a longer duration with mixed local and external, possibly climatic, controls.

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Fractal clustering analysis and numerical modeling results from Firsoff Crater (Mars)

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Keywords: Mars, Firsoff Crater, Impact simulations, fractal modelling, fluid source depth.

Arabia Terra is dominated by heavily cratered terrains, and some peculiar landforms can be found mostly in craters interior. With high-resolution images from HiRISE (25 cm/px) and CTX (6 m/px) cameras pitted cones, mounds and knobs can be easily recognized. Those are intepreted as the surface espression of pathways for subsurface fluid. It is commonly hypothesized that Arabia Terra is an area of past fluid activity, being crater central bulges a place of sulfate precipitation (Andrews-Hanna, 2011, Pondrelli et al, 2011, Franchi et al., 2013).

We investigated the presence, origin and timing of mounds formation as well as the depth of the fluid source according to their fractal clustering. In fact, the spatial distribution of eruptive structures within volcanic areas on Earth has been linked to fracture systems with hydraulic connection between surface and magma reservoirs. Self-similarity in vents distribution is described by a power law distribution with fractal exponent D and defined over a range of lengths comprised between a lower limit (lower cutoff, Lco) and an upper limit (upper cutoff, Uco). On Earth, volcanic vents as well as mud volcanoes have shown that the Uco of their fractal distribution scales with the depth of pressurized fluid reservoirs (Mazzarini et al., 2011). The same approach has been applied to mounds mapped at Firsoff and Crommelin craters assuming a similar relation between the surface distribution of mounds and the depth of the connected deep pressurized water table.

431 mounds (most with a central orifice) were mapped on Firsoff Crater's floor and 160 on Crommelin Crater's floor. Preliminary result on the Uco depth estimation shows that a shallow and common reservoir for Firsoff e Crommelin is likely.

We also investigated the origin and pristine shape of Firsoff crater depending on the Martian target composition.

The aim of simulating an impact process on a complex environment such as the Martian surface (due to erosion and strong degradation) is to reproduce a pristine realistic crater shape in order to better understand the geologic processes that led to its latter modification. We simulated two endmembers depending on the rheological structure and composition of the Martian upper crust in order to understand which type of target layering (basalt layering vs basalt/anorthosite layering) is more likely. Interestingly the best fit has been obtained with a jointed basalt/anhotosite transition at the same depth of the pressurized water table predicted by the surface mound distribution.

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Correlation between chaotic terrains and impact craters on Mars

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Keywords: chaotic terrains, impact craters, sub-ice lake.

In this contribution we present the results of a statistical analysis performed on 50 chaotic objects around Xanthe Terra. For each object we measure the diameter and the maximum and minimum depth respect to the surrounding non-collapsed area. We also measure the maximum collapse as the difference between the maximum and minimum depth.

The most part of the measured objects has a maximum depth greater than 1.2 km. The latter represents the maximum collapse achievable by complete pore-space closure of 20 km depth cryosphere after groundwater release. This indicates that the groundwater outflow process is not responsible for the high collapse observed in the most part of the chaotic terrains. Only 5 have a maximum depth greater than the pristine depth of impact crater, calculated from 4 different diameter vs depth relations. Furthermore, the relation between diameter and maximum depth is statistically similar to the relation between diameter and pristine depth of impact craters. This similarity is much more significant when the minimum collapse achieved by chaotic terrains is taken into account vs diameter. In fact, the difference in slope between chaos and crater relations is less than the statistical interpolation error.

The high collapse shown by the most part of the chaotic terrains and strong correlation between diameter vs collapse relation and the same relation for pristine crater suggest that they can be formed on older impact craters, after the collapse of sediment partially filling the craters. Of the four major processes proposed to explain the evolution of the chaotic terrains, only the buried sub-ice lake scenario seems to match the results of this statistical analysis. The scenario starts with the partial filling of the crater by water ice and the subsequent burial under a thick overburden sequence. The buried ice unit starts melting as a result of the thermal insulation by the overburden in combination with the planetary heat loss, creating a subsurface lake. When the melt layer reaches a remarkable thickness the overburden collapses, resulting in massive expulsion of liquid water to the surface (Roda et al., 2014). This scenario can explain the high collapse of chaotic terrains, the similarity with impact craters and the shifting between the chaos collapses and the pristine crater depths relative to the same diameter. The latter can be explained by the partial filling of crater by sediments. Magma cryosphere scenario can only explain the high collapse but not the strong correlation between chaos and impact craters, while gas-hydrated and aquifer scenarios disagree with both observations (Roda et al., 2014).

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Analysis of reflectance spectra from Proclus and Copernicus craters

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Keywords: Moon, plagioclase, spectroscopy.

The Moon is one of the most studied planetary body in the Solar System. A large portion of lunar rocks has been classified as ferroan anorthosite (Warren, 1985) and contain up to 90% plagioclase (PL). So, PL is widespread on the surface.

Several missions spectroscopically analyzed the lunar surface, e.g. SELENE and Chandrayaan, and detected the presence of an absorption band at ca. 1250 nm, due to Fe2+ transition in PL, in central peaks of impact craters (Matsunaga et al., 2008; Cheek at al., 2012; Cheek & Pieters, 2012). Ohtake et al. (2009) recognized areas with PL amount higher than 98%.

Here we analyzed reflectance spectra from Proclus and Copernicus craters, relating the spectral parameters to the mineralogical composition, particularly focussing on PL.

Proclus is a 28 km crater situated in the west of Mare Crisium. We recognized regions with different spectral behavior: 1) PL regions located mainly in the crater walls; 2) pyroxene (PX) regions in both the walls and the floor of the crater; 3) olivine (OL) region in the south-east portion of the crater walls; and 4) PL+PX regions in the crater wall. Reflectance spectra from 1) are comparable with PL with iron content of 0.1 and 0.5 wt.% (Serventi et al., 2013b), and spectra from 4) are comparable with mixtures composed with more than 90% PL and low PX (Serventi et al., 2013a).

Copernicus is a 93 km crater located in the eastern portion of the Oceanus Procellarum. We recognized: 1) OL-bearing regions in the central peak and in the north-west wall; 2)PX-rich areas outside the crater; and 3) featureless spectra and spectra with a broad absorption at ca. 2000 nm in the crater floor. A detailed analysis of spectra from the central peak suggests the presence of PL in 1), where spectra indicate more than 90% iron-poor PL (Serventi et al., 2013a).

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Pedogenetic processes on Mars

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Keywords: Mars,soils,clay minerals.

Clay minerals may provide important information on the rock/fluid interaction and, thus, on the climatic conditions under which they formed. We have compared the mineralogy detected on Mars from CRISM data and terrestrial analogues samples. These data reveal clay minerals in the eastern part of Valles Marineris and Margaritifer Terra regions and we compared the mineral assemblages with soils sampled on the Etna volcano (Sicily) and Cerviero Mount(Calabria, Southern Italy). Our integrated approach of combining remote sensing observations with real pedological, petrographical and mineralogical analyses can help to identify the main alteration processes (wheathering vs. hydtrothermal) in the Martian study area.We found good analogies between the Andosols developed on the 600-700 years old basaltic substrates of Etna (Branca et al.,2011) and on the Upper Jurassic- middle Cretaceous pillow basalts of Cerviero Mount (Iannace et al.,2007), and the Martian soils, based on their spectral response and propose similar formation processes.CRISM data show limited evidence of illite and smectite in the eastern part of Valles Marineris, but these phases are widely exposed in Margaritifer Terra, where we also detected allophane (poorly crystalline clay) as well as vermiculite, chlorite and smectite. This suggest an intense and widespread water-bedrock interaction.The analysis of terrestrial soil profiles using X-ray diffraction shows similar characteristics to Martian terrains in terms of bedrock composition and clay mineralogy inferred from remote observations. We relate the different clay minerals to different formation processes such as: a) chemical weathering of the main primary minerals present in the bedrock (i.e. plagioclase and pyroxenes);b) neoformation processes of different clays; c) hydrotermal alteration of volcanic glass. Although we cannot totally exclude hydrothermal events at places due to the presence of chlorite and smectite, the geological setting of the studied region of Mars seems to support the presence of standing bodies of water and thus the formation of clay minerals after weathering processes, which implies a humid climate in the past.According to our analysis of the Etnean soils, the formation of clay minerals from weathering started on lavas of about 600 years under warm temperate, humid climatic conditions. This time range can be scaled to Martian-like conditions to find a minimum time for the permanence of water in the Martian study area.

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The meteoritical collection of the Parma mineralogical museum

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Keywords: meteorites, Parma Museum, historical samples.

In the internet site of the Mineralogical museum of Parma, the existence of an interesting metoritical collection is reported, coming from former late 18th-beginning 19th century private collections (Linati, Piroli), later gathered in the mineralogical museum. However the samples were almost disappeared since recently, when they were found in the drawer of a retired professor. A preliminary observation showed that most samples were mislabeled, or even not labled. For instance an olivine-metal meteorite, which turned out to be the Krasnojarsk historical pallasite, wes labled as Ensisheim, which is the locality of the fall in 1492 of a chondrite.

A hint for the correct attribution was given by the "Cocconi catalogue" (1867-70) of the mineralogical museum of Parma, where 16 samples are cited: 2 as ferri nativi (native iron), 4 ferri metorici (metallica meteorites) and 10 aeroliti (silicatic meteorites). Of the 10 aerolites two (Pieve di Cisignano-Borgo san Donnino) are a pairing. Also in the Cocconi catalogue we find several misreported names, which could be hardly referenced to an existing sample. However, combining the historical locality, internet imaging of the candidate meteorites, the date of the fall (only when reported), and finally petrographic evidence we could assign each sample the historical name.

Two samples are absent from the Cocconi catalogue: one is a native iron labled as "Incerta" by Cocconi, the other loss is of the Siena metorite, already absent in 1870, according to the note of the museum curator Prof. Strobel. For the other the actual weight is much lower than reported in the sample description. The only addition is a small piece of the Alfianello meteorite fall in 1883. Second younger is the Juvinas eucrite, which fell in 1824.

Metallic metorites were examined by SEM-EDS; of them two were discarded as non-metorites (Brianza and Florac), one is likely the smelting product of a larger mass (Bitburg), and only Zacatecas IIIAB iron and Krasnojarsk pallasite are confirmed.

Among the silicatic metorites we have two achondrites (Juvinas and Stannern eucrites) and seven chondrites (Borgo san Donnino, Alfianello, Renazzo, Benares, Salles, L'Aigle, Ensisheim). Most interesting is the large mass of the Borgo san Donnino (now Fidenza) LL6 chondrite, which is one of the very few falls in the Provincia of Parma. The analysis of the silicatic samples is underway.

Morphometric analysis comparison of differently degraded simple craters on the Moon

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Keywords: morphometry,craters,degradation.

In this research we analyzed DTMs from LROC (Lunar Reconnaissance Orbiter Camera) NAC (Narrow Angle Camera), which have a mean resolution range from 0.5 to 1.5 m/pixel and WAC (Wide Angle Camera), that is providing a global lunar surface coverage with a resolution of about 100 meters/pixel. (http://lroc.sese.asu.edu/about).

The morphometric analysis was carried out using a multiscalar approach, by testing different ranges of window kernel size (e.g. 15-35-50), in order to retrieve morphometric variables such as slope and curvatures, calculate along different planes, which can be potentially used to characterize the different sectors of a crater (rim crest, floor, slopes and related boundaries) and to evaluate its degradation. For example, a rheological boundary at a depth of 200 m within the small fresh Linné crater (diameter: 2.22 km), firstly hypothesized throughout numerical investigation (Martellato et Al.), has been well identified as a bland morphological step on the inner crater scarp, by using slope and curvature maps derived from a NAC DTM, also this discontinuity, located on the inner crater scarp, is expressed by a very low topographic relevance (8-10 meters).

A change in morphometry values is also expected in relation to craters‘ages and diameters. Indeed degradation is influenced by gravitative processes, as well as space weathering, that induce a smoothing effect on the morphological features with the main results of lowering and enlarging the rim crest. We have quantified this variations using morphometric variables derived by NAC and WAC DTMs of several craters with different diameters, that can be considered representative of the 4 relative age classes of degradation, firstly defined in literature (Arthur et al., 1963).

SESSIONE S35

Poster - Open Session

CONVENORS

B. Cesare (Univ. Padova)

E. Erba (Univ. Milano)

The "Geoitaliani" project: history of geology as a key for the spreading of scientific knowledge in Italy

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Keywords: History of geology, communication strategies, science outreach, Geoitaliani.

"Geology has been an Italian science" ("Principles of Geology", proem to 1st edition, 1830). Sir Charles Lyell's tribute to forerunners in earth sciences field seems today neglected by Italian society, whose relationships with geoscientific community in the last decades have been compromised by several tragic events. In such a context, promoting public awareness and understanding of earth sciences importance is thus a crucial issue for a 'geologically young' country, constantly facing the consequences of natural hazards.

The history of geological thought and its evolution through time can play a key epistemological role for the spreading of a more holistic and multidisciplinary science knowledge in Italy. In our country other scientific disciplines (e.g. medicine, biology, physics and mathematics among others) rely on a consolidated awareness of the importance of their own tradition, whereas contribution by Italian earth scientists to this cultural operation is still subordinate.

The Italian Geological Society has recently established a History of Geosciences Section and then a website (*www.geoitaliani.it*) activated in March 2013. The site has been conceived as a common space for the "storytelling" of people, places and events representative of the Italian geological culture, by means of texts, images, photos, historical maps and multimedia. About one hundred contributions by nineteen different authors (researchers, teachers, geologists, historians) have hitherto been published.

Precious information come from the historical archives of both the Italian Geological Society and the library of the Italian Institute for Environmental Protection and Research (ISPRA), which represent the principal collections of original bibliographic and cartographic material (about 50.000 maps) belonged to the Geological Survey of Italy. The digitalization process of about 1.000 historical maps, catalogued according to the International Standard Bibliographic Description for Cartographic Materials, has almost been completed.

Participation to meetings and publication of thematic papers is part of the cultural process. History of Geosciences section members also cooperate with the Institute of the Italian Encyclopedia as authors of geoscientists biographies published in the Italians Biographic Dictionary (*www.treccani.it*).

Since its activation, GEOITALIANI has been consulted by more than 28000 visitors from Italy and all over the world. Social networks (Facebook: *www.facebook.com/geoitaliani*; Twitter: *@geoitaliani*) represent strategic communication tools, reaching younger audience and trespassing boundaries of the geological community: the majority of the almost 800 Facebook followers are indeed "non geologists", actively involved in general discussion.

In our vision, a new meaning of the Actualism principle should thus be considered for the future of the Italian Geosciences: *"the present is the key to the past, and the past is the key to the future"*.

The utilization of the electron microprobe analyses to non-silicatic systems: examples of applications

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Keywords: electron microprobe, non-silicate systems.

In the last five years the JEOL-8600 electron microprobe hosted in the new labs at the Department of Earth Sciences of the University of Florence has been updated in both software and hardware components. The instruments is controlled by the XMAS, IDFix, HiMax, MaxView software packages (developed by SAMx) which allow to perform quantitative analyses utilizing the equipped four spectrometers, each constituted by two analyzing crystals. In addition to be involved in routine analysis, such as those performed to characterize the mineral chemistry of silicates, in the recent past the instrument has been used to "non-conventional" researches who have interested different fields of Earth Sciences *sensu lato,* such as Paleontology and Archeometry. In this context, the importance of analyses on materials such as bones, teeth, bryozoa, and phases such as apatites and oxides are invaluable in the interpretation of the processes responsible of their formation and evolution. The optimization of the analytical conditions was therefore properly approached adjusting several different instrumental parameters such as accelerating voltage, beam current and counting times. Besides adjusting these parameters, the calibration included the choice of the appropriate emission lines to be analyzed and the consequent selection of the analyzing crystal (and spectrometer) to be used in WDS analyses. For this purpose the calibration was mainly concerned in the minimization of the detection limits of the elements to be analyzed.

The aim of this communication is to provide some examples of analytical set-up utilized during analyses of "non conventional" material. Thus, the acquired analyses of teeth (either enamel and dentin) and bones fossil remains of *Ursus spelaeus* from Grotta all'Onda cave (Camaiore, Italy) were invaluable to reconstruct the paleo-environment in which the animal lived. Similar information was obtained after analyzing *Chiastosella* bryozxoa from different depth in Southern Ocean (Antarctica). Appropriate analytical setting allowed to estimate $MgCO_3$ mol% contents to be related to water temperature variations and climate changes. Further researches involved analyses on apatites from a pseudotachylite sample and its host rock collected south of Terranova Bay (Antarctica). These analyses have the aim to verify the depletion in minor and trace elements due to the pseudotachylite formation, as suggested by the variation of U contents in the pseudotachylite and its host rock, derived from apatite fission-track analysis. As a final example, an appropriate calibration procedure was necessary to measure out trace elements (e.g. W) in oxides and metallurgical slag, thought to be valid tracers in ancient metallurgical processes finalized to the production of Fe in Tuscany.

A “group of Oil&Gas Geology" within the Geological Society of Italy. Why? What? How?

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Keywords: Oil, Gas, Geologial Society of Italy, Social Responsibility.

Italy has always been a strong consumer of Oil and Gas. It was also, and potentially it is still now, a major producer of hydrocarbons; we could be the 5th largest European producer of oil, following the countries bordering the North Sea, ie Norway, Netherlands, UK and Denmark. Oil&Gas are a strategic resource of the State, an indispensable good of the community, or all of us.

The “Italian oil history” began in 1802 with chemical studies from Giuseppe Mojon: the streets of Genoa were illuminated with the "nafta" naturally outcropping along the Taro River near Parma. The early production of Oil in Italy was finalized to this kind of use, as reported by Abbot Antonio Stoppani (1824-1891), author of "Geology of Italy" and of the most famous "Il Bel Paese".

Gas has a similar story, which began in the late eighteenth century with the studies of the Abbot Lazzaro Spallanzani and Alessandro Volta on the properties of hydrocarbons. The agreement between the City of Turin and "Society of Gas Lighting for the City of Turin", funded in 1837 to brighten the first capital of Italy with gas distilled from solid fuels, is dated 1846.

Since the beginning, these activities were based on scientific and technical knowledge, on the professional skills of the men and women who devoted themselves. The presence and the excellence of Italian science was important, giving global footprint in all the innovative processes that guided the development of energy sources.

WHY A GROUP OF OIL&GAS GEOLOGY?

Underground resources and Earth Sciences. An indissoluble union, an enviable school of geosciences, a huge hunger for energy, an incredible dependence on imported energy resources and a very important domestic potential. The need to operate in full respect of the surrounding territory, the material contribute a hydrocarbon geologist can give to a proper dissemination of knowledge and to increase awareness of our surrounding land, the need of a Corporate but also Personal Social Responsibility.

All this is at the base for creating the Group for Oil&Gas Geology within the Geological Society of Italy. A section that wants to have the aim to contribute to the knowledge of the territory and the development of our country.

WHAT TO DO?

Promoting knowledge on the scientific and technological aspects of the exploration and production of hydrocarbons, on their importance in the context of a proper energy mix, and on their contribution to a sustainable development of the country. Dissemination and sharing of knowledge, awareness of the importance of Geosciences, accurate information.

HOW?

Through the combination of the following possible actions:

- Organisation of, and participation in, seminars and conferences
- Publications
- Visits to facilities and production sites
- Lecturers to schools and universities
- "Twinning" with similar sections and / or foreign companies and associations

Rus in Urbe: GIS for archaeobotanical data collection of green spaces of ancient Pompeii

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Keywords: Archaeobotany search, ancient Pompeii, GIS systems, soil anthropization.

The creation of a GIS information system for the green spaces of Ancient Pompeii is intended to support the development of a coordinated and consistent system of useful data to realize enhancement projects based on contents of recognized scientific validity. The setting up of analytical methods, inspired to the principles of geography, is aimed at producing information layers to be used in geo-referenced modeling of physical spaces. The analysis and processing of data extracted from the observation of the real world, is performed using advanced technologies, designed to dynamically produce information, data and procedures useful for the knowledge of natural and cultural resources. The current debate on the use of GIS tools in the field of archaeological studies, since a few years finds a significant acceleration, thanks to the increasing awareness of the analysis potential of this technology. To support this development means to intensify the debate and discussion between all the different specialists involved in the issues, placing in the foreground the premises and conditions necessary for a scientifically correct development for the diffusion of geographical knowledge of the historical territory (Scarpa, 2012). Based on the census of plant elements, found in ancient Pompeii (Ciarallo, 2004), a GIS platform was developed aiming at making archaeobotanical data accessible and usable. The list of the collected plant specimens, amounting to 13,680 referred to 1,710 entities (Ciarallo, 2012) was compiled on the basis of all available data: archive, bibliographic and analytical data. The achieved ecodata come mainly from the study of vegetation (paleobotanical analysis and pollen analysis) and provide the reconstruction not only of the vegetative cover of the archaeological site but also the analysis of the human impact on the vegetation and soils that support it. The inclusion of archaeobotanical data in a digital environment will make the realization of a software possible able to collect and organize data in a consistent, rational and organic manner (Farinetti, 2012). The ability of GIS systems to integrate information layers concerned with the environmental context allows to check and assess the relationship between archaeobotanical data and environmental data, bringing the archaeobotanical research back to an environmental determinism.

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Hunting for a putative trackmaker: "élite prints" 3D morphology as an objective tool to recognize osteological patterns and to infer locomotor functionality

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Keywords: *Dimetropus,* "pelycosaurs", photogrammetry.

Tetrapod footprints referred to the ichnogenus *Dimetropus* have been traditionally attributed to carnivorous eupelycosaurian synapsids (*i.e.*, Sphenacodontidae; see Gand & Haubold, 1984; Haubold, 1971; Tilton, 1931; Voigt, 2005). Despite the broad agreement on this attribution, the characters connecting the ichnogenus to specific osteological features of "pelycosaurian" (non-therapsid synapsids in the new cladistics conception) autopods have never been clearly identified.

The discovery of superbly preserved footprints referable to *Dimetropus* from the Lower Permian Midco Member of the Wellington Formation (Perry, Noble County, Oklahoma, USA), has allowed to define these features, emphasizing their intimate correlation with autopod structure and inferred functionality in non-therapsid synapsids.

In a first analysis, digit length in considered footprints has been morphometrically compared with digit length in known "pelycosaurian" autopods. The analysis has been conducted separately for the manus and pedes impressions and the respective fore and hind autopods. Subsequently, the impression differential depth has been studied in detail. For each considered footprint portion, the osteological pattern mirrored in the impressions has been recognized, and the possible path of weight loading during a complete cycle of locomotion has been highlighted. To obtain a more quantitative and objective appraisal of differential depth of impression, the method of photogrammetry has been applied and a high-resolution three-dimensional model of the footprints, through the VisualSFM and MeshLab softwares, has been obtained.

The ichnological characters, in connection with the comparative analysis of known skeletal remains and tracks, highly suggest the attribution of the studied material to a new *Dimetropus* ichnospecies and allow inferring a putative trackmaker within the Family Caseidae (Synapsida, Caseasauria), even if an edaphosaurid affinity cannot be completely excluded. In addition, as a more general conclusion, the study has shown that footprints ascribed to *Dimetropus* are characterized by a substantial variability, which is most likely a direct reflection of a wide range of different zoological taxa among non-therapsid synapsids.

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Petrographic features of foliated leucocratic body in the Migmatite Complex from northeastern Sardinia

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Keywords: Foliated leucogranite, migmatite, Variscan Sardinia.

At Punta Bados, a few kilometers north of Olbia city, an elongated foliated leucocratic body striking N160°-170°, characterized by coarse-grained garnets up to 4-5 cm in diameter is hosted in a sequence of igneous and sedimentary derived migmatite and fibrolite-rich metapelites with minor metabasite and metaultramafics (Cruciani *et al*., 2002, 2008). The leucocratic body shows an alternation between poorly and moderately foliated domains, as well as a great variability in garnet size and abundance. Rock grain size is strongly variable reaching up, locally, a pegmatitic texture. The contact between the leucocratic body and the metapelites is marked by a 30 cm-thick cataclastic band with S-C structures and kinematic indicators suggesting a dextral shear component. It mainly consists of quartz, plagioclase, microcline, muscovite, biotite and garnet, with zircon, apatite and tourmaline as accessory minerals. Plagioclase is mainly unzoned albite ($An_{\sim 5}$). Garnet is unzoned to poorly zoned with composition Alm_{75}, Pyr_{10}, Sps_{15}, $Grs_{<1mol.\%}$. It is free from inclusions and/or from other microstructural relics. Muscovite occurs as centimetre-sized crystals with Si content near to 6.15 a.p.f.u. and $X_{Na} = 0.10$. The whole-rock composition of a few representative samples shows following major element content ranges: SiO_2: 72.8-74.7; Al_2O_3: 15.0- 15.4; Fe_2O_3tot: 0.5-0.7; MnO: 0.05-0.08; MgO: 0.1-0.7; CaO: 0.4-2.0; Na_2O: 4-5; K_2O: 3.2-4.8 wt.%. The rocks are peraluminous with normative composition matching those of granite/trondhjemite. Preliminary data suggest that barium ranges from 71 to 634 ppm, whereas Rb and Sr vary between 36-252 and 54-327 ppm, respectively. Rare earth element (REE) content of the leucocratic body is ~50 ppm with moderately fractionated pattern for light and medium REE, and flat for heavy REE (Ce_N/Yb_N ~1.5, La_N/Sm_N ~1.5, Gd_N/Yb_N ~1.0) with no Eu anomaly. Field geological data and petrographic features indicate that the leucocratic felsic body of Punta Bados resembles the foliated leucogranites described in Golfo Aranci and Arzachena areas (northern Sardinia) interpreted as anatectic bodies emplaced during the late deformative event related to the exhumation of the metamorphic basament.

Cruciani G., Franceschelli M., Jung S., Puxeddu M., Utzeri D. 2008. Amphibole-bearing migmatites from the Variscan Belt of NE Sardinia, Italy: partial melting of mid-Ordovician igneous sources. Lithos, 105, 208-224.

Franceschelli M., Carcangiu G., Caredda A.M., Cruciani G., Memmi I., Zucca M. 2002. Transformation of cumulate mafic rocks to granulite and re-equilibration in amphibolite and greenschist facies in NE Sardinia, Italy. Lithos, 63, 1-18.

The Variscan (?) Settiballas "Micaschists" (SW Sardinia): geological and petrographical investigations

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Keywords: Variscan chain, Metamorphic rocks, Sardinia.

In SW Sardinia crops out the Monte Filau Complex, a Variscan medium-grade metamorphic complex built by the Monte Filau Orthogneiss and the Settiballas "Micaschists" (Minzoni, 1981): this complex intrudes the clastics of the Variscan Bithia Complex (Junker & Schneider, 1983). While the Monte Filau Complex is referred to the amphibolitic facies, the enclosing Bithia Fm pertains to the greenschist metamorphic facies (Franceschelli et al., 2005). The Monte Filau Orthogneiss is a Middle Ordovician granitoid metamorphosed by the Variscan events. The Settiballas "Micaschists", whose age is still uncertain (Precambrian?), are mainly surrounded by the Monte Filau Ortogneiss (Monte Settiballas area) except for a few outcrops (Monte Cogoni coastal area) that are surrounded by the Variscan intrusive complex. Thermometamorphic evidences due to the intrusion of the orthogneiss protolith and/or of the Variscan granitoids are evident in the Monte Settiballas area where the "micaschists" are turned into hornfels. Conversely, in the southern Monte Cogoni area the "micaschists" show a stronger regional metamorphic imprint. Besides, in this area intercalations of metavolcanics and carbonate and mixed carbonate-siliciclastic beds (now turned into marbles and calcsilicate rocks) have been found. The geological survey evidenced in the "micaschists" a variable schistosity trend; in the western outcrop it strikes about NS dipping West. Conversely, in the eastern area it is meanly N°150 dipping East. An antiform structure is thus evidenced. Petrographic investigations in the studied areas indicate that the micaschists are well-foliated rocks characterized by an alternation of granoblastic and lepidoblastic millimetric layers. The most common minerals are quartz, muscovite, biotite, and Al-silicates. Andalusite is partially replaced and pseudomorphosed by muscovite. Chloritized biotite still retains significant titanium content. Accessory minerals are ilmenite, monazite and, sometimes, tourmaline. Calcsilicate intercalations show a layered microstructure consisting of dark-coloured phyllosilicate-rich layers alternated with light-colored epidote rich layers. The geological features suggest that the "micaschists" may be a thin cover over Ordovician and Variscan intrusives. The original nature and age of the protolith is still matter of debate.

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The high-grade metamorphics from Pittulongu to Golfo Aranci (NE Sardinia): an attempt of lithological reconstruction

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Keywords: igneous-sedimentary sequence, northeastern Sardinia, Variscan orogeny.

In NE Sardinia, along the coastline from Olbia to the Capo Figari southern side, crops out a high-grade metamorphic complex pertaining to the Axial Zone of the Southern Variscan chain. The main outcrops are formed by migmatitic paragneisses, orthogneisses, eclogites, and mafic to ultramafic amphibolites (Franceschelli et al., 2002, Cruciani et al., 2008). Orthogneisses dated 469 ± 3.7 Ma prevail in the northern part (Capo Figari), while migmatitic paragneisses, minor amphibolites with relic eclogite parageneses (this latter with an age of 460 ± 5 Ma) and rare lenses of orthogneisses are present in the southern part. In the paragneisses, swarms of calc-silicatic nodules probably representing former carbonate beds (?) now completely shattered are locally concentrated. By a detailed geological mapping along the coast, an attempt has been made to unravel the pre-metamorphic sequence: we tried to refer every metamorphic rock to its former protolith. The mapping evidenced the presence of alternations of metamorphic rocks passing frequently from each other through gradual or alternated boundaries: this could be related to the original boundaries of the former sedimentary or igneous protoliths, thus probably suggesting the original composition of the succession. This may be composed by acidic and basic volcanics and immature siliciclastics. The geometrical upper part of the succession may be located in the Capo Figari area (Cala Moresca), where the thick augen-orthogneiss outcrop may be related to the Middle Ordovician volcanic complex widely outcropping along all the Variscan Sardinian transect. These rocks show also the oldest radiometric age ever found in the area and are characterized by primary/interdigitated contacts with paraderivates (paragneiss with calcsilicate nodules). In the lower part of the succession, in the M. Nieddu-Pittulongu beach area, alternations of migmatitic paragneiss with calcsilicate nodules and amphibolites could be related to former immature siliciclastics intercalated by carbonate beds (?) and basic volcanics. Thus, this work could allow to relate the low- to middle-grade metamorphics of the Variscan Nappe Zone with the ones of the Variscan Axial Zone and to confirm the local persistence in the Olbia area of the same sedimentary environments existing during lower Paleozoic times in the south and central part of the island.

Cruciani G., Franceschelli M., Jung S., Puxeddu M., Utzeri D. 2008. Amphibole-bearing migmatites from the Variscan Belt of NE Sardinia, Italy: partial melting of mid-Ordovician igneous sources. Lithos, 105, 208–224.
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The Lower Pleistocene Arda river invertebrate fauna: palaeoecology, palaeoclimatology and biochronology

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Keywords: Palaeoecology, Arda River, Boreal guests.

The Arda River succession, cropping out in Western Emilia, Northern Italy, is a marine succession of Early Pleistocene age; it is composed mainly of sandstones, siltstones and claystones and it is bounded at its top by continental conglomerates, representing a major sea level drop and the establishment of a continental environment with vertebrate faunas and fresh water molluscs.

Numerous fossiliferous levels very rich in macroinvertebrates are present along the marine succession; the very diverse fauna comprises bivalves, brachiopods, gastropods, corals, serpulids, bryozoan, echinoderms, scaphopods and barnacles. Fossils are generally well preserved with several articulated specimens in life position and often preserving the color and the spiny fragile ornamentation.

The results of the analysis of the faunal association are the following:

Palaeoecologic implication. The Arda fauna is characterized by both infaunal and epifaunal species, mainly of infra- and circalittoral environment. The higher biodiversity has been recorded in fine sandstones, which contain the typical shallow water association with *Chamelea gallina, Acanthocardia tubercolata* and *Glycymeris insubrica*; a lower biodiversity has been instead recorded in siltstones barren of sedimentary structures and characterized by a deeper water fauna, mainly typified by the bivalve *Venus multilamella* and the gastropod *Turritella tricarinata*. The palaeoecological analysis of the fauna confirms the general regressive trend of the marine succession; several alternation of lower order transgressive and regressive sedimentary cycles are present, but no event of emersion or shift to very deep water setting has been recorded.

Palaeoclimatic implication. The occurrence of boreal guests, such as *Arctica islandica, Pseudamussium septemradiatum, Mytilus edulis* and *Acanthocardia echinata*, suggests that a climatic change occurred in the section causing a shift from warm to cold seawater temperatures. The evolution of this climatic deterioration is complex, but it prepares the ground for the onset of the continental glaciation of the Middle and Late Pleistocene.

Biochronologic implication. Based on the analysis of its fauna, the Arda river succession entirely belongs to the Early Pleistocene age (Gelasian and Calabrian). The extinction of the bivalves *Aequipecten scabrella* and *Flabellipecten flabelliformis* and the first occurrence of *Arctica islandica* allow to better constrain the age in some part of the section.

The late Variscan Monte Linas Pluton (SW Sardinia): a source of granophile element ore

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Keywords: Fayalite, hydrothermal ore deposits, Corsica-Sardinia Batholith.

The Monte Linas Pluton (MLP) and its host rocks offer a good chance in unveiling the relationships between late-Variscan geodynamics, magmatism and ore formation. Late-Variscan ore deposits are known since pre-historic ages; however, some petrological features of MLP such as the occurrence of uncommon fayalite bearing terms and their association with hydrothermal ore deposits remain unclear. The MLP emplaced at 289 ± 1 Ma in the Sardinian Variscan Foreland, between the allochtonous Arburese Unit and the underlying para-autochtonous Iglesiente Unit. The pluton consists of coarse-grained monzogranite permeated by medium- to fine-grained co-magmatic monzogranites. These fine-grained facies form an almost continuous sub-horizontal sheet, up to 50 m thick. The magmatic fabric is poorly defined by the shape preferred orientation of biotite, feldspar and plagioclase; however, a flat or gently dipping overall geometry is defined by the geometry of concordant porphyritic sheets, metamorphic xenoliths and pegmatites at the top of the pluton, and by the shape of rare micro-granular mafic enclaves. The MLP emplaced within already exhumed very low grade basement. A shallow level of emplacement is also inferable from the occurrence of andalusite in the metamorphic aureole. The composition of MLP is characterized by the occurrence of large, idiomorphic, zoned plagioclase and Fe-rich Ti-biotites, ipidiomorphic ortoclase and quartz. Common accessory phases include ilmenite, zircon, monazite fluorite and apatite. Fayalite has been rarely observed and is generally replaced by pseudomorphic patches of Fe oxides/hydroxides. Medium to fine grained rocks, instead, are characterized by plagioclase with inverse zoning often containing drop-like inclusions of Y- and Ta-oxides. Fayalite generally appears as a fundamental phase in pegmatites associated to these fine-grained rocks.

A wide range of ore deposits are associated to MLP, including Mo-W/Mo-Cu greisens, Fe ± Sn skarns, and W-Sn, Sn-Pb-Zn-Cu and F-Pb-Zn hypothermal to mesothermal veins. A striking metallogenic feature is the occurrence Mo and Sn in the same vein swarm, pointing to probable variations in the oxidation state of magma (from ilmenite-dominated to magnetite-bearing), which involved also the metal bearing fluids during a late intrusive phase. Field relationships and petrographical observations suggest that: i) MLP emplaced along a first order tectonic discontinuity (i.e., a major thrust plane developed in the more internal part of the Variscan Foreland), ii)the more evolved melts, relatively enriched in W-Sn-Pb-Zn-Cu, emplaced in the apical part of MLP in response to filter pressing processes enhanced by thermal contraction and fracturing of the already solidified monzogranitic terms. Hence, the MLP shares the same metallogenesis of equivalent late-Variscan plutons exposed in Cornwall, Herzgebirge and the Central Iberian Zone.

Foraminiferal assemblages in active volcanic areas: two study cases from Azores Archipelago (Atlantic Ocean) and Pantelleria Island (Mediterranean Sea)

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Keywords: benthic foraminifers, recolonisation, marine volcanic areas.

Recent studies demonstrated the capability of foraminifers to adapt to a wide range of environmental conditions and to give a response to environmental stress due to natural or human origin as environmental indicators (Alve, 1991; Hess et al., 2005; Carboni et al., 2009; Schönfeld et al., 2012). This work aims to document the benthic foraminiferal response to natural stressed environments in two areas, Azores Archipelago and Pantelleria Island, interested by similar active volcanism. The Azores area has been affected by a recent volcanic activity occurred in 2001, while the last submarine eruption of Pantelleria Island dates at 1891. The different periods of eruption of the two areas allow to investigate on the way and time of the re-colonisation process by foraminiferal assemblages. Petrographic, sedimentological and microfaunistic analyses were conducted on selected samples in order to obtain an environmental characterisation of the two active volcanic areas.

The inorganic fraction of samples collected in both areas is constituted of blackish, sand-sized glass shards, whereas the organic component is mainly constituted by foraminifers. Faunal composition, diversity and density highlight two different structure of the assemblages relatively to the two areas. In fact the foraminiferal assemblages of the Azores area are dominate by opportunistic species (*Angulogerina angulosa*) and represent the first stage of re-colonisation after the eruption occurred in 2001, while the associations of Pantelleria Island (*Globocassidulina subglobosa*, *Lenticulina rotulata*, *Lobatula lobatula* and miliolids) have to be considered as an advanced stage of resettlement with stable rich and well diversified assemblages. Moreover, in the Azores area many morphological abnormalities were recognised confirming a more stressed environment than Pantelleria bottom. In both areas a lot of specimens showed test alterations probably due to hydrothermal fluids that lead to the dissolution of calcium carbonate.

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Living foraminiferal assemblages in two submarine canyons (Polcevera and Bisagno) of the Ligurian Basin (Italy)

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Keywords: Foraminiferal assemblages, submarine canyons, Ligurian basin (Italy).

Recently the scientific interest is focused on the deep marine ecosystem because they can play an important role to recycle of the global carbon cycle. Particularly the submarine canyons act as sediment and organic matter traps into which material originating from the continental shelf is conveyed (Van Weering et al., 2002). Therefore, canyons, compared to the adjacent continental slope, represent areas characterized by more eutrophic conditions.

This study is part of the RITMARE Project: BioLig - Biodiversity, ecosystem functioning and pelagic-benthic coupling in Ligurian submarine canyons. In this work two types of environmental settings (from 200 to 2000 m depth) were investigated: the Polcevera and Bisagno canyons and the adjacent open slopes (Ligurian Sea). Living (Rose Bengal stained) and total benthic foraminiferal assemblages, collected by mean box corer, were analyzed and processed by statistical analyses (Cluster Analyses). The data results highlight different foraminiferal assemblages in slope and canyon areas due to the quantity and quality of organic matter fluxes.

The main difference consists of high frequencies of *Bolivina* spp., typical low oxygen taxa, in canyon sites. Moreover a comparison between the benthic foraminiferal assemblages of the studied sites and other canyons in the Atlantic (Nardelli et al., 2010) and Mediterranean basins (Schmiedl et al., 2000), showed similarities in compositional and structural features.

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Geochemical constraints on late Variscan granitoid magmatism in central Calabria (Southern Italy)

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Keywords: Petrogenesis, Serre Batholith, Calabria.

The Serre Batholith, in central Calabria, is a Late Variscan granitoid complex that makes up the middle portion, c. 13 km thick, of an almost complete and continuous section of continental crust. Petrogenetic studies on these granitoid rocks, although providing important advancements, highlighted the difficulty of elaborating reliable and univocal models and stopped ultimately the mid nineties. In this study, major and trace element analyses of 300 literature samples and 60 new samples have been investigated by means of classical petrological tools, but also in the light of recently proposed, or recently modified, classification schemes. Geochemical data indicate that the batholith rocks range with continuity in composition from quartz diorite and quartz monzodiorite to tonalite, granodiorite and monzogranite, with minor syenogranite samples; a well distinct group of leucotonalites also occurs.

The granitoids are on the whole magnesian and calcic to calc-alkalic, with only some of the more evolved rocks (two-mica granites) showing a ferroan calc-alkalic to alkali-calcic composition. Quartz diorites, quartz monzodiorites and tonalites are metaluminous to weakly peraluminous, while granodiorites and granites are weakly to strongly peraluminous, with two-mica porphyritic types being the only population with a genuine strongly peraluminous character. Fe*-number, MALI and ASI features highlight a strong affinity of the Serre Batholith rocks with Cordilleran granitoids, inherited from the compositions of the source rocks rather than reflecting the real tectonic environment of the magmas. Silica-rich peraluminous granites show also affinity with leucogranites formed by pure decompression melting of crustal rocks.

Major and trace element clusters and trends in Harker diagrams are consistent with an origin of the Serre Batholith from the assembling of several batches of magmas with different original compositions. Multielement diagrams and literature Sr-Nd isotope data also provide evidences for large heterogeneites within the magma sources. This does not exclude that the resulting magmas did interact between them, as indeed suggested by the diffuse presence of mafic microgranular enclaves in the weakly peraluminous granitoid rocks and by geochemical trends consistent with mixing processes.

A role for fractionation is also not ruled out and it appears indeed as the main process involved in the production of leucotonalites and in the geochemical variations within a population of weakly peraluminous granodiorites. Comparison with mixing curves and with compositions of experimental melts produced by partial melting of metasedimentary and intermediate-mafic metamagmatic sources suggests a general derivation of studied rocks from mixing, in varying proportions, of mantle- and metasediment-derived melts. It also confirms a pure crustal origin of the strongly peraluminous porphyritic granites, by partial melting of dominantly metagreywacke sources.

^{40}Ar-^{39}Ar results on amphibole and biotite of an anatectic amphibole-bearing migmatite from the Variscan basement of NE Sardinia, Italy

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Keywords: ^{40}Ar-^{39}Ar age, amphibole-bearing migmatite, Variscan Sardinia.

The amphibole-bearing migmatite forms a decametric lens-shaped body at Punta Sirenella, a few km north of Olbia in NE Sardinia. The leucosomes are coarse-grained granoblastic rocks occurring as elongated, tightly folded leucosomes, ranging in thickness from 2 to 4 cm, or as pods or patches up to 30-50 cm long. Both leucosome and mesosome mainly consist of variable proportions of quartz, plagioclase, biotite, ± amphibole, ± garnet. Accessory minerals are apatite, zircon, titanite, Fe-oxides, Fe-sulphides, and epidote. The mesosomes show an oriented fabric defined by the alignment of biotite and amphibole parallel to the D_2 foliation. Amphibole abundance is strongly variable from one leucosome to the other, or even along the same leucosome. In amphibole-rich leucosomes, amphibole occurs as large, green porphyroblasts (up to 4 cm in size) with several inclusions mainly of plagioclase, quartz, garnet, and biotite (Cruciani et al., 2008). According to Massonne et al. (2013), the migmatite protolith was an intermediate igneous rock metamorphosed at high pressure. At the final prograde metamorphic stage, the migmatite was heated to reach P-T conditions of about 1.3 GPa and 700°C. Close to these P-T conditions, melt separated from the rock to form leucosomes. Subsequently, pressure release and slight cooling resulted in the crystallization of the leucosome melt to form, among other phases, relatively large amphibole crystals that were partially resorbed later. Probably, the resorption process occurred at about 0.9 GPa and 680°C, just prior to the final crystallization of the leucosome melt. This implies that melt must have resided in the rock from about 45 km to 30 km depth. Pb–Pb zircon dating yielded a mean value of 452±3 Ma and an isochron age of 461±12 Ma which is interpreted as the emplacement age of the migmatite protolith (Cruciani et al., 2008). In order to improve our knowledge on the age of the amphibole-bearing migmatite, we analysed by the ^{40}Ar-^{39}Ar laser step-heating method amphibole and biotite separates. Amphibole yielded a slightly discordant age profile, characterized by a concordant segment representing ~75 % of the ^{39}Ar$_K$ released, yielding an error-weighted mean age of 317.4±2.0 Ma. We interpreted the measured age of amphibole as the age at which the migmatite passed, during exhumation, through the temperature 450-520 °C. In contrast, biotite gave a hump-shaped age spectrum, most probably due to the presence of minor interlayered chlorite. The total gas age is ~283 Ma and is taken as a minimum argon age for the biotite.

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The role of flavonoids on the weathering of iron and manganese minerals in the rhizosphere

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Keywords: flavonoids, Fe (hydr)oxides, Mn oxides, X-ray diffraction.

Iron (Fe) and manganese (Mn) are essential micronutrients for plants but, in most agricultural soils, they are present in scarcely bioavailable forms. Iron occurs mainly as Fe(III) in poorly soluble oxides (hematite, maghemite), oxyhydroxides (goethite, lepidocrocite), amorphous hydroxides and poorly crystalline minerals like ferrihydrite, or is included as Fe(II) or Fe(III) in the lattice of primary and secondary minerals. Manganese is present mainly as Mn(IV) and Mn(III) in amorphous secondary phases as well as in crystalline oxides (birnessite) and hydroxides (manganite), but it is taken up by plants only in the reduced form Mn(II).

To increase the bioavailability of these nutrients, plants have developed different mechanisms, among which the active release of flavonoids into the rhizosphere. Flavonoids are polyphenolic compounds with multifunctional properties, such as the protection of plants against pests and diseases, the regulation of root growth and function, and the induction of allelopathy. Very few studies have focused on the mechanisms of Fe and Mn mobilization operated by flavonoids in the soil and, particularly, in the rhizosphere.

It can be hypothesized that flavonoids dissolve Fe and Mn minerals by means of reducing or complexing processes, or by a combination of these two mechanisms. In a recent experiment, we observed that rutin mobilized a high amount of Fe from an alkaline soil by reducing it to Fe(II), and quercetin was very efficient in Mn solubilisation from an acidic soil by reducing it to soluble ions Mn(II). When quercetin was used in combination with citrate, Mn solubilisation further increased due to reduction and complexation processes.

On the basis of these experimental evidences, the present study aims at investigating the effects of some flavonoids (rutin, quercetin and genistein), both alone and in combination, on the alteration of some of the most representative Fe and Mn (hydr)oxides of the soil (goethite, hematite and birnessite). For each flavonoid, saturated aqueous solutions are prepared, containing Na_3N (10 mM) as bacteriostatic agent. Synthetic Fe and Mn minerals are mixed at 20% (w/w) with an inert glass powder and let to interact for 24 h with 30 mL flavonoid solutions under continuous stirring. After centrifugation, the liquid fraction is filtered and analysed to determine: (i) the amount of Fe and Mn by ICP-AES and voltammetry; (ii) the concentration of flavonoids and other secondary products by HPLC analyses. The solid fraction is dried and analysed by (iii) XRD and (iv) SEM-EDX in order to study any structural modification of the minerals. Results are compared to a control without flavonoids and a control prepared using citrate, a well-known complexing molecule in plants.

Complex electrical resistivity measurements on alluvial sediment samples toward sedimentological and petrographic properties estimation

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Keywords: hydrogeophysics, complex electrical resistivity, alluvial sediments.

In the last decades, geophysical methods have been increasingly used for groundwater exploration to gain information on geometry and properties of the subsurface. However, the knowledge on petrophysical relationships achieved with the longstanding experience in hydrocarbon exploration and available for reservoirs characterization cannot be applied in a straightforward way for near-surface environments, due to typical lower temperature, pressure and consolidation degree. Moreover hydrogeological studies have less financial support and higher interactions with human activities than hydrocarbon exploration, so that different techniques are used, e.g. surface instead of well-log acquisitions.

Essentially, hydrogeophysics is based on the relationships of electrical resistivity and hydraulic conductivity with the porous medium texture. In this work the resistivity-texture relationship is investigated through laboratory measurements of complex electrical resistivity on reworked alluvial sediment samples, texturally ranging from slightly sandy mud to gravelly sand, and saturated with NaCl and $CaCl_2$ solution with electrical conductivity varying between 20 and 1400 S/cm. Data are collected in the frequency range between 10 mHz and 100 kHz with a spectrometer connected to a sample holder, which allow to investigate a volume of about 2500 cm^3. Amplitude and phase spectra are modelled through the Cole-Cole analogue electrical circuit, in order to obtain the best-fitting parameters (direct current resistivity, chargeability, relaxation time and frequency exponent) describing conduction and polarization processes within the samples.

The fit of the experimental data is performed not only with a standard least-squares approach, but also with a multi-objective approach, which considers separately the amplitude and the phase spectrum. The latter approach allows to emphasise polarization phenomena primarily linked to the amount and the dispersion degree of the silty-clayey fraction, even if phase values for sediments free from metallic particles are usually smaller than a few mrad. Moreover, the multi-objective approach permits the identification of upper and lower limits for model parameters. However, preliminary results show that the superposition of comparable effects originated from different variables (e.g. both the decrease in the water electrical conductivity and the increase in silt and clay content yield an increase of polarization) prevents one-to-one correlations among the model parameters and the sediments' litho-textural properties; a multivariate statistical analysis could be a valid support in the interpretation of experimental data.

Quantitative phase analysis of clay soils via the Rietveld-RIR method and thermal analyses coupled with evolved gasses mass spectrometry

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Keywords: Rietveld-RIR, soil, thermogravimetry.

The present study deals with Quantitative Phase Analysis (QPA) of clay soils obtained via the Rietveld-RIR method, the General Structure Analysis System (GSAS; Larson & Von Dreele, 2000), and thermal analyses coupled with evolved gasses mass spectrometry.

As far as we know, there are very few applications of the Rietveld method to the estimation of quantitative mineralogical composition of soils (Brinatti et al., 2010; Prandel et al., 2014). The application of the Rietveld method represents a major step forward in QPA with respect to conventional methods, especially as far as accuracy and detection limits are concerned. The GSAS is a comprehensive and detailed system for refinement of both structural models and quantitative mineralogical composition of powder mixtures, starting from X-ray or neutron diffraction data.

Thermogravimetry (TGA) allows the determination of the mass as a function of temperature or time; this thermal technique provides information concerning thermal stability and composition of the sample and of any intermediate compound which may be formed. When these measures are combined with chemical analysis of evolved gases, it is possible to determine the reactions that are at the base of each thermal effect.

During the GSAS refinements, a Chebyshev polynomial of the first kind was used for background modeling. For peak shape modeling a multi-term Simpson's rule integration of pseudo-Voigt was adopted. The amount of amorphous phase present in the analyzed powder mixtures was estimated via the combined Rietveld and Reference Intensity Ratio (RIR) methods. Corundum NIST SRM 674a was used as internal standard.

Identified phases in analyzed soil samples include tectosilicates, layer silicates, carbonates, and in minor amount sulphates. Irregular interstratified phyllosilicates were also detected. Since treatments with ethylene glycol did not enhanced any appreciable changes in the low angle peaks of the pattern, it is conceivable that no expandable interstratified phyllosilicates are present in the analyzed soils. One or more amorphous phases were detected.

In selected samples the amount of carbonates and hydrated phases measured via X-ray diffraction was then compared with the values estimated via TGA by measuring the quantity and type of the reaction products (i.e., H2O and CO2) released.

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Prospecting and assessing structurally controlled bentonite deposits by employing Electrical Resistivity Tomography

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Keywords: Mineral exploration, Electrical Resistivity Tomography, bentonitic deposits.

Sardinian bentonite deposits are commonly linked to hydrothermal alteration of thick sequences of pyroclastic flows and epiclastites, associated with the Oligo-Miocene calcalkaline volcanic cycle. Faults represents an efficient hydrothermal plumbing systems, which combined with textural features (mainly open porosity) of the pyroclastic pile, controls the geometry of the deposits. Making out this interplay between faults, rock texture and the resulting clay deposits is not easy. Conventional methods, such as structural and stratigraphic studies followed by drilling investigations and trenches, despite high costs, can fail predicting the actual three-dimensional structure of a deposit. The geoelectrical methods, instead, provide an important contribution, not only in prospecting but also in defining the volume of mineralized bodies. The effectiveness of these techniques depends on the high-resistivity contrast between hydrothermally altered pyroclastites and the host rocks. In this paper we propose the application of Electrical Resistivity Tomography (ERT) to localize and evaluate a smectite clay deposit in northern Sardinia. 2D ERT surveys were performed close to a faulted area, to define the location, thickness and lateral continuity of the clayey body and to define its relations with faulting and stratigraphy. A quasi-3D ERT data acquisition was carried out in a selected area to estimate the available clay reserves. The reliability of the resistivity models was assessed by means of cross-checking with boreholes data. Finally, the interpretation of field survey has been optimized through synthetic modeling of the electrical resistivity imaging technique. The ERT surveys were carried out using a multielectrode system, consisting of an Abem Terrameter SAS1000 device combined with an ES 10-64 electrode selector. The results allow defining, with good accuracy, the extent and geometry of the deposit and evidenced its genetical relationships with both faults and definite pyroclastic horizons. Overall, the suitable conditions under which the ERT method might provide optimal results for prospecting clay deposits were defined.

Depositional environment of calcite-alabaster: two compared case studies

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Keywords: calcite, alabaster, karst.

Calcite-alabaster is a sedimentary orthochemical rock which forms in karst environments as a consequence of the precipitation of consecutive layers of calcium carbonate crystals (mostly calcite, rarely aragonite). In some cases, calcite-alabasters are characterized by the presence of bands irregularly disposed between the layers. These consist of detrital material deriving from the surrounding rocks and deposited on the surface of calcite layers. Their presence is probably due to transport events e.g. episodic flooding of cave passages (Lascu & Feinberg, 2011). The aspect and the properties of every layer, as well as calcite fabric, are strongly influenced by the fluctuations of environmental parameters through time. Changes in factors, such as temperature, water composition (trace elements, presence of dissolved organic matter), detrital material, drip and precipitation rates, affect the features of calcite-alabaster at both microscopic and macroscopic levels. This preliminary study aims to compare two calcite-alabaster *varieties* along with their formation sites, observing similarities and differences of the rocks and of their depositional environments. We compare two Italian sites: Busca (Piedmont) and Belmonte Mezzagno (Sicily); both exploited in past times as quarries. Effectively, calcite-alabaster has been used since ancient times in churches and historical buildings as a construction and ornamental stone. From a geological point of view Busca area belongs to the southern sector of Dora-Maira Massif (Pennidic domain of Western Alps), the deposits are hosted in a Liassic-Triassic cover of dolomitic marble (Sandrone et al., 1993). Belmonte Mezzagno district belongs to the Famusi Formation (Noric age); in this case, the host rock is a microcrystalline porous dolostone. The macroscopic appearance of both calcite-alabaster samples is extremely heterogeneous: white translucent bands of pure calcite of variable thickness (few mm to 2 cm) are alternated with brown bands full of dissolved organic material, likely humic and fulvic acids deriving from decomposed vegetal matter. In both cases one can recognize merged speleothem structures, such as stalactites and stalagmites. A multi-technique approach has been chosen to start this project. Calcite-alabaster samples of both localities have been petrographically examined and described. The mineralogical characterization has been done by micro-Raman spectroscopy; while geochemical analyses have been carried out by trace elements identification using micro-XRF. Furthermore, stable isotope analysis has been done in order to acquire data on ^{18}O and ^{13}C isotopic fractionation, to reconstruct the ambient temperature in the time of deposition.

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Petrography, major-trace elements and isotopic compositions of the lavas from El Tigre volcano (Fonseca Gulf, Honduras): increasing data on the Central America Volcanic Front

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Keywords: El Tigre, Honduras, Central America Volcanic Arc, calc-alkaline magmatism.

El Tigre volcano is located within the Fonseca Gulf, Honduras, where there is a break in the strike of the Central America Volcanic Front (Walker et al., 2000; Carr et al., 2003; Bolge et al., 2009). The origin of this gulf arise from the intersection of three first-order tectonic structures, and such a complex tectonic setting is the result of the oblique subduction on the Central American trench (Carr et al., 2003; Burkart & Self, 1985). For these reasons, the knowledge of El Tigre is of paramount importance for unravelling the magmatological and volcanological evolution of this area.

Lavas from El Tigre consist of basalts and basaltic andesites with calc-alkaline affinity. The fundamental mineralogical assemblage is typical of relatively primitive subalkaline rocks, and is made of plagioclase, olivine, clinopyroxene, orthopyroxene and opaques. Lavas show a significant LILE enrichment and Nb depletion, a strong slab signature and incompatible element contents similar to those in the main front of the adjacent volcanoes from El Salvador and Nicaragua (e.g. Ba/La up to 80). However, a small group of basalts from El Tigre, with higher MgO content (> 5 wt%) and lower Ba/La, Ba/Nb and Zr/Nb ratios (34-39, 35-49 and 5-7, respectively), emphasizes that mantle-derived magmas were not produced by the same source or process throughout the span-time activity of the volcano.

El Tigre lavas are characterized by higher $^{87}Sr/^{86}Sr$ (0.7038) and lower $^{143}Nd/^{144}Nd$ (0.51301) with respect to arc volcanoes of El Salvador and Nicaragua, whereas $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ isotope ratios are very similar (38.2 and 18.5, respectively).

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Geochronology of travertines and calcite veins in the Tafone Graben area (Manciano, southern Tuscany)

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Keywords: hydrothermalism, travertine, southern Tuscany.

The Tafone Graben is a key area to study the interaction between active tectonics, hydrothermalism and travertine deposition in southern Tuscany. Moreover, the graben is known for the occurrence of stibnite ore deposits, whose origins are related to the rise of hydrothermal fluids (Dessau et al., 1972). The Tafone Graben formed as consequence of the Miocene-Quaternary crustal thinning that operated in the inner domain of the Northern Apennines and led to diffuse volcanism (e.g. the Vulsini Volcanic District) as geothermal anomalies (Larderello, Amiata, Latera) along the Tyrrhenian side of the belt.

A preliminary geological-structural survey in the area revealed that a complex fault array controls the tectonic relationships between the main exposed lithotypes that, locally, show evidence of intense hydrothermal alteration. A main travertine body, characterized by a tabular geometry and sub-horizontal layering, is positioned on top of a fault-related damaged zone and a few hundred meters away from an active degassing spot. N-S-striking, sub-vertical calcite-sulphide vein arrays cut through the Quaternary deposits surrounding the travertine body. By the means of the Uranium-series disequilibrium method ($^{230}Th/^{234}U$) we obtained an age older than 350 ka for the travertine body, whereas the calcite-sulphide veins reported an age of 148±21 ka. Stable isotopes analysis shows a positive $\delta^{13}C$ range (5-7‰, PDB) confirming the hydrothermal origin of both the dated carbonates. The field and geochronological data presented in this work provide further constraints to the age and the structural control on the hydrothermal mineralization in southern Tuscany (cf. Minissale et al., 2004; Brogi et al., 2010). Specifically, the 148±21 ka can be referred to the fluid-rock interaction processes responsible for the ore deposition in the Tafone Graben area.

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Burial contexts in the protohistorical necropolis of Torano Castello: SEM and XRF spectroscopy analyses

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Keywords: Calabrian Iron Age, XRF spectroscopy analysis, X-ray, archaeometric studies.

The archaeological and protohistoric site of Torano Castello is a hill site located at Cozzo la Torre. The excavations that took place in 1965 discovered an indigenous necropolis dating to the 8th century BC and lying on the plateau just below the hill: a mound and twelve burials were exposed. The modalities of deposition and the typology of grave goods exhibited features typical of the necropolises of the Calabrian Iron Age. The most important artefacts recovered were SEM-EDX analysed at the Dipartimento DiBEST of the Università della Calabria; whereas XRF spectroscopy was carried out at the Dipartimento di Fisica e Scienza della Terra of the Università della Calabria. The materials that were analysed were: iron and bronze rings; brooches; an iron and bronze knife; decorated bronze pendants; weapons of various kinds. The XRF spectroscopy analysis aimed to distinguish the composition of a pendant, some brooches and a dagger, while the superficial analysis conducted through the use of an X-ray beam over the surface of the objects provided information on the most representative elements in the composition of the sample.

Overall, this research highlighted a series of innovative aspects that had never been shown before and that distinctly differentiated from analogous contexts belonging to the same period that had previously been investigated. The archaeometric studies put in evidence the fine decorations and high level of standardisation reached in the creation of the analysed objects. For instance, it was possible to note that all the iron rings exhibited a specific decoration that was eventually revealed to be characteristic of the place, known as to small botton.

A global crustal model from the inversion of GOCE gravity observations

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Keywords: Global crustal model, GOCE satellite, inverse gravimetric problem.

The boundary between Earth crust and mantle, the so called Moho, is commonly estimated by means of seismic or gravimetric methods. The former methods can be locally very accurate since seismic profiles give an almost direct observation of the actual crustal structure, but can be quite far from reality in large regions where no data are available. The latter methods, although often based on simplified hypotheses to guarantee the uniqueness of the solution, are nowadays becoming more and more important thanks to the improved knowledge of the gravitational field. In particular satellite gravity missions, like the European Space Agency mission GOCE (Drinkwater et al., 2003), provide a very accurate and spatially homogeneous dataset that can be used to validate the existing global crustal models or to estimate a new one by constraining the relation between Moho depth and crustal density (Reguzzoni et al. 2013).

In this work the GEMMA1.0 crustal model (Reguzzoni & Sampietro, In Press) with a spatial resolution of 0.5°x0.5° and constrained with GOCE observations is presented. For this purpose several additional external information has been used, such as topography, bathymetry and ice sheet models from ETOPO1, a recent 1°x1° sediment global model and some prior hypotheses on crustal density. In particular the main geological provinces, each of them characterized by its own relation between density and depth, have been considered. A model describing lateral density variations of the upper mantle is also taken into account. Starting from this prior information, an inversion algorithm is applied to the GOCE space-wise grid of second radial derivatives of the gravitational potential (Reguzzoni & Tselfes, 2009) to estimate the bottom of the crust. The computed Moho global model is well consistent not only with other global/regional models, but also with the actual gravity field, thus overcoming the main limitation of seismic Moho models, like the CRUST1.0.

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Using PCA and standard deviation analysis to evaluate the reliability of digit length impression as sound ichnotaxonomical character

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Keywords: Principal Component Analysis, Standard Deviation analysis, tetrapod ichnology.

In tetrapod ichnology, relative length of digit impression is often adopted as a binding character, both for ichnotaxa discrimination and in the search for a putative trackmaker (*e.g.*, Voigt et al., 2007; Voigt & Ganzelewski, 2010).

To evaluate the reliability of this character in ichnotaxonomy, a Principal Component Analysis and a standard deviation analysis have been performed on well-preserved footprints referred to as *Ichniotherium sphaerodactylum* from the Early Permian Tambach Formation (Thuringia, Germany). The studied footprints can be referred with a good chance to a unitary kind of trackmaker within Diadectidae (Diadectomorpha), as suggested by a functionality analysis recently performed on the same material. Therefore, the peculiarities observed in different slabs can be traced to differences in posture and locomotion of the same typology of tetrapod, rather than to a real taxonomic diversity.

Despite the soundness traditionally ascribed to this character, digit impression relative length has proved to vary consistently even within the same trackway, due to mode of locomotion and substrate conditions. Overall, the digit relative length in manus impressions results much more variable with respect to the condition observed in pedes impressions, indicating a less biomechanically constrained front autopods, probably linked to their greater exploratory attitude during the progression of stroke. The analysis has also highlighted a substantial variability in digit impression length even as regards digit IV, often adopted as reference in ichnotaxonomic studies.

The obtained results clearly indicate the need to conduct a preliminary explorative analysis on the whole available ichnological material, in order to detect which digit is the most consistent by an ichnotaxonomical standpoint (*i.e.*, the less variable digit impression, and maximally connected to the actual functional prevalence of autopods) and, therefore, to avoid an arbitrary selection. In this regard, a standard deviation analysis and a multivariate one are strongly recommended as an empirical basis for sound and communicable studies and diagnoses. Such a preliminary analysis, obviously case-specific, should provide a greater control on ichnotaxonomy, particularly in the case of allied footprints, and can also be considered an enlightening tool, if associated to biomechanical analysis, in improving and refining trackmaker identification.

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Voigt S. & Ganzelewski M. 2010. Toward the origin of amniotes: Diadectomorph and synapsid footprints from the early Late Carboniferous of Germany. Acta Palaeontologica Polonica, 55, 57-72.

Forensic Geosciences

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Keywords: Forensics, Criminalistic, Criminology.

Forensic Geosciences are the set of all disciplines that focuses on Earth system and that can play a resolutive role in law enforcement and in intelligence activities. The word "Forensic Geosciences" replaces the obsolete "Forensic Geology" because the latter gave a reductionistic and misleading image of all the possible applications and outcomes of Earth Sciences in Criminalistic and Criminology. Geosciences more often used in Forensics are Geology "*sensu stricto*", Paleontology, Mineralogy, Petrography, Geological engineering, Geophysics and Geochemistry. Leading countries in Forensics, such as United States, Canada and Germany among the other, have a long tradition of Forensic Geosciences used as a standard procedural tool in investigations and in court, while such discipline are only scarcely applied in Italy.

Only recently, a new section of the Italian Geological Society dedicated to this topic has been opened, taking into account that Forensic Geosciences are still scarcely known in Italy. The new section aims to be a lively forum for communication between geologists working in different fields of the Earth Science, who want to approach and provide their valuable contribution to this new horizon of Geosciences.

New foundings of contourite deposits in an active continental margin (Southern Tyrrhenian Sea)

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Keywords: Contourites, Bottom Currents, Loop Current.

Contourites are marine sediments deposited or reworked by bottom currents which are able to erode, transport and deposit the sediments on the seabed (Rebesco and Stow, 2001).

They have been recognized in different variety of context, ranging from the abyssal plain to the outer-shelf or upper slope. Elongated-mounded drifts represent one of the most common recognized typologies especially in the Mediterranean Sea (Faugeres et al., 1999; Martorelli et al. 2010).

This study is based on high and very high resolution seismic reflection profiles and Multibeam data collected along the northern Sicily continental margin, in the sector between Palermo and Castellammare Gulfs, during 2009 MaGIC Project oceanographic cruise, by using CHIRP, Sparker and MultiBeam acoustic systems.

The data show the occurrence of different types of structures with highly contrasting seismic and morphologic signatures, but we have been focused attention on those who have lenticular, convex-upward shapes, and internally are characterized by sub-parallel, moderate to low-amplitude reflections, interpreted as deriving from contourites. In particular, we recognized these structures, which comprise drifts and associated erosional elements (moats), in the eastern Castellammare Gulf. Contourites were found in depth range of 350-600 m, are about 3 km wide, up to 20 m thick from basal erosional surface, have asymmetric profile and divergent reflectors resulting in a non-uniform thickness between drift and moat. On the basis of several examples documented in other basins we classified them as elongated-mounded drifts.

Their deposition and distribution is mainly controlled by effect of continental climate on bottom currents, sediment avalaibility and morphostructural context. Offshore northern Sicily the dominant wind-driven current flows eastward but in proximity of the gulfs can form loop current. In particular, in the western Castellammare Gulf it curves to south where it hits warmer water so the denser water sinks to the bottom running parallel to the coast and finally exits towards northeastern. This anticlockwise deep path acts as a bottom current, therefore contourites depositional systems can be formed.

These data allow us to document for the first time the presence of contourites along the northern Sicily continental margin, revealing that the morphology of the margins is one of the main controlling factor for their deposition.

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Rebesco M. & Stow D., 2001. Seismic expression of contourites and related deposits: a preface. Marine Geophysical Reaserches, 22, 303-308.

Structural analysis of the Laguna Blanca basin in the Central Andean Plateau (Catamarca, Argentina)

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Keywords: strike-slip tectonics, pull-apart basin, Southern Central Andes.

The Southern Central Andes are characterized by an oblique subduction between the Nazca and South-America plates, with a ENE-WSW convergence, determining a transpressive stress regime. The aim of this study is to define the nature of the rhomb-shaped Laguna Blanca basin (26°35'S-66°49'W), which is located along the SE margin of the Puna plateau. Indeed, the Neogene tectonic evolution of this area is a debated topic. According to a first model a polyphase compressive tectonics, probably reflecting a change in plates convergence, involved the entire region where a former NW-SE shortening was followed, at 4-2 Ma, by a ENE-WSW contraction continuing in the Present (Marrett & Strecker 2000). Alternatively, a second model excludes large-scale stress field variations, but suggests a simultaneous activation of differently oriented faults within a heterogeneous deformation of the upper crust. In this view, the deformation of the Puna plateau appears dominated by a southward-increasing crustal strength, related to the absence of Quaternary magmatism south of 27°S, accordingly to the abrupt change in the subduction angle. This strength gradient is responsible for the southward mid crustal flow and the related formation of sinuous transpressive zones and rhomb-shaped domains, bordered by N-S and NE-SW fault systems (Riller et al. 2012). In this context the N-S faults should have left-lateral transpressive kinematics, contrary to what is expected from the general ENE- WSW convergence between plates.

In order to evaluate the two models a series of meso-structural data were collected during the fieldwork, analyzing the major fault zones that bound the Laguna Blanca basin. These data were used to retrieve local paleostress fields through stress-inversions methods. The results have shown a general NW-SE horizontal shortening, compatible with the left-lateral strike-slip kinematics of the N-S faults bounding the Laguna Blanca basin. On the other hand, a pure extensional regime has been recorded within the basin, although the maximum horizontal axis holds steadily along a NW-SE trend. All these results, together with macro- and meso-scale morphological and structural evidences, support the interpretation of the Laguna Blanca basin as a pull-apart basin generated at a releasing stepover along N-S sinistral strike-slip master faults. Hence, our results agree with Riller et al. (2012) since the formation of a pull-apart basin at the scale of tens kilometers is compatible with a stable sinistral strike-slip regime along N-S faults.

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Riller U., Cruden A. R., Boutelier D. & Schran C. E. 2012. The causes of sinuous crustal-scale deformation patterns in hot orogens: Evidence from scaled analogue experiments and the southern Central Andes. J. of Structural Geology, 37, 65-74.

Gentle sample preparation methods for specimen contained in complex matrix

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Keywords: TEM sample preparation, asbestos, complex matrix.

The target of this work is to present different sample preparation methods that permits to characterize, by different TEM techniques, the inorganic fibers or particulate matters contained in an organic or artificial complex matrix.

We will present two type of methods: the first kind includes the complete removal of the matrix component, in order to concentrate the analyses only on the target fibers or particles; the second kind, is planned in order to conserve and allows to characterize also the matrix component.

The used method has to avoid any damage to the inorganic material extracted from the matrix. Moreover, it should not generate artefacts through chemicals or mechanical stress.

In this study, different techniques of preparation have been evaluated and tested, giving priority to the most rapid and simple ones.

For organic matrix, we preferred chemical digestion for the first kind methods and embedding techniques combined with microtomy for the second kind. The digestion of the biological component of the sample was performed by sodium hypochlorite ($NaClO$ 14%) in an oven at 60 C for 6-24 hours. The embedding was made in paraffin and epoxy resin.

For the artificial matrix (in this case cement), we choose to use different amount of mechanical stress to partially or totally separate the matrix from the fibers/particles. The mechanical stress in this case is represented by grinding and sonication.

The cement pieces was suspended in acetone to avoid dispersion and the possible chemical interaction between the sample and the suspension medium.

Substantially, a simple preparation allows an appreciable flexibility of applications. With the possibility to modify and adapt the steps at the different biological (e.g. urine, intestine tissues etc) or artificial samples (concrete, wallpaper, ropes etc).

This technique allows to make TEM detailed investigation to fully characterize exogenous inorganic materials that enter the organism or lies in manufacts and the transformations that occur during mineral-matrix interactions. The extrapolated data can be used in an interdisciplinary study (by mineralogists, chemists, biologists, pathologists) to better understand the pathological effects caused by the inorganic materials penetrated into human body.

Regional unconformities in the Plio-Pleistocene sedimentary successions of the Calabrian Block (central Mediterranean)

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Keywords: Unconformity, Pliocene, Pleistocene, Calabria, Tectonics, Forearc basin.

Three main unconformities typify the Plio-Pleistocene fill of the basins that lie in both onshore and offshore areas of the Calabrian Block, an arcuate terrane migrating to the SE above the Ionian lithosphere, between the southern Apennines and Sicily (Malinverno & Ryan, 1986; Sartori, 2003). These surfaces consist of the mid-Pliocene unconformity (developed between late Zanclean and early Piacenzian), the early Pleistocene unconformity (Gelasian) and the mid-Pleistocene unconformity (late Calabrian) (Zecchin et al., 2012). Their occurrence varies significantly depending on the considered location, so that one to three unconformities may be recognizable at a given basin. Several lines of evidence suggest that the three unconformities are the result of main tectonic events related to interferences between the Calabrian Block and adjacent microplates, which led to deformation and uplift, and interrupted phases characterized by tectonic subsidence in the Calabrian basins and forward migration of the entire Block (Zecchin et al., 2012). The discontinuous occurrence of the unconformities is inferred to be related to the position of the basins with respect to the areas that underwent tectonic disturbance, which varied during the Plio-Pleistocene interval. Important implications arise from the recognition of a synchronicity in the development of the unconformities in the Calabrian basins, as this allows to define key references for the study of the geodynamic evolution of the central Mediterranean.

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SESSIONE S36

Poster - Geoscience outreach: a challenge to be faced

CONVENORS

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The secret to *lustro* between art, science and mineralogy

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Keywords: problem based learnin, clay, clyuster, ITC.

The European Reference Framework of Key Competences for Lifelong Learning (OJEU, 2006) defines key competences as knowledge, skills and attitudes applied appropriately to a given context (Pepper, 2011). The Framework identifies eight key competences as necessary for personal fulfilment, active citizenship, social inclusion and employment; languages; mathematical competence and basic competences in science and technology; digital compete nce; learning to learn; social and civic competences; sense of initiative and entrepreneurship; and cultural awareness and expression. Each has a concise definition of its scope and all emphasise critical thinking, creativity, initiative, problem solving, risk assessment, decision taking, communication and constructive management of feelings. The latter are also known as 'transversal skills'.

Earth sciences are an example of the teaching-learning based on problem-based learning. The question to which students must answer is what secret lies behind the preparation of Luster, from where the clay rich in silver and copper. As through the chemical and mineralogical analyzes can solve a riddle of the Renaissance. The first step is setting, students are divided into groups of three or four boys; each of them is assigned a specific role as a geologist, archaeologist, historian, chemist, physicist. It operates attivaziine context of asking a question apperentemente extraneous What is the luster when this technique was born in Umbria who was Piccolpasso. After an initial investigation students will visit a master potter in Deruta. Here you will learn the practical technique to achieve the luster. By means of a physical-chemical analysis, it turns out the nature of microcrystalline clusters of silver or copper immersed in an amorphous matrix a colloidal system that undergoes a redox environment in a non-oxidizing. The secret that allowed the production about luster was the clay with which to make the Bolo, that is, a colloid clay and vinegar. From which location came the clay. questionnaire secret has been handed down from father to son and is lost. Today, thanks to a geological and petrographic study has identified the region in Siena from which to draw useful material.

Seismological literacy, a contribution to the mitigation of seismic risk. The educational project for the schools of Arezzo (Italy) and its province

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Keywords: educational project, seismology, Arezzo.

In the last six years an educational project has been developed involving seismologists of the local Seismological Observatory of the Istituto Nazionale di Geofisica e Vulcanologia (INGV), geologists and experts of civil defense from the Municipality of Arezzo and of a local cultural association, the “Associazione di Promozione Sociale La Voce dei Piccoli” from Anghiari (Arezzo, Italy). The aim of the project is to address the pupils from the earliest years of school (from preschool to the junior high school) to the knowledge of the dynamics of the Earth. In this context, the main subjects of geophysics and seismology are illustrated during courses of four weekly lessons.

The contribution of local geologists allows to drop the scientific information directly to the places where pupils live, in order to increase their knowledge about the local geological and seismological peculiarities and to make them aware of the environmental hazards, especially of the local seismic hazard. In this perspective, the project is an important cultural contribution to the mitigation of seismic risk. From the beginning of the project more than 1500 pupils have attended the courses. The strict cooperation between researchers, local experts and teachers has allowed to target the school activity in producing tangible results. Small books of short stories about earthquakes, brochures to illustrate the correct behavior to undertake before, during and after an earthquake, essential handbooks of seismology are examples of the final products of the courses. Pupils have diffused what they have learned to their peers and to adults organizing scientific popular conferences and participating with their posters at the scientific exhibitions promoted by the Seismological Observatory. The project and its products have been supported by the local administrative authorities, the Province and the City of Arezzo, conscious of the importance of the diffusion of the knowledge as first stage in a successful plan toward risk mitigation.

Dissemination through InFEA Project: the water, an inalienable right

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Keywords: hydrogeology, dissemination, Friuli Venezia Giulia Region, groundwaters.

While drawing up the Water Protection Plan, the Water Resources Department of the Friuli Venezia Giulia Region jointly with the Mathematics and Geosciences Department of the Trieste University has carried out a three-year study aimed at assessing the sustainability of the groundwater use in the Friuli Venezia Giulia Region. In this territory is still very common to get water from artesian wells for domestic purposes and to leave them flowing free. These so called “fountains”, widespread located in the Low Plain, can be considered an integral part of the popular culture, a sort of cultural heritage to be preserved. Their density varies considerably according to the geographic settlements distribution and to the boundary conditions. The withdrawals interest the artesian aquifer systems and being free flowing, withdrawals are real and much more than the needs. The unsustainability lies in the fact that, high quality waters, withdrawn from medium to high depths, end up in the sea through irrigation and drainage canals or go to feed the shallow phreatic aquifer system of the Low Plain without producing any recharge for the groundwaters. The study highlighted that more than 50% of the total used groundwaters come from the domestic wells that get the waters from the deep aquifer systems. These withdrawals are approximately 70 times more than the estimated demand (250l/day per person, for a European citizen). In the Friuli Venezia Giulia Region, even if do not exist a problem of water quantity, going on with the same way of living, there will be, for sure, a quality problem. In the system in fact, through the effective infiltration, worse quality waters go into the water cycle. Furthermore, this great discharge that reaches the drainage system causes malfunctions in sewage plants and an increase of the pumping costs. Then comes the need to raise awareness on this specific subject. Thanks to the national InFEA Project, Friuli Venezia Giulia Region, jointly with researchers of the Trieste University, started a dissemination program in the hydrogeology field. The foreseen activities, within the time, will involve all the Low Plain municipalities. The methodological approach involve all the primary schools (class 4 and 5), teachers, local administrators and citizens. To the scholars, after a starting front lecture (two hours for each class), a field daily activity is offered. At the end of the cycle, all the students are involved in an active cooperation allowing to realize posters, models, poems and short stories that are later presented during an evening dedicated to a discussion among researchers, politicians/administrators and citizens. The involvement of the young students (9-11 years old) with the constant and active participation also of the teachers, authorities, parents and citizens, can be considered an educational experience for everybody. At the same time, this creates a conscious awareness of the critical issues of our fragile territory.

Because the ERN belongs to public: lesson learned at INGV

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Keywords: European Researchers Night, interactive outreach, scientific theatre, educational games.

"The European Researchers' Night (ERN) aims to bring researchers closer to the general public and to increase awareness of research and innovation activities, with a view to supporting the public recognition of researchers, creating an understanding of the impact of researchers' work on citizen's daily life, and encouraging young people to embark on scientific careers." This is the objective of European Commission, as shown in the Participant Portal for funding opportunities (ec.europa.eu/research/participants/portal/).

Since 2009, the Istituto Nazionale di Geofisica e Vulcanologia (INGV) participates to ERN in the framework of Associazione Frascati Scienza (www.frascatiscienza.it) with activities on Earth Sciences outreach aimed at intriguing and stimulating audiences of all ages.

For the September 27th 2013 Night, INGV contributed with programs in the INGV headquarters in Rome, including guided tours to laboratories, seminars held by researchers, exhibitions, educational games. Other activities took place in Frascati, the main venue of the Night at the Museo Geofisico in Rocca di Papa, and in L'Aquila, the city stroken by the 2009 earthquake. For the latter location, INGV is participating to the renaissance of the city with on site researchers and special research projects.

Activities combined education with entertainment.

In Frascati, children and adults attended a science theatre performance "When the sky flashed red". The plot invites general public to consider science as a big story of pioneering ideas. The theatrical experience survey was aimed investigating emotions and learning. Other activities concerned a novel hands-on educational activity for kids curious about science. They learned about Earth inner structure, fragile lithosphere, waves propagations, impact of waves on building etc, handling eggs, cookies, honey, sugar and pudding. People of all ages and professions came, giving us the opportunity to evaluate different types of audience. Evaluation of impact on different type of audiences was performed. Appreciation surveys, compiled by visitors at INGV headquarter and by the scientific theatre's audiences, supplied our team with feedback, revealing some precious hints about users themselves, appreciation, emotions, learning and margins of improvement. The most frequent comment was the invitation to repeat more frequently such events.

The science venue was the result of common efforts among scientists that found themselves enjoing the challenging public. About forty people participated, and beyond the authors, they were: C. Acerra, G. Alessio, L. Alfonsi, A. Bannoni, S. Bucci, P. Burrato, F. Caprara, A. Caramelli, S. Conte, D. Di Luigi, G. Ferrari, R. Forsinetti, G. Galli, V. Gallotti, G. Gaudiosi, I. Hunstad, V. Lazzarini, N. Lo Bue, M. Miconi, R. Nappi, R. Nave, M.C. Piazza, C. Piccione, D. Pietrangeli, S. Pinzi, V. Pirro, M. Puppio, L. Raimondi E. Rocchetti, E. Spagnuolo, L. Spogli, R. Tozzi, M. Vallocchia, A. Winkler.

A National Civil Service project at INGV: for contributing to Earth Sciences outreach

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Keywords: science outreach, civil service, learning by doing.

INGV – Istituto Nazionale di Geofisica e Vulcanologia is one of the major Italian public funded Research Institute and the largest European body dealing with research in Geophysics and Volcanology. Its main mission is the monitoring of geophysical phenomena in both the solid and fluid components of the Earth. INGV accredited with the National Civil Service since 2011 and has subscribed its ethical commitment describing values, goals, rights and responsibilities of the volunteers.

The aim is to involve young generations in "homeland defense" that is in social services which enforce the relationships between people, territory and living. Volunteers will spend one year fully involved in the activities of the organization, taking the opportunity to grow up, perform a real work experience and learn by doing. Among the projects funded in 2014 there is the project *"Science and Outreach: a comprehensive approach to the divulgation of knowledge of Earth Sciences "*, designed by the Laboratorio Divulgazione Scientifica e Attività Museali of INGV, Roma.

The project, dedicated to initiatives of earth sciences outreach, started in May 2014 and will last one year. Among its aims: 1) to contribute to the increase and the diffusion of a correct and informed scientific culture especially with regard to seismic and volcanic phenomena; 2) to extend to cultural associations, universities and citizens, scientific information on events for wider dissemination of basic information and for a correct approach to geophysical issues; 3) to extend the dissemination of scientific information on the Web and social media.

To achieve these objectives, the project involves an initial part of general and specific training, a phase of planning and sharing of the activities, the formation of working groups, and a part of the activities in which the volunteers are included.

From the point of view of volunteers there is a wide series of motivation including: increase knowledge in the field of science communication to share with the public; acquire specific skills to improve communication between the research organization and the citizen.

The outreach activities carried out by the Laboratory in the initial period included participation in dissemination events in and around Rome like: Scienza Aperta 2014 Open Day, 5 April, Albano Insieme, 18 May; Roma Drone , 24 – 25 May, to which volunteers participated.

During the "Albano Insieme" event, volunteers proposed the game: What shall I do in case of an earthquake? involving children in the activity and giving insight on appropriate behavior in case of earthquake meanwhile playing a game. Volunteers also participated to educational courses and workshops with schools, performed in Rome INGV headquarter.

Volunteers were pleasantly surprised by the interest and participation shown by the public to the issues raised. Participation to events of different nature has given them the opportunity to work alongside experts from various fields and interact with a diverse audience.

"I luoghi di Mercalli": a travelling exhibition as a tool for scientists to dialogue with the public on volcanoes and earthquakes

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Keywords: exhibition, Giuseppe Mercalli, seismic hazard, volcanic hazard, history of volcanology.

On March 19, 1914 Giuseppe Mercalli, a seismologist and volcanologist, well-known around the world for the Intensity scale of earthquakes bearing his name, died tragically. A hundred years after, the Istituto Nazionale di Geofisica e Vulcanologia (INGV) has promoted a variety of activities and cultural events that will take place under the Patronage of the President of the Italian Republic within a year, the so called "Anno Mercalliano" (the Year of Mercalli).

The opening ceremony took place in Naples, Italy, on March 19, 2014, in the Convitto Nazionale Vittorio Emanuele II. A scientific conference was held with the participation of experts from INGV and the university of Milano – Bicocca, and presentations of students. On that day the exhibition entitled "I luoghi di Mercalli" (Mercalli's places) was also inaugurated, at the presence of local authorities.

The exhibition, organized by INGV, was realized in collaboration with the high school Vittorio Emanuele II, where Mercalli has been teaching for 19 years, and the Università degli Studi Suor Orsola Benincasa, where he was professor of natural sciences.

A biographical and geographical description of the places where Mercalli operated introduces the exhibition, which is organized in sections:

- Mercalli educator (he taught at high schools in Reggio Calabria and Naples);
- Mercalli volcanologist (Mercalli studied Vesuvius volcanic activity for more than twenty years, he was a scientific witness of the Vesuvius 1906 eruption, and of the eruptions occurred at Vulcano (1888-90) and Stromboli (1891) islands.
- Mercalli seismologist (Mercalli Intensity scale definition, based on his experience as witness of catastrophic earthquakes, such as Casamicciola in 1883 and Messina in 1908).

Another section deals with the Vesuvius Observatory, directed by Mercalli between 1911 and 1914, and the description of the three active volcanoes of the Campania region (Vesuvius, Campi Flegrei and Ischia island), which have been the subject of studies by the well-known scientist. The exhibition is enriched by documents, manuscripts, photos and field notebooks of Mercalli.

It is not intended to be only a celebratory exhibition; rather it is designed as a tool for dissemination of scientific culture and to raise awareness about seismic and volcanic hazards.

In the exhibition path a continuous thread between the figure of Mercalli as a researcher and the role of an Earth Science researcher today is highlighted, pointing to the development of scientific knowledge in the past century. The goal is to improve the capability of learning from the disasters occurred in the past to implement preventive actions to safely deal with future events.

The exhibition is travelling and will be provided on request to institutions and schools.

The island of Ustica, an open-air geoscience museum: the role of geoparks in the dissemination of the Earth Sciences

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Keywords: Ustica, Volcano, Geopark.

In the Earth sciences, as well as in many other scientific disciplines, the availability of experimental laboratories is of paramount importance for the transfer of knowledge through the performance of practical experiences, which must be conveniently conducted and founded on a firm footing. In geology, in particular, the contact with rocks and landforms exposed in the field, is an irreplaceable tool to understand the processes that lie at their origin.

In this sense Geoparks may play a leading role, as, from the definition of the UNESCO European Geoparks Network, "*a Geopark must comprise a certain number of geological sites of particular importance in terms of their scientific quality, rarity, aesthetic appeal or educational value"*. Therefore, as Geoparks contain these sites in quite restricted areas, they have a great educational potential, if conveniently organized in a series of easy enjoyable and well equipped paths, thought to be interlinked to each other.

In recent years, following extensive geo-volcanological studies, the island of Ustica was gratified by two flattering definitions: "emerging singularity " and "open-air museum of volcanology".

The first definition derives from the consideration that the island is the only anorogenic volcano emerged in the Southern Tyrrhenian Sea, in a context dominated by the presence of the orogenic Aeolian Islands volcanic arc. For more, Ustica preserves the signs of the geodynamic processes that led to the oceanization of the Tyrrhenian Sea and to the opening of fractures that fed its volcanism. Ustica is, at the same time, the fruit and the precious witness to these events.

The second definition, refers to the wealth and variety of volcanic landforms and products that sightseers can observe in conditions of absolute safety, as the Ustica volcanism has been extinct for over one hundred thousand years. Moreover the marine transgressions that have alternated during Pleistocene generated marine terraces, and leaved typical fossiliferous deposits.

With an area of 8.6 km^2, a circuit of about 12 km and a maximum height of 248 m a.s.l., Ustica lies 60 km north of the Palermo coast and represents the emerging small part of a vast submerged volcanic complex, rising more than 2,000 m from the Southern Tyrrhenian Sea bottom.

At Ustica, submarine and subaerial lava flows, pillow lavas, monogenetic volcanoes and strovolcanoes, relics of ancient craters, deposits of ash and other pyroclastic rocks, lava tubes, bombs of various sizes , dykes, extinct fumaroles, faults, and spectacular morphologies, unfold the researcher and the student as the pages of a manual that can be browsed through the roads and trails of the Island, or diving in its waters.

With this paper we want to float the proposal to institute a new Geopark, aimed at enhancing the value of Ustica geo- volcanological aspects, by presenting a collection of illustrated routes, which lead the visitor through the geological and volcanological history of the island.

Volcanoes, a window into the Earth's interior: the dissemination of scientific knowledge in the new exhibit of the Royal Observatory of Vesuvius (ROV)

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Keywords: Earth Sciences, Outreach, Volcanoes.

Southern Italy has the largest concentration of high-hazard active volcanoes in Europe, with nine volcanoes in the densely inhabited areas of Campania and Sicily. These volcanoes have long been objects of study, destinations for cultured travelers and provided inspiration for works of art that may be found in numerous collections the world over. The Royal Observatory of Vesuvius (ROV) currently houses a remarkable scientific, historical and cultural heritage that at present is partially displayed in its historical building.

The INGV (National Institute of Geophysics and Volcanology) has a long tradition in the study of volcanoes and has produced an enormous quantity of scientific works from 1841 onwards, the foundation date of the Vesuvius Observatory, the first institution of this kind in the world and now the Naples section of the Institute.

This huge cultural production led to the inauguration of many educational activities, aimed at promoting a more modern view of the science dissemination.

Presently, one of the main INGV goals is to improve and expand the extent to which this important legacy may be put to use, in order to reach the widest possible audience.

This task can be accomplished only by the previous performance of a sociological study, inspecting the expectations of sigthseers divided by age, education and origin.

However, the use of museum collections is still linked to a concept of exhibits accompanied by brief explanations ending in itself, and directed towards making the material accessible only to specialists and enthusiasts, without any broad-based educational aims.

The innovative idea that animates the reorganization plan of ROV is to convey correct information concerning the earth sciences, the dangers of volcanoes and the strategies for risk mitigation, drawing on collections, documents and historic scientific instruments, together with the appeal exerted by volcanic activity itself, by means of the combined use of traditional methods, modern multimedia and interactive techniques. The ROVE exhibit provides the implementation of the wonderful collections of rocks and minerals, old books, instruments and paintings, with computer graphics reconstructions, HD and 3D documentaries, scenographic decors reproducing in virtual and increased reality volcanic eruptions, and their effects on the environment, interactive dioramas showing the evolution of Italian volcanoes, multimedia systems of communication to guide the visitors throughout the exhibition, digitalizing of old books and documents for the creation of a virtual library, aimed at sharing the huge cultural heritage of the Vesuvius Observatory.

The use of volcanoes and related phenomena to provoke interest in the earth sciences is undoubtedly a successful tool, which has significant implications especially in active volcanic areas, where volcanism strongly affected the landscape and influenced the development and life of human communities.

The trust of Italian students in geoscientists: a quantitative pilot study

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Keywords: science outreach, education.

If the Layman is to fulfil his responsibility as a citizen in this globalized modern society he will have to know about science in an understandable form. Geosciences may deeply impact on everyday lives as it relates to natural hazards. However there is a stringent paradox that drives to underestimate the potential of Geosciences to help people live with natural hazards, take decision towards land use and vulnerability of infrastructures. We might argue that one of the reasons for geoscience not playing a major role in modern society is due to incomplete or inefficient communication and the consequent lack of trust of citizens toward geoscientists. High school students represent a specific kind of Layman as they are close to become "adult" citizen entitled to take decisions or contribute to them.

In this study we present the results of a poll conducted on high school students (age 14-19) aiming at estimating the trust of the young Italian citizens in the geoscientists and their studies. The sample refers to Northwestern Italy, in areas prone to natural hazards from low to moderate intensity. Although limited to about 180 students and then not representative of the whole nation, the information, collected directly in schools before conferences or laboratories, can be used for a rough picture of level of trust of a part of the society towards the Geosciences.

The poll contained very few questions, the form in fact was organized in three sections only. The first to collect age and region of the compilers, the second to know about the sources students usually use to get info about catastrophes and natural phenomena and the last aiming at estimating the trust towards the scientists and their studies.

First results show that, students get their information mainly from the internet (about 60%) in its various forms (social media, Wikipedia) and TV (31%). However newspapers (17%) and schools (10%) still represent a significant fraction of sources of information.

In regard to the trust in science, some 87% believe that scientists are reliable but only 73% consider their research also useful. Only less than 5% declare that both scientists and their studies are not reliable and not useful.

Finally, about 75 % of the sample believe in the potential of future studies in Geoscience to help the society face natural catastrophes.

It must be remarked that the regions where the poll took place were not hit by main earthquakes in the last years. However the pool is part of an ongoing research that will include regions prone to higher level of natural hazards and recently hit by earthquakes, which will allow to compare the relationship between preparedness, hazard and the role of scientists in different contexts. Additionally, it would be necessary to estimate the bias introduced by the fact that the poll, although anonymous, is conducted before a scientific talk given by scientists. This may in fact introduce a sort of "respect" that could in turn influence the answers. For this reason we plan to propose the questionnaire to schools that had no relationships with geoscientists in the last five years.

The Serra d'Ivrea (NW Italy) as a didactic example of lateral moraine devoted to the scientific dissemination

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Keywords: Ivrea Morainic Amphitheatre, geoheritage, Piedmont.

The Ivrea Morainic Amphitheatre (IMA) is well-known worldwide among the European south-alpine end moraine systems for its remarkable geomorphology. The *Serra d'Ivrea,* its most typical evidence, constitutes an unusually straight, continuous and long (16 km) set of lateral moraines, which crests gradually decline from 937 m to 250 m asl. The *Serra d'Ivrea,* regarded as the biggest moraine of the Alps, represents a very didactic example of a marginal glacial landform result of the glacial sedimentation. However, until now it has not been the subject of many specific researches (Forno & Gianotti, 2005) and its age, ranging from the Middle Pleistocene to the Late Pleistocene, still remain a controversial issue.

The PROGEO-Piemonte Project, promoted by the Turin Earth Sciences Department, points to increase the scientific knowledge of the IMA geological features. A 55 m long core was drilled in 2013 into the sedimentary sequence. The radiocarbon dating and the palinological analysis of two superimposed lacustrine bodies, in addition to the study of soils developed on the outcropping glacial sediments, are going to strongly revise the *Serra d'Ivrea* stratigraphy. Moreover, researches on the petrographic composition of clasts forming the different glacial deposits are carrying out to define the clast source and the relation between clast features and transport/deposition processes.

A significant aim of this project is the dissemination of the results by geological brochures, posters and itineraries books, as well as lectures, workshops and short courses for teachers and naturalistic guides. A travelling exhibition on the IMA geology (supported by the IMA Ecomuseum since 2012) is going round the local municipalities and schools, with a series of lectures and the publication of a popular book (Gianotti & Marra, 2012). The scientific dissemination is essentially based on sketches of geologic elements and processes. A permanent exhibition on the IMA geology was also placed (May 2014) in a strategic site offered by the Caravino Municipality. This location is closed to the frequently visited Masino castle, on a panoramic moraine crest rising above the IMA internal depression. The exhibition consists of display panels regarding the IMA geology, a big plastic model and some old and modern geological maps. It will be soon supplemented with other materials also concerning the Serra d'Ivrea. This institution has to become, according to our intention, an active centre of vulgarization of the IMA geological knowledge, managed by the Ecomuseum.

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The Eco-Museum an innovative educational methodology to discover the earth sciences

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Keywords: eco-museum, proactive educational methods, geoscience outreach.

The eco-museum is a revolutionary concept compared to traditional museum because it considers the social dimension. The environment is described through history, culture, landscapes and human activities linked to the places that generated them.

The work describes the realization of the pilot project "Towards an Eco-Museum of the Castelli Romani". The project conceived by a group of researchers of the Laboratory of Education and Science Communication of Istituto Nazionale di Geofisica e Vulcanologia (INGV) in collaboration with the Regional Park of the Castelli Romani, involved students of the Classic and Socio-Psycho-Pedagogical High School of the Mancinelli Falcone Institute of Velletri (RM).

The project aimed at promoting the knowledge and the awareness of the territory by using innovative and proactive educational methods.

The educational activities carried out in the school year 2009-2010 have been structured in multidisciplinary training programs designed to create eco-museum routes.

These training programs have been organized in several areas: historical, archaeological, literary, geological, city planning, ecological and naturalistic representative of the geological and anthropological complexity of the Nemi Lake's territory.

It is a highly innovative educational project. Promote participatory planning. Led by experts and teachers, students participate in all the stages of the design, by choosing the itinerary, identifying the training needs, playing scenic actions and evaluating the effectiveness of the project.

The proactive techniques used in the project (dramatization, creative writing, music, etc.) facilitated the acquisition of knowledge and skills enhancing the territorial resources improvement and the sharing with the community.

Last but not least, the innovative project methodology places the school world not as the final recipient of knowledge but as a viewer and at the same time a partner who takes an active role in the dissemination of knowledge.

Teachingearthsciences: a website for teachers without a geological background

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Keywords: Web, geosciences, high school.

In the last decades the development of virtual and useful tools for teaching science at school has increased really fast and "even without going totally virtual, the Internet can provide a rich and valuable learning environment for anyone interested in the sciences" (Doherty, 1996). Anyway the largest part of the web production is in English and it seems not to be really well known by Italian teachers. The purpose of this research is: 1) to evaluate the need of an updated web tool for Earth science teachers in Italian, 2) to select the main themes it should contain, 3) to build it, 4) to test its usefulness.

The project is to make virtual lessons that are a sort of "repository" for the most interesting and useful Earth science existing tools, adapt them to Italian school system, organize them in different sections with animations, movies, hands-on activities, but also tests and evaluation papers for Italian teachers. The final aim is to provide an effective support to the Italian Earth science teachers without a geological background.

The first step of the project consisted on the development of a questionnaire for investigating the effective use of educational multimedia activities in the Earth science teaching in Italian high schools. Moreover the purpose of the questionnaire was also to select the Earth science topics of greater interests. The sample chosen was the group of teachers who inscribed their school at the 2012 edition of Natural Science Olympiad (more that 350 teachers).

On the basis of the preliminary results we designed a website trying to respond to all the needs showed by the teachers. Within the selected Earth science topics we collected the existing web teaching material (hands-on activities, simulation, models, animations, etc.) that best fit the real teachers needs. In this regard, the selection criteria are defined as the relevance to the selected topics, the scientific validity, the ease of use, the economic and logistical needs, the link with everyday life and the relation with the territory.

At the moment the website hosts different kind of files that undergo the Creative Common Licence, and that are free to be used and even modified by the registered teachers. The idea is that teachers can find in the website most of the material they said were interested about.

Right now the first 4 unit are complete and they are structured in different lessons, each one formed by different learning objects:

- a power point file, consisting on a key point text with a list of web links to the most useful external materials and the most interesting images available in the web
- a pdf file, consisting on the transcript of the whole lesson
- a set of exercises, consisting on a group of multiple choice and a group of open answers questions
- a video of the lesson, consisting on a MP4 file lasting about 10 minutes and describing the entire content of the lesson
- a set of specific short movies concerning key concepts.

Actually the website is in a experimentation phase and it is tested by in-service teachers, in order to evaluate its usefulness and efficiency. After that a new data will follow to report the results.

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Using narrative to disseminate Earth sciences culture

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Keywords: narrative, earth sciences, science communication, sustainability.

Since ancient times, narrative have been used not only as a way of experiencing the world but also as a vehicle of culture and values. Ancient myths and legends, poetry, and today literature, theatre and movies very often deals with the relation of human kind with nature.

Today industrialization have brought men to be day by day ever more detached from nature at the point to be not able to survive outside civilization and with consequences for the environment. Narrative can be a valid tool to convey messages and values for re-awakening in the inhabitants of the Earth the sense of beauty and responsibility for a better planet sustainability.

The present work gives examples of how narrative is used to this aim. Examples include the work done within the Laboratorio di Didattica e Divulgazione Scientifica in Rome in the past four years using narrative in different formats. Some preliminary consideration will concern the evaluation of narrative as a vehicle of science communication.

ScienzAperta: Earth Science for everyone... finally in Milan!

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Keywords: Science outreach, special venue, open days.

ScienzAperta is an outreach science venue that the Istituto Nazionale di Geofisica e Vulcanologia started in 2011 as the spring of science: the doors of the headquarters of science were finally opened to public.

A number of events, conferences, seminars, guided tours through the Institute and its laboratories are every year offered to general public. The venue is held in most of the cities where the Institute is located, giving a special priority to high seismic and/or volcanic risk regions.

On May 2014 we held ScienzAperta for the first time in Milano and open up the doors to schools specifically dealing mostly with seismic hazard in a region where general public not necessarily think it might be of any need. We offered students conferences, seminars and educational activities to highlight the fun of science and jet raise awareness on proper behaviours in case of earthquake shaking. We asked students and teachers, ranging from elementary to high schools, to fill in a questionnaire that we use to evaluate the appreciation the venue had. One hundred years after Giuseppe Mercalli's death we could not forget to celebrate his science in Milano, the city where he was born.

The Geophysical Museum of Rocca di Papa: between knowledge and scientific research

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Keywords: Geophysics, Seismology, Museum.

The Geophysical Museum of Rocca di Papa is located in an historical, three floor building, of the small town Rocca di Papa, twentyfive kilometres from Rome. The edifice was, until 1931, the place of the Geodynamic Observatory, created in 1889 by the famous seismologist Michele Stefano De Rossi. The museum is due to an agreement between the Town Council of Rocca di Papa and the Istituto Nazionale di Geofisica (INGV, one of the most important European Research Institutions operating in geophysics) signed in 2000. After bureaucratic passages and two years of important restoration the Museum was open to the public at 26th February 2005. During last two years, in 2013 have been completede other major restructuring that have expanded the Museum display capacity.

The main aim of the Geophysical Museum is to illustrate how experimental data and information, accumulated by science in the course of time, led to new hypotheses on the internal structure of the Earth.

The target of the educational and of the scientific disciplines of the Museum is mainly school students of all ages, but also local residents, and tourists: since its opening, the Museum has been visited by thousands people by year. Posters, movie presentations, plastics, games and interactive experiments explain to visitors the main topics of geophysics and the stages of scientific research which led to the modern concept of the Earth internal model. Seismic instruments and games are easily accessible so that the visitor can interact with them: experimental data are recorded in real time and displayed through different monitors placed throughout the rooms. The museum has also a small cinema for three dimensional projections which allow visitors to experience a virtual tour on the Alban Hills, the seismic zone where the museum is located, and also on some other Italian tectonic belts where earthquakes occurred in past.

In addition, the Museum maintains the typical skills related to activities observatory due to the presence of modern seismic station of the national seismic network, as well as a GPS station, managed by INGV.

In addition to this, The Museum is located on the top of southernmost Quaternary volcano, the Alban Hills (Italian Colli Albani) which is considere a quiescent volcanic complex in Italy, located 20 km (12 mi) southeast of Rome. So guided visit tours, are organized at the Museum for showing at the visitors walking around the dominant peak (but not the highest) *Monte Cavo* at 950 m, two small calderas which contain lakes, Lago Albano and Lake Nemi. The rock of the hills sourced by explosion of theese calderas is called Peperino (lapis albanus) a particular Tuff, a combination of ash and small rocks that is useful for construction, and provides a mineral-rich substrate for grape vines.

The Tree of Natural Hazard Education

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Keywords: natural hazard, science outreach, education.

Natural hazards are often thought as being, beside a difficult issue, a major problem forcing the community to deal with the economic and social development. For this reason they require specific actions tailored on the local environment. It is fundamental to build a ground to rely on when dealing with the governance of a territory and when the economic factors intersect scientific knowledge and available technical solutions. Science outreach could usefully focus on simple, clear and yet accurate information. The social projection of natural disaters is not just the faith of careless attitude towards hazard as it might get strongly influenced by emotions triggers by an event close in time. On the other end people might misperceive risks ineffectively choose recovery over prevention, when the latter is proved to be far less costly.

There is a general mindset of people towards a culture of prevention and the relationship established between the concepts of *hazard* and *disaster*, as if one would automatically always turn into the other just as like a nature curse towards which humans have no power.

There is much of emotions involving hazards response so that to be effective education should not only convey information in *strictu sense* (to explain natural phenomena and their causes), but drives the understanding through interpersonal skills and explicitly use the language of emotions (and in particular the positive ones, eg. reassurance, confidence, serenity, optimism, etc...).

The Istituto Nazionale di Geofisica e Vulcanologia is a scientific institution monitoring of geophysical phenomena through networks of technologically advanced equipment which approach outreach and education to the dissemination of scientific culture through publications for schools and web pages, exhibitions, special venues and open-days.

We envisage a virtual tree of natural hazard education where science actively interacts with general public to implant awareness on the urge of science knowledge in modern society when it comes to help citizens to have independent opinions or participate to crucial decisions. Here we display on a tree several ways of doing outreach and education towards natural hazards.

Activities encompass volcanic, seismic, hydrogeological hazard and risk education to explore and understand natural processes lying behind the hazard. The general concept of risk is also exploited, where children and teachers will have to think on what could be the actions to be taken to avoid risks, weather there are risks we are willing to take, what we think we cannot avoid and, above all, how do we behave facing a risky situation. We definitely remark the link between inhabitants and their land emphasizing on the sense of responsibility towards land preservation.

SESSIONE S37

Poster - Le geoscienze a scuola

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Geosciences in virtual worlds: a path in the volcanic area of the Phlegraean Fields

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Keywords: teaching, geosciences, virtual worlds.

Today, virtual worlds represent an innovative strategy and an educational opportunity to learn in a socially-interactive learning community and in a immersive environment. To experience this approach, this research aims at introducing digital contents in geosciences and, in particular, to address the theme of volcanic hazard, taking as an example the area of the Phlegraean fields (Napoli, Italy).

The project makes use of a MUVE (multi user virtual environment), addressed to students of various ages (13-15 and 15-18 years old). A virtual island, called UNICAMearth, was created in 3d on the University of Camerino server, using the software open SIM and the singularity viewer. Through an online access, using a role play, learners go through activities built using inquiry based science education (IBSE) with a adaptive path. Students, in a serious game, must pass ability and expertise steps/tests, solving paths and pre- and post-tests. By following the path and answering to tasks and questions, they acquire scientific skills.

The simulations in virtual environments recreates contexts similar to reality, which can be used to study an area and its transformations with time. For example, it is possible to recreate in 3d environments a volcanic environment, where the student as an avatar, can learn with an immersive training the different types of volcanoes, simulate volcanic eruptions and earthquakes, to understand which events may occur in an area at risk of eruption. The first of these paths is currently being tested in the secondary schools of grade I and grade II of the Napoli area. The path is divided into 6 areas of investigation: the distribution of volcanoes, interior structure of the earth and the formation of magma, the classification of volcanoes and eruptions, igneous rocks, volcanic phenomena in the Solfatara and the volcanic history of the Phlegraean fields. In each area there are animations and interactive chats. In this way the student plays the role of a scientist - a geologist studying a volcano. Experimentation has shown that students learn in a more engaging way by using these environments, especially if they can be changed by the user.

Dal laboratorio al palcoscenico: il teatro-scienza per apprendere e divulgare le discipline scientifiche

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Keywords: Scienze polari, Teatro scienza, Laboratori didattici.

Spesso i percorsi di scienze vengono proposti agli studenti seguendo l'organizzazione per nuclei tematici suggerita dal libro di testo. A questa si agganciano esempi di collegamenti con la realtà, disciplinari e solo a volte interdisciplinari.

In questo progetto l'ottica è stata ribaltata.

Partendo dalle testimonianze di esploratori e ricercatori polari gli allievi sono stati coinvolti in attività *hands-on* e in *role plays* e sono diventati essi stessi gli sceneggiatori di un copione teatrale. E così la mirabolante avventura di E. Shackleton e della sua nave Endurance (1914/16) intrappolata dai ghiacci antartici è diventata il pretesto per imparare come si forma il pack, in cosa si differenzia dal ghiaccio continentale, quali dati può fornire quest'ultimo sul clima del passato, come si originano le correnti oceaniche, quale relazione esiste tra l'inclinazione dei raggi solari e i climi polari, come spiegare la durata notte-dì a diverse latitudini o per comprendere alcuni fenomeni termici legati agli adattamenti degli organismi polari.

Il teatro è stato il luogo per "mettere in scena" alcuni degli esperimenti effettuati nelle lezioni di scienze ma anche per spiegare le attuali ricerche compiute nelle zone polari e la loro importanza per la ricostruzione del passato della Terra.

In questo lavoro viene messo in evidenza "un percorso" proprio perché spesso a scuola è soprattutto quello che è importante più del prodotto finale. Un percorso che è partito, con la collaborazione delle insegnanti di lettere e geografia, dalla lettura di diari di esploratori del Polo a cui sono state agganciate attività di laboratorio riguardanti le Scienze Polari e una riflessione sull'utilità della ricerca in Antartide e che si è concluso con l'allestimento di uno spettacolo teatrale realizzato dagli alunni di due prime classi di una scuola secondaria di primo grado.

Lo spettacolo, realizzato con la collaborazione del Piccolo Teatro di Milano e dell'associazione Scienza Under 18, è stato rappresentato per altre scolaresche in occasione dell'evento "La Statale incontra la scuola" presso l'Università Statale di Milano e all'Auditorium del Comune della scuola per la cittadinanza.

Questo percorso mette in evidenza come approcci alternativi come quelli del teatro scienza possano veicolare, in maniera efficace, contenuti scientifici non solo all'interno del gruppo classe ma anche nella comunità locale.

La storia avvincente facilita il coinvolgimento e il teatro l'immedesimazione. La messa in scena richiede un uso attento della parola: agli studenti è richiesto di saper suscitare curiosità e interesse attorno ai temi scientifici proposti e di saperli presentare utilizzando un linguaggio che si mantiene in equilibrio tra rigore e semplicità.

Infine a teatro è permesso mettere in scena il valore universale della ricerca e della scienza promuovendo l'educazione scientifica nel senso più ampio.

Star bene per far star bene la terra

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Keywords: ecological footprint, carbon footprint.

Atmosfera, idrosfera, geosfera, biosfera: basta poco per turbare il difficile equilibrio che mantiene in salute il nostro pianeta. I nostri consumi quotidiani possono provocare cambiamenti climatici e mettere a rischio le riserve di acqua utilizzabile. Per far sì che sulla terra la vita continui bisogna partire dalla consapevolezza che "siamo tutti sulla stessa barca": dobbiamo individuare i problemi e cercare di risolverli con una progettualità diffusa e una condivisione di significati. Il C.R.E.A. (Centro Regionale Educazione Ambientale) del Comune di Pavia, è un organismo di riferimento per l'educazione ambientale. Innumerevoli progetti e attività sono offerti alle scuole e ai cittadini, con lo scopo di favore buone pratiche per uno stile di vita più sostenibile. Da anni collabora con l'Università di Pavia e con l'ANISN (Associazione Nazionale Insegnanti Scienze Naturali). Il progetto "Star bene" invita gli studenti di scuole di diverso ordine e grado a riflettere criticamente sulle conseguenze del proprio stile di vita attraverso laboratori interattivi, con l'utilizzo di giochi, per i più piccoli, di semplici fogli di calcolo e/o di siti Web. Sono state calcolate: **l'impronta ecologica** (ecological footprint), la superficie di terra e acqua necessaria per rigenerare le risorse consumate da una popolazione umana e per assorbire i rifiuti prodotti, **l'impronta di carbonio** (carbon footprint), la misura in unità di anidride carbonica dell'impatto che le attività umane hanno sull'ambiente in termini di ammontare di gas serra prodotti, e **l'impronta idrica** (water footprint), la quantità di acqua consumata da un processo, un ente o una nazione. Nell'anno scolastico 2013-2014 sette classi quinte elementari e tre seconde medie hanno partecipato ai laboratori. Con gli alunni della scuola elementare è stato realizzato un gioco a squadre: **"La mia piramide per la salute della terra"**. Ogni squadra deve rispondere a domande sui gruppi di alimenti, sull'alimentazione mediterranea, sull'impronta ecologica, sulle conseguenze legate a una impronta eccessiva. Ogni risposta esatta dà diritto a una scheda raffigurante la porzione di un alimento o a un jolly con cui si possono "comprare" porzioni dei diversi gruppi. Sul retro di ogni scheda sono scritte le diverse impronte: ecologica, della CO_2, dell'acqua. Le squadre devono costruire una piramide con le porzioni dei diversi gruppi che un bambino/a di 10 anni mangia in un giorno. Una volta completata la piramide bisogna girare le carte e calcolare le impronte relative alla dieta giornaliera. Vince chi ha la piramide più equilibrata, ricca di frutta e verdura colorate, e con l'impronta minore.

http://www.comune.pv.it/site/home/canali-tematici/ambiente-e-territorio/c.r.e.a./

Familiarizzare gli studenti del Liceo Scientifico con le geoscienze attraverso attività seminariali e di terreno

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Keywords: geoscienze, didattica, metodologie.

La ricchezza delle Geoscienze, che utilizzano una vasta gamma di metodologie di indagine per lo studio del pianeta Terra e che hanno un ampio spettro di applicazioni, non è facilmente valorizzabile nell'ambito delle attività previste dai programmi ministeriali. Per questo, numerose attività di carattere seminariale o dimostrativo vengono organizzate in collaborazione tra le scuole medie secondarie superiori e gli Atenei.

A partire dal 2007, e poi regolarmente dall'A.S. 2009/10, in collaborazione tra l'Università degli Studi di Milano e il Liceo Scientifico "G. Bruno" di Melzo (MI) è stata svolta un'attività per familiarizzare gli studenti con la conoscenza della geofisica, e in particolare dei suoi aspetti applicativi. Il progetto, che nell'A.S. 2011/12 è stato inserito anche nel POF dell'istituto scolastico, prevede: (1) una lezione introduttiva di carattere seminariale sulla geofisica e in particolare sui suoi aspetti applicativi per indagini a piccola profondità; (2) l'esecuzione di misure geoelettriche, sismiche e magnetiche dimostrative nel prato della scuola; (3) una lezione in cui vengono presentati e discussi i risultati delle misure eseguite dagli studenti. La realizzazione del progetto ha previsto la partecipazione e la collaborazione: (a) di dottorandi, assegnisti di ricerca e ricercatori dell'Università degli Studi di Milano a supporto della giornata dedicata alla esecuzione delle misure sul terreno; (b) di docenti di diverse materie, prevalentemente scientifiche, del Liceo "G. Bruno", per permettere ai ragazzi di diverse classi di partecipare alle attività.

Con alcune classi è stata svolta anche un'ulteriore attività di approfondimento delle metodologie di studio proprie delle Geoscienze, consistente in una visita guidata dei laboratori analitici del Dipartimento di Scienze della Terra, affiancata da una esercitazione di osservazione di minerali e rocce in campioni macroscopici ed al microscopio.

Il riscontro è in generale positivo, in quanto i ragazzi da un lato possono familiarizzare con alcuni argomenti meno conosciuti e meno approfonditi delle Geoscienze e dall'altro entrare in contatto con aspetti meno "astratti" e più "concreti" di discipline scientifiche, che spesso vengono viste dai ragazzi come "aride" e poco attraenti. Si ritiene quindi che questo tipo di attività possa effettivamente fornire un contributo alla diffusione della cultura scientifica e più in particolare delle Geoscienze tra le giovani generazioni.

Teachingearthsciences: un sito web per insegnanti

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Keywords: web, docenti, geoscienze.

In prevalenza gli insegnanti di scienze naturali della scuola secondaria sono biologi e solamente una piccola parte sono geologi (Costa & Zauli, 1982). Questa formazione disciplinare e le poche ore di lezioni a disposizione, hanno portato a sacrificare l'insegnamento delle scienze della Terra a favore di biologia e chimica (Massa & Pedemonte, 1983). Il presente progetto ha lo scopo di fornire un supporto agli insegnanti di scienze delle scuole secondarie che non sono geologi, al fine di rafforzare la loro sicurezza verso questa disciplina.

Nel web sono presenti numerosi strumenti virtuali per l'insegnamento delle scienze della Terra, ma sono per lo più in inglese e non sembrano essere ben conosciuti e sfruttati dai docenti italiani. Quindi gli scopi di questa ricerca sono: 1) valutare la necessità di uno strumento web in italiano per insegnanti di scienze della Terra, 2) selezionare i temi principali che dovrebbe contenere, 3) sviluppare lo strumento nel complesso, 4) valutare la sua utilità.

Il progetto è creare lezioni virtuali che siano una sorta di meta contenitore per gli strumenti didattici di scienze della Terra più interessanti e utili, adattati al sistema scolastico italiano.

Nella prima fase del progetto è stato formulato un questionario per indagare l'utilizzo delle attività multimediali nel campo delle scienze della Terra nella scuola secondaria e per selezionare i relativi argomenti di maggior interesse per gli insegnanti. Il campione è stato il gruppo di docenti che ha iscritto la propria scuola all'edizione 2012 delle Olimpiadi di Scienze Naturali (più di 350).

Sulla base dei primi risultati è stato progettato un sito web, il più possibile rispondente alle esigenze mostrate dagli insegnanti. A tale proposito è stato creato materiale ad hoc ed è stato raccolto quello già esistente nel web, che meglio si adatta alle necessità degli insegnanti. I criteri di selezione sono stati: la validità scientifica, la facilità di utilizzo, le esigenze economiche e logistiche, il legame con la vita quotidiana e con il territorio.

L'unità didattica sulla tettonica delle placche è stata la prima ad essere caricata sul sito; quindi un questionario di gradimento è stato inviato agli insegnanti registrati. Il campione ha fornito una valutazione nel complesso positiva, dichiarando di trovare il sito utile per aumentare il proprio background geologico e di volerlo estendere ad altri argomenti.

Dopo la fase di sperimentazione altre tre unità didattiche sono state caricate e attualmente sono in valutazione da parte di insegnanti in servizio, per estrapolare l'utilità e l'efficienza dell'intero sito. Al termine del presente anno scolastico seguiranno i risultati di questa ultima parte dell'indagine.

Costa M. & Emiliani Zauli F. 1982. Indagine sui titoli di studio degli insegnanti di "Scienze matematiche, chimiche, Fisiche e Naturali" in servizio presso la scuola media – COASSI, quaderno n.1, 1-20.

Massa B. & Pedemonte G.M. 1983. L'insegnamento delle Scienze della Terra nella scuola secondaria superiore: Una indagine su scala regionale. Ed. Tilgher, Genova, 1-97.

Darwin, il geo-investigatore - Ripercorrere in chiave inquiry based alcuni esperimenti storici del teorico dell'evoluzione

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Keywords: Darwin, geo-esplorazioni, IBSE

Forse i più non sanno che Charles Darwin fu prima di tutto un geologo, come egli stesso si definì nei suoi taccuini "Io, un geologo…"(Darwin, 1838).

Fu proprio la passione per le scienze della Terra che gli permise di osservare l'ambiente con lo sguardo attento alle trasformazioni, consentendogli di elaborare la teoria dell'evoluzione.

In questo poster si presentano due elaborazioni sperimentali che Darwin condusse per risolvere questioni geologiche. Da un lato egli misurò la profondità alla quale si trovavano i coralli negli atolli (Darwin, 1842), per poterne definire il meccanismo di formazione, mentre dall'altro misurò la velocità dell'erosione di depositi gessosi, per datare l'età delle scogliere del Sud Est britannico "recuperando" tempo profondo, necessario ai tempi dell'evoluzione (Darwin, 1859; Burchfield, 1974).

I due esperimenti sono proposti in modo semplificato, con materiale di semplice reperibilità. L'approccio utilizzato è quello IBSE (Bybee et al., 2006), nel quale lo studente si comporta da *geoinvestigatore*, mentre l'impiego di documenti originali e risorse multimediali (Google Earth; DVD "Nel giardino di Darwin", 2010) rende l'attività fruibile anche nel contesto CLIL (Coyle et al., 2010)

Di seguito sono sintetizzati i due laboratori didattici.

Darwin e il problema dell'origine degli atolli corallini

L'esperimento simula quanto realizzarono Darwin e Fitzroy, per provare che i coralli non crescono oltre ad una certa profondità. Le misure compiute servirono per dimostrare che i coralli si formano a basse profondità e lentamente sprofondano e non, come si credeva allora, sul fondo del mare per poi risalire spinti dai vulcani sottomarini.

Gli alunni realizzano uno scandaglio con una vasca piena d'acqua, dello spago e un peso. Con questo modello, sono invitati a eseguire rilevamenti sulle profondità dei diversi tipi di fondale e a compiere deduzioni su quali ospitino i "coralli" vivi.

Darwin e il dilemma del tempo geologico

Attraverso alcune osservazioni sulle formazioni geologiche dei terreni circostanti la sua abitazione di Down House, e alcuni assunti sulla loro velocità di erosione, Darwin calcolò che il tempo necessario alla formazione delle scogliere gessose dei South Downs doveva essere estremamente lungo, circa 300 milioni di anni. Pertanto l'età della Terra doveva essere di sicuro maggiore. Solo un tempo così lungo poteva dare ragione del lento svolgersi dei processi evolutivi attraverso la selezione naturale.

Gli alunni ripercorrono, attraverso un semplice esperimento di corrosione di una roccia calcarea con soluzione acida, il concetto che sta alla base del calcolo utilizzato da Darwin, mettendo in evidenza quali sono i punti critici del ragionamento e venendo condotti alla scoperta della necessità di una datazione relativa e assoluta delle rocce.

Scuola terra e fantasia: un progetto sperimentale per la diffusione delle geoscienze nelle scuole dell'infanzia

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Keywords: bambini, geoscienze, didattica, laboratori, sperimentazione, apprendimento.

Il progetto didattico "Scuola Terra e Fantasia" nasce dalla collaborazione tra il mondo universitario, quello della professione del geologo e le scuole statali; da questa unione è nata l'associazione IL GECO, una collaborazione tra geologi e insegnanti che propone alle scuole di ogni ordine e grado tematiche di carattere scientifico. L'associazione IL GECO si sviluppa dalla passione per la geologia e dalla consapevolezza della necessità di un coinvolgimento più dinamico degli studenti verso le materie scientifiche e in particolare verso le scienze della Terra; una disciplina estremamente complessa e di fondamentale importanza nella vita dell'uomo. Da esse, e in particolare dalla geologia, dipende anche una parte importante della qualità della vita di un'intera comunità, grande o piccola che sia. Purtroppo questo concetto spesso non è percepito né dalla popolazione né dalle pubbliche istituzioni; ne sono un triste esempio le immani catastrofi naturali a cui si assiste sempre più spesso e in cui l'uomo, con il suo sfruttamento sconsiderato del suolo, è l'unico vero responsabile. La geologia deve essere spiegata e raccontata alla popolazione per riuscire a fare quel grosso cambio di mentalità che permetterà ai singoli individui e alla comunità intera di sintonizzarsi sui tempi e i modi in cui la Terra evolve. Per ottenere questi importanti obiettivi è necessario educare, fin dalla più tenera età, il cittadino a comportamenti "ambientalmente corretti".

In particolare il progetto "Scuola Terra e Fantasia" è stato sperimentato per un periodo di tre mesi alla scuola materna Alessandrini di Zibido San Giacomo di Milano. Con questo progetto si è voluto sfidare l'abitudine di rimandare tematiche di carattere scientifico in età esclusivamente scolare. I bambini fino ai 5 anni di età sono generalmente più liberi da stereotipi e preconcetti e maggiormente predisposti al contatto con la natura e l'ambiente circostante facilitando il processo di comprensione e assimilazione di esperienze anche molto complesse. La base quindi del progetto "Scuola Terra e Fantasia" è stata la sperimentazione sfruttando gli ambienti circostanti come laboratorio nel quale verificare tutti quei concetti alla base di un corretto approccio scientifico.

Le scienze della terra nelle scuole dell'infanzia sono state introdotte in modo semplice con l'ausilio di un personaggio, Mariolino, creato appositamente per far rispecchiare ogni bambino nelle sue esperienze. Mariolino è stato introdotto tramite il racconto del suo viaggio molto particolare, che parte dal pianta Terra verso l'intero Sistema Solare per andare a scoprire quale sarà il pianeta in cui vorrà fermarsi. In ogni sua tappa Mariolino propone sempre attività differenti da realizzare con i materiali che ci circondano e chiede sempre ai bambini di verificare anche le cose più ovvie tramite la percezione sensoriale che costituisce la base del programma didattico e favorisce la manipolazione dei materiali a disposizione.

Earth-net: una rete per la didattica delle scienze della terra

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Keywords: didattica, scuole-università, rete.

La comprensione del sistema Terra contribuisce alla formazione della coscienza ambientale tra i giovani che, come futuri cittadini, con le loro azioni determineranno la qualità dell'ambiente e della vita sul Pianeta. La conoscenza dei fenomeni naturali permette una migliore prevenzione dei rischi e una riduzione dei danni alle persone e alle cose, mentre la consapevolezza della fragilità del Pianeta suggerisce un uso più sostenibile delle risorse e un'attenzione all'inquinamento ambientale. È quindi necessario migliorare la sensibilità dei giovani verso questi temi, aumentando l'interesse verso le Scienze della Terra lungo tutto il curriculum scolastico tramite uno studio attivo, evidenziando i riscontri e le implicazioni per l'ambiente naturale e la vita dell'uomo.

Cosa può fare l'insegnante per affrontare questi temi? Può: a) utilizzare metodi e materiali ben testati e sperimentati, ma disponibili spesso solo in inglese sul web e difficilmente esportabili, b) creare e sperimentare percorsi e materiali propri. In ambedue i casi, gli insegnanti sono lasciati da soli a investigare, testare, sviluppare ed applicare, con spreco di energie e tempo, che spesso porta a rinunciare alla sperimentazione. Alcune Università, Musei e enti di ricerca hanno attivato progetti didattici e attività per le scuole. Questo sforzo individuale e' lodevole, ma non piu' sufficiente: i fondi sono pochi, ma soprattutto le iniziative, seppur utili e coinvolgenti sono spesso locali, si concludono e purtroppo si perdono. Bisogna ottimizzare il lavoro svolto da singoli gruppi pubblicizzandolo, come in una cassa di risonanza, in modo che il lavoro di pochi sia un beneficio per tutti. È necessario costruire delle relazioni concrete tra i vari attori, per facilitare lo scambio di risorse, conoscenze e competenze, da condividere con scuole, insegnanti, educatori.

L'Università di Camerino, ha creato il gruppo UNICAMearth, che svolge ricerca e divulgazione nell'ambito delle scienze della Terra e collabora con le scuole, con attivita' specificamente dedicate agli insegnanti e un dottorato di ricerca in "Teaching Earth Sciences", ha un sito web e una mailing list per divulgare le iniziative. UNICAMearth ha lanciato una proposta che e' stata raccolta da alcuni gruppi di ricerca (UNIMI, UNIPI, UNITO, UNIUD, INGV,...). A luglio 2013, al workshop di Camerino, è stata lanciata la creazione di **EARTH-NET,** una rete nazionale per la didattica delle Scienze della Terra, che nasce per "avviare sinergie di risorse umane e scientifiche con lo scopo di promuovere la cultura delle Scienze della Terra, con particolare attenzione al tema dei rischi naturali, tra gli studenti di Istituzioni scolastiche del territorio". Il successo del meeting di LE GEOSCIENZE A SCUOLA di Pisa 2013 e la nuova edizione di Milano 2014 sono la dimostrazione che c'è interesse a **"FARE RETE".**

Le scienze della terra sul campo: applicazioni didattiche per la comprensione dell'evoluzione del paesaggio

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Keywords: Geoscienze, itinerari didattici, attività in campo.

Lo scopo di questo lavoro è di raccogliere alcune applicazioni didattiche predisposte e sperimentate, aventi come obiettivo l'osservazione e la comprensione dell'evoluzione del rilievo e del paesaggio geografico fisico a diverse scale spaziali e temporali, mediante contatto diretto con la realtà geologico-geomorfologica. Molte delle attività realizzate sono state testate su vari campioni di studenti della scuola secondaria: i) attraverso l'osservazione di pareti rocciose, attrezzate per l'arrampicata sportiva, la cui struttura condiziona le tecniche di progressione, sono stati proposti approcci per la comprensione sia dei litotipi sia delle forme erosionali di origine glaciale su cui le stesse sono impostate (Bollati et al., 2014); ii) l'analisi della morfologia e dei depositi fluviali in siti didatticamente strategici ha rappresentato lo strumento per un approccio alla paleogeografia, al controllo strutturale e al modellamento fluviale (Bollati et al., 2011); iii) itinerari in ambiente alpino e appenninico si sono rivelati uno strumento chiave in termini di attività didattico-laboratoriali sul terreno. L'applicazione di tecniche dendrocronologiche semplificate su scansione di campioni lignei prelevati da alberi ubicati su depositi di diversa origine hanno favorito una miglior comprensione dei processi di modellamento del territorio e dei tempi di evoluzione del paesaggio (es. Garavaglia & Pelfini, 2011; Bollati et al., 2011). Il collegamento con i concetti di pericolosità geomorfologica ha rappresentato inoltre un'occasione per l'educazione al rischio geologico (Bollati et al., 2013).

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Canale Geotube

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Keywords: Geoscienze, misconcezioni, video, media.

Le Geologia è una Scienza poco conosciuta al grande pubblico e che genera l'accumulo di una serie di misconcezioni errate. Una delle criticità che abbiamo evidenziato, sulla base di pluriennali studi dei risultati di apprendimento degli studenti in uscita dalle scuole secondarie in termine di competenze nella lettura e nella gestione dei territorio, è da attribuirsi ad una didattica della disciplina di tipo "statico", decontestualizzata e che promuove un tipo di apprendimento nozionistico e riduzionistico. Partire dalla tassonomia è senz'altro un elemento necessario per la comprensione dei fenomeni naturali ma non è sufficiente per promuovere la visione "olistica" di spessore evoluzionistico. Lo scopo di questo lavoro di ricerca, avviato in un Liceo Scientifico della provincia di Monza e Brianza in collaborazione con il Dipartimento di Scienze della Terra dell'Università degli Studi di Milano, è stato quello di indagare nuove forme di comunicazione delle geoscienze con la creazione di un canale digitale attraverso il quale poter trasmettere i classici contenuti del programma ministeriale. La comunicazione mediata dal video ha permesso di partire dal protagonismo degli studenti rendendoli attori/maestri; di ritornare a spirale sul contenuto, sia nella fase di " scrittura " del copione che nella fase di "registrazione" delle diverse repliche; di trasmettere il dinamismo spazio-temporale dei fenomeni naturali attraverso l'uso di immagini e spezzoni cinematografici utilizzati nella fase di montaggio; di promuovere competenze progettuali nella realizzazione della scenografia; di sviluppare forme di apprendimento collaborativo ("cooperative learning"); di sviluppare capacità critiche nella fase di revisione del prodotto finito; di render consapevoli dell'esistenza di luoghi comuni radicati (le "misconcezioni"); educare ad un uso consapevole dei media grazie alla condivisone di protocolli e di regole da assumere nell'approccio all'uso dei diversi ambienti disponibili in rete. I risultati ottenuti, soprattutto in termini di interesse e di motivazione, ci convincono dell'efficacia della strategia oltrechè della possibilità che tale canale possa avere una diffusione maggiore e diventare uno strumento di divulgazione della scienza al grande pubblico.

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Preparazione indagine sull'insegnamento delle Scienze della Terra nei licei italiani post-riforma

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Keywords: Geoscienze, licei, didattica.

Dopo la recente riforma della scuola secondaria di II grado (2010), in quasi tutti i licei è presente un curricolo di Scienze Naturali di 5 anni, per il quale il Ministero ha fornito indicazioni di massima scandite in 1°, 2° biennio e 5° anno, senza separazione cronologica predefinita tra le discipline di Scienze della Terra, Biologia e Chimica. Data la novità del contesto, si è voluto indagare come i docenti stiano effettivamente costruendo il nuovo curricolo di Scienze della Terra, che attualmente dovrebbe essere insegnato nell'intero quinquennio. La ricerca è stata condotta su un campione stratificato casuale di docenti di Scienze Naturali di licei pubblici italiani, suddivisi per regioni in proporzione al numero di scuole. Si è utilizzato un questionario anonimo somministrato on-line nei primi mesi del 2014. Sono stati raccolti 120 questionari da 76 licei (pari al 4,5% dei licei pubblici italiani).

Da essi risulta che le indicazioni ministeriali dei temi da trattare sono state seguite fedelmente nel 1°biennio e un po' meno nel 2° biennio, mentre le scelte tematiche per 5° anno di corso risultano più diversificate. Nell'intero quinquennio vengono considerati come più importanti i temi già presenti nel curricolo pre-riforma. L'organizzazione didattica sembra risentire del limitato monte-ore settimanale, e le attività pratiche (di laboratorio e sul campo) dichiarate dai docenti sono estremamente ridotte. Per quanto riguarda le scelte dei libri di testo, pochi autori sono presenti in alte percentuali, mentre i rimanenti figurano molto distanziati dai primi. Interpellati sulla propria preparazione nelle Scienze della Terra, i docenti esprimono un'auto-percezione complessivamente soddisfacente, accompagnata da apertura alle proposte di formazione in servizio, preferibilmente in forma mista (in presenza + on-line).

Il quadro fornito dal campione mostra un lavoro di costruzione dei nuovi curricoli di Scienze della Terra realizzato in modo autonomo e sostanzialmente basato sull'esperienza di quelli del vecchio ordinamento. Le scelte tematiche eterogene per l'ultimo anno di corso potrebbero essere condizionate dalle incertezze sull'esame di stato per il nuovo ordinamento. Lo studio suggerisce la necessità di intraprendere e potenziare le attività di formazione in servizio dei docenti per sfruttare a pieno le potenzialità insite nei nuovi curricoli di Scienze Naturali: interesse e motivazione appaiono presenti. Occorre fare perno su questi punti di forza per promuovere il superamento di prassi didattiche che a tutt'oggi sembrano fondate quasi esclusivamente sull'approccio teorico alle Scienze della Terra.

Le argille, protagoniste del paesaggio attorno a Baiso (RE)

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Keywords: argilla, calanchi, melange, impermeabilità

Dovunque si giunga a Baiso, si notano pendii interrotti da vistose erosioni: i calanchi, dissesti che interessano i terreni argillosi e che si sviluppano in tempi lunghi, dell'ordine di migliaia di anni. I calanchi sono per il geologo una preziosa occasione per osservare in affioramento la composizione del sottosuolo. I terreni argillosi che compaiono sembrano molto simili. ma in realtà si differenziano fra loro per struttura ed età. Ad esempio, le cosiddette "Argille varicolori" hanno sfumature rossastre, rosate o violacee che lasciano intravvedere la stratificazione: si sono depositate su una piana abissale oceanica da 95 a 75 milioni di anni fa. Altra formazione è il "Melange di Baiso": si tratta di depositi di mare profondo di circa 40 milioni di anni, a prevalente composizione argillosa, dovuti a frane sottomarine, per colata o lento scivolamento, che hanno inglobato lembi di altre formazioni, calcaree o arenacee. Il colore è generalmente grigio scuro, con frequenti chiazze e focature di colore rossastro, violaceo o verdino. Abbiamo infine le "Marne di Monte Piano", argille marnose in strati molto sottili ma poco evidenti, di colore passante dal rossastro, al verdino ed infine al grigio, depositatesi da 40 a 35 milioni di anni fa su una scarpata oceanica profonda e sul bacino abissale contiguo.

L'argilla è una roccia sedimentaria, di solito pseudocoerente: si comporta cioè in condizioni asciutte come una roccia compatta, mentre quando è impregnata d'acqua assume le caratteristiche di un fluido. È costituita da granuli di dimensioni piccolissime, inferiori a 2 millesimi di millimetro, aventi composizione chimica differente; tuttavia i più frequenti sono illite, caolinite, clorite e montmorillonite, tutti appartenenti al gruppo dei silicati idrati di alluminio, con quantità variabili di altri elementi metallici, quali magnesio, sodio, potassio, calcio e ferro. La loro struttura microscopica è formata da strati di atomi o molecole combinati a formare solidi geometrici riuniti in "pacchetti", che costituiscono l'unità fondamentale del minerale. Tra gli interstrati dei pacchetti, oltre ad elementi come sodio e potassio, risiedono alcune molecole d'acqua tipiche dei minerali argillosi. All'interno di queste strutture geometriche sono presenti gruppi ossidrile OH. Il basso valore delle dimensioni medie dei granuli, unitamente alla loro struttura fogliare, implica una caratteristica importante, ossia l'elevata superficie per unità di peso. Questi minerali argillosi hanno proprietà uniche:

a- immersi in soluzioni acquose fissano sulle loro superfici molecole di acqua e di alcune sostanze disciolte nella soluzione, aumentando in peso e volume;

b- danno facilmente masse plastiche quando sono mescolati con poca acqua; tuttavia in condizioni particolari questi minerali favoriscono la formazione di masse quasi liquide, incoerenti;

c- trattengono molti elementi, fra cui il potassio, che dapprima si legano alla loro superficie in modo debole, ma poi si fissano in modo più forte all'interno della struttura chimica.

Il learning cycle delle 5e per introdurre l'IBSE nella didattica delle Scienze Della Terra

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Keywords:, didattica, IBSE, geoscienze

Negli ultimi tempi anche in italia si è cominciato a parlare di educazione scientifica basata sull'investigazione (IBSE, inquiry-Based Science education). Con il termine inquiry si intende una serie di processi messi in atto dagli studenti in modo intenzionale come: saper diagnosticare problemi, commentare in modo critico gli esperimenti, individuare soluzioni alternative, saper pianificare un'indagine, formulare congetture, ricercare informazioni, costruire modelli, saper discutere e confrontarsi tra pari, formulare argomentazioni coerenti. Una tale rivoluzione nell'insegnamento/apprendimento non può essere compiuta in breve tempo per cui le ricerche suggeriscono di avvicinarsi all'inquiry attraverso un percorso progressivo in quattro livelli – confermativo, strutturato, guidato e aperto – che si differenziano per il grado di responsabilità dato agli studenti, ossia per quante informazioni (domande da investigare, procedure, risultati attesi) vengono fornite dall'insegnante. Uno degli approcci più efficaci per progettare lezioni inquiry-based è il cosiddetto learning cycle. Ne esistono molte varianti, tra cui il modello delle 5E, dove ciascuna e descrive una fase di apprendimento: engage, explore, explain, elaborate ed evaluate. Nel poster vengono descritte le fasi di un percorso di inquiry (strutturato) sviluppato con il modello delle 5E.

Un’esperienza didattica di studio del paesaggio geologico con il supporto dello smartphone

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Keywords: patrimonio geologico, didattica, nuove tecnologie, paesaggio

Nell’a.s. 2013/2014 due classi prime hanno sperimentato un’attività preparata e guidata dalla Dott.ssa Alessandra Magagna, nell’ambito della sua ricerca di dottorato e del progetto GeoMedia-web: multimedialità e reti per la diffusione della conoscenza sul patrimonio geologico e sui rischi naturali (L6/2000).

Durante un incontro preliminare sono state valutate preconoscenze e misconoscenze degli studenti ed è stato presentato il progetto ed il funzionamento della Applicazione Trimble Outdoors Navigator free per la successiva escursione in Val Sangone (TO). Sul terreno, i ragazzi hanno svolto, in gruppi di 4/5, attività pratiche di osservazione, fotografia, raccolta campioni, cartografia, rilevamento di punti nelle 6 tappe del percorso e registrazione dell’intera traccia con lo smartphone. Al termine i gruppi hanno svolto una riflessione guidata con l’aiuto di una scheda. L’attività sul campo è stata approfondita con un incontro in laboratorio di informatica, quando è stata scaricata la traccia registrata, quindi analizzata e visualizzata su Google Earth e confrontata con quella segnata sulla carta topografica.

Il focus delle attività è stato condurre i ragazzi alla scoperta del paesaggio con la raccolta di indizi utili per ricostruirne l’evoluzione geologica (caratteristiche e le dimensioni spaziali e temporali) e per acquisire consapevolezza sul rapporto tra agenti, processi e forme del paesaggio. Il percorso è stato concluso con un questionario di gradimento sottoposto agli studenti, una verifica di conoscenze e competenze acquisite e un questionario di valutazione sottoposto all’insegnante.

Dall’esperienza vissuta sono emersi alcuni risultati significativi, che suffragano l’ipotesi di partenza: gli studenti hanno partecipato con interesse alle diverse attività proposte e la loro attenzione è stata catalizzata dalla possibilità di usare in modo nuovo smartphone o tablet; l’uscita sul campo ha consentito l’apprendimento ex-novo e/o il consolidamento di alcune conoscenze/competenze; la partecipazione ad un progetto di ricerca a livello universitario è stata stimolante per docente e studenti e si è rivelata perfettamente integrata nella programmazione curricolare del docente stesso.

L’esperienza didattica ha evidenziato l’importanza e il valore aggiunto dell’interazione e della collaborazione tra l’Università e il mondo della ricerca e la scuola, secondaria di II grado, in particolare.

Ammoniti: gli abitanti più famosi dell'appennino accompagnano gli studenti alla scoperta dei fossili

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Keywords: ammonitI, didattica, paleoambienti

Le ammoniti erano molluschi molto diffusi nelle acque del mare della Tetide durante l'era Mesozoica. Sono comparse sulla Terra nel periodo del Devoniano (era Primaria o Paleozoica), circa 415 milioni di anni fa e si sono estinte alla fine dell'era Secondaria o Mesozoica, al termine del periodo Cretacico, circa 65 milioni di anni fa, insieme ai dinosauri terrestri e marini. Esse vengono rinvenute in tutte le formazioni rocciose della successione umbro-marchigiana del periodo Giurassico.

Lo scopo di questo laboratorio è di far conoscere alcuni elementi di paleontologia e di stratigrafia ad alunni e docenti delle scuole delle Marche, tramite attività di tipo "hands on" che prevedono l'osservazione e la manipolazione delle ammoniti.

Man mano che il laboratorio si svilupperà, sarà possibile conoscere le abitudini di vita degli ammoniti e la loro evoluzione nel tempo. Diversi kit di ammoniti, quasi tutti provenienti dalle rocce giurassiche dell'Appennino umbro-marchigiano, sono stati allestiti per simulare delle attività da poter svolgere in campagna durante una escursione scolastica o in classe. Il laboratorio puo' essere svolto per studenti di diverse eta'. Il prerequisito di questa attivita' e' un'introduzione alla vita e alla storia della Terra, alla fossilizzazione e alle rocce sedimentarie.

Per familiarizzare con le ammoniti sono mostrati alcuni caratteri che i paleontologi esaminano per riconoscerli e classificarli. L'attività inizia con l'analisi della conchiglia dell'ammonite, divisa in camere separate tra loro da setti sinuosi (linea di sutura) e continua con l'esame del profilo e della presenza o meno delle ornamentazioni, protuberanze o inflessioni del guscio. Si introducono gli studenti al concetto di classificazione. Successivamente si pongono i fossili all'interno di una ricostruzione dei paleoambienti del periodo Giurassico, sottolineando il fatto che si tratta di ipotesi basate su diversi parametri ed evidenziando le caratteristiche di ciascun ambiente di vita, con confronti con gli ambienti attuali.

Infine si studia il tipo di avvolgimento degli ammoniti (da evoluto a involuto) e il loro significato, quindi, grazie a un modello in polistirolo, si esamina una delle proprietà di questi fossili più utili ai paleontologi, ossia quella di fossile guida dell'era Mesozoica, in particolare del periodo Giurassico. Un cenno ai principi della stratigrafia e della cronologia relativa completano l'argomento.

Al termine dell'attività gli alunni dovrebbero aver acquisito i concetti di fossilizzazione e di evoluzione di queste specie, avere familiarita' con i metodi di osservazione e studio dei fossili e sul loro significato, e avranno potuto riflettere sulle caratteristiche degli ambienti e dei paleoambienti.

Viaggio spazio-temporale nel geosito del Monte Conero (Marche): uno strumento per la didattica delle geoscienze nelle scuole

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Keywords: geositi, didattica delle geoscienze, scuole.

Lo scopo di questo progetto di ricerca è quello di promuovere lo studio delle Scienze della Terra nelle scuole delle Marche utilizzando i geositi più rappresentativi dell'evoluzione geologica della regione. Dopo la preparazione di materiali didattici sul sito di Frasassi, già disponibile on-line in http://d7.unicam.it/teachingearthsciences/, che racconta la storia geologica del periodo Giurassico (da 210 a 140 milioni di anni fa) e degli ultimi 2 milioni di anni, il secondo geosito scelto per questo progetto è quello del Monte Conero in cui è rappresentata la storia geologica da 140 milioni di anni fa ad oggi.

Nel geosito del Monte Conero sono stati scelti diversi luoghi e percorsi che permettono agli insegnanti di affrontare lo studio delle Scienze della Terra, sia approfondendo i temi del curricolo scolastico con un'attenzione alla geologia della regione, sia con la possibilità di trattazioni degli argomenti in maniera interdisciplinare, secondo lo spirito dei nuovi programmi. Analogamente a quanto predisposto e già testato sul geosito Frasassi, è stato preparato materiale didattico di supporto e di approfondimento per gli insegnanti e gli studenti su una serie di temi di ampio respiro, che prendono spunto dalla geologia del Monte Conero.

I seguenti percorsi-argomenti, sono stati già proposti agli insegnanti per mezzo di seminari di presentazione dell'attività e visite guidate, in preparazione della sperimentazione con le classi:

1) Passo del Lupo, dove in un'anticlinale asimmetrica si può osservare l'Evento Anossico Oceanico 1 "Livello Selli", riferibile a circa 124 milioni di anni fa (periodo Cretacico);

2) Passeggiata al limite K-T (nella formazione della Scaglia rossa), con il Livello Marchesini e il limite K-T di 65 milioni di anni fa, quello dell'estinzione non solo dei dinosauri marini e terrestri, ma anche degli ammoniti, delle belemniti e delle rudiste;

3) Cava di Massignano, nella Scaglia cinerea, nota per il GSSP (Global Stratotype Section Point) di 33,7 milioni di anni fa, che indica il passaggio tra l'epoca dell'Eocene con quella dell'Oligocene;

4) Punto panoramico su Monte dei Corvi, per lo stratotipo di 11 milioni di anni fa nella F.ne dello Schlier;

5) Spiaggia di Mezzavalle dove un affioramento della Formazione della Gessoso-solfifera illustra la crisi di salinità del Mediterraneo di 6 milioni di anni fa;

6) Baia di Portonovo, per osservare e comprendere i meccanismi dei fenomeni franosi dell'area avvenuti nelle ultime centinaia di anni.

I percorsi scelti sono facilmente utilizzabili per escursioni scolastiche e permettono di poter effettuare raccolte di dati da rielaborare in classe, oltre che esperienze hands-on. Nell'ambito di questo progetto gli insegnanti potranno usufruire di un sito web con il materiale didattico prodotto, esempi di esperienze e progetti per gli studenti, approfondimenti, una guida virtuale alle escursioni, un tutorato on line.

Le scienze della terra nei libri di testo della scuola secondaria di secondo grado italiana: cambiamenti ed evoluzione

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Keywords: Scienze della Terra, libri di testo, attività sperimentale.

L'approccio alle tematiche delle scienze della Terra nell'insegnamento nella scuola secondaria di secondo grado ha subito un'evoluzione consistente in relazione sia alle direttive ministeriali sia agli sviluppi della ricerca scientifica. I libri di testo rappresentano uno strumento fondamentale a supporto dell'attività didattica (Keine, 2014) e seguono anch'essi l'evoluzione complessa del settore scolastico. Nell'ambito del dottorato in Scienze Ambientali, dell'Università degli Studi di Milano, è in corso un progetto di ricerca che, sulla base di una ricostruzione storica degli approcci ai singoli argomenti oggetto di insegnamento, dei testi disponibili e dell'ampliamento del settore multimediale, si pone come obiettivi di analizzare l'impatto e l'efficacia delle diverse impostazioni su un vasto campione di studenti, verificare la percezione dell'immagine della disciplina negli studenti, elaborare proposte didattiche basate sui più innovativi strumenti di comunicazione e sull'attività sperimentale in campo.

I primi risultati mostrano come nell'ultimo ventennio si è assistito a un incremento significativo dell'offerta editoriale, particolarmente differenziata a partire dal 2010-2011, anno in cui le tematiche relative alle Scienze della Terra compaiono nei programmi già dal primo biennio. Sensibili cambiamenti si osservano anche nei titoli dei testi dove termini come *Sistema*, *Gaia* prendono il posto dei tradizionali *geografia*, *geografia generale,* e compaiono verbi come *osservare, capire, scoprire,* a supporto di un approccio più sperimentale. I cambiamenti osservati e in fase di analisi aprono a una necessaria discussione sui fattori che possono averli determinati e sulla necessità di ampliare l'approccio sperimentale sul terreno come indicato sia dalle ultime indicazioni ministeriali sia dalla ricerca in didattica delle Scienze della Terra (es.Bollati et al., 2011; 2013).

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Microcosmo suolo

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Keywords: Suolo, ecosistema, didattica

Il suolo è un comparto ambientale complesso, poco conosciuto e poco tenuto in considerazione dai non addetti ai lavori. Non si tratta di un semplice substrato ma di una componente viva, essenziale al compimento dei principali cicli biogeochimici e inaspettato serbatoio di biodiversità. Il suolo svolge un ruolo determinante negli equilibri ambientali e riveste innumerevoli funzioni; i servizi garantiti dall'ecosistema suolo sono indispensabili per l'uomo: basti pensare che l'umanità dipende dal suolo per la propria alimentazione e che il suolo è un importante serbatoio di carbonio con rilevanti conseguenze sui cambiamenti climatici. Capirne l'importanza è cruciale per sviluppare l'attenzione necessaria nei confronti di questa preziosa risorsa e per contribuire allo sviluppo di una cultura della sostenibilità che dipende anche da come consideriamo ciò che si trova sotto i nostri piedi.

Il C.R.E.A, centro regionale di educazione ambientale del comune di Pavia, da alcuni anni propone agli insegnanti ed alle classi delle scuole secondarie di primo grado un progetto che si propone di far scoprire il mondo nascosto che sta nel suolo attraverso un approccio sperimentale ed il ricorso a modalità di coinvolgimento diretto dei ragazzi. La presenza di aria ed acqua e l'evidenziazione delle diverse componenti (attraverso una prova di sedimentazione) sono condotte su campioni di suolo raccolti dai ragazzi. L'osservazione è mediata da schede di lavoro che non anticipano il risultato ma che, attraverso una serie di domande, guidano i ragazzi nella formulazione di ipotesi. Molto spazio viene lasciato all'osservazione della pedofauna intesa come spaccato della biodiversità che il suolo può ospitare. Le attività prevedono in questo caso l'estrazione della pedofauna dai campioni di suolo raccolti e l'utilizzo di chiavi dicotomiche semplificate per l'identificazione degli organismi. Presentazioni e video didattici accompagnano e preparano l'attività sperimentale. Analizzando i risultati dei campioni di suolo raccolti si introduce il concetto dell'utilizzo della pedofauna come bioindicatore della qualità del suolo stesso e di come questa qualità non debba assolutamente darsi per scontata.

Addendum

Crustal modelling of the Ivrea-Verbano Zone in Italy re-examined: new observations preclude lower-crustal extension and 90° rotation

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Several independent lines of evidence prevent crustal tilting of the previously proposed Ivrea-Verbano – Serie dei Laghi crustal section in northern Italy. The Ivrea-Verbano zone (IVZ) is separated from the Serie dei Laghi (SdL) by the Cossato-Mergozzo-Brissago (CMB) and Pogallo lines and from the Alpine belt in the north-west by the Insubric Line (IL).

New observations of the supposed rotated, lower crustal extensional shear zone system in the IVZ reveal that this consists of localized, mostly brittle teleseismic deformation on the SE side of the Insubric line. Widespread crushing, intense planar microjoint fabrics, tectonic deformation lamellae in quartz, dm-scale block rotation, fluidised, dyke-like microbreccias and associated pseudotachylites are observed, but we have not found evidence of a major shear zone. We ascribe all these features to early Alpine, earthquake-induced, in-situ seismic reverberation in a broad belt south-east of the IL, without significant lateral displacements outside the IL itself.

Recent geological mapping also shows that the CMB Line is not just a fault but a major dextral shear zone, clearly visible from the Sottoceneri (Canton Ticino, CH) to Lago d'Orta; its best exposure is in Valle Cannobina. Its thickness is about 6 km; its activity postdates Variscan regional metamorphism and predates the Permian intrusion of mafic stocks and dykes. After the Permian the CMB shear zone and the entire crustal section cannot have been tilted by more than 20°, as indicated by the low dip of the upper, miarolitic layer of the Baveno-Mottarone granitic pluton and by the vertical attitude of Permian mafic dykes with chilled margins. The CMB shear zone juxtaposes two units (the IVZ and SdL) that had nothing in common until the Lower Permian. It is a major Lower Permian discontinuity that could be part of the dextral megashear between Gondwana and Laurasia (Muttoni et al.,1996). The Pogallo line is a steep sinistral Permian fault that cuts across the CMB shear zone with an offset of 12 km. Our field observations show that it is coeval with the intrusion of the mafic dykes along it. We conclude that the IVZ and SdL are not parts of a coherent crustal section. Furthermore, the previously proposed Variscan lower crustal extensional shear zone system is re-interpreted as Alpine teleseismic deformation features without major displacement. A thorough re-evaluation and simplification of the crustal structure in the IVZ seems to be appropriate.

Muttoni G., Kent G.V. & Channel J.E.T. 1996. Evolution of Pangea: paleomagnetic constraints from Southern Alps, Italy. Earth and Planetary Science Letters, 140, 97-112.