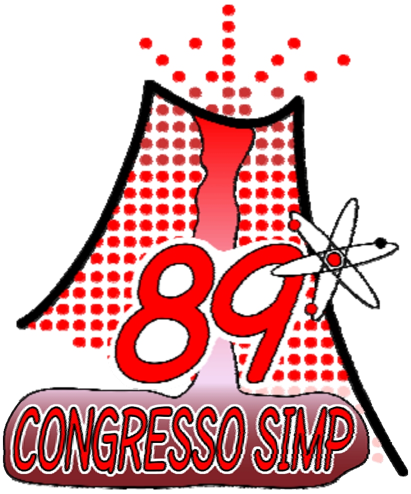

L’EVOLUZIONE DEL SISTEMA TERRA DAGLI ATOMI AI VULCANI

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PLENARY LECTURES

STROMBOLI, ETNA AND VESUVIUS: EXAMPLES OF VOLCANIC RISKS MANAGED BY DPC

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Italy's national territory is exposed to a broader range of natural hazards than other European countries. For this reason, Italy has implemented a coherent, multi-risk approach to civil protection. This approach fully integrates the scientific and technological expertise within a structured system aimed at forecasting natural disasters, providing early warning and immediately managing the emergency. With regard to its delayed time activities, the Department of Civil Protection (DPC) provides strong support to the knowledge of natural hazardous phenomena through a network of Competence Centres (Centres for technological and scientific services). DPC supports research efforts on the assessment of vulnerability and exposure of population, buildings and critical infrastructures to the risks associated with these phenomena.

The early warning system for volcanic events, floods, landslides, hydro-meteorological events and forest fires includes prevention activities. It is provided by the DPC on the basis of the network of "*Centri Funzionali*" (Functional Centres). These centres are in charge of the forecast and assessment of the risk scenarios, in order to provide a multiple support system to the decision makers of the Civil Protection Authorities. The Functional Centres are organized in a network which consists of operative units able to collect, elaborate and exchange any kind of data (meteorological, hydro-logical, volcanic, seismic and so on), and it is supported by selected Competence Centres involved in the analysis of a specific risk.

The southern part of Italy has the highest concentration of active volcanoes of entire Europe: Etna, Vesuvius, Phlegrean Fields, Vulcano, Stromboli. More than 2 millions people are exposed to the volcanic risk.

Stromboli is characterized by a typical "strombolian" activity, with explosions every 10-20 minutes, and it represents a major attraction for the tourists in the Aeolian archipelago. On the December 30th, 2002, a landslide along the Sciara del Fuoco flank triggered a tsunami that severely affected the Stromboli coasts and reached the other Aeolian islands and the northern part of Sicily, although with lower intensity. Since that catastrophic event the DPC, in cooperation with the scientific community and the local population, funded the improvement of a multiparametric monitoring system and undertook several countermeasures to mitigate the volcanic risk. Nowadays DPC provides a daily bulletin of criticality in order to estimate the impending risk.

Etna volcano, with the strong ash emissions of 2002 - 2003 and 2006 eruptions, brought severe problems to the air traffic management, in particular to the Catania international airport (located about 30 km SE of the Mt. Etna). In order to support the local airspace authorities for the air traffic management in case of eruption, DPC daily provides simulation maps of the probable plume direction and ash dispersion every three hours.

Due to the extensive urbanization of its surroundings, Vesuvius represents one of the areas with highest volcanic risk in the world. The DPC, through a dedicated expertise Commission, is updating the National Emergency Plan for the Vesuvius, which foresees the total evacuation of the "red area" (about 500.000 people) within 72 hours. In 2006 the Vesuvius emergency plan and its procedures were successfully tested by a European civil protection exercise (M.E.SIM.EX).

THE COMPOSITION OF THE TERRESTRIAL PLANETS AND THE EARLY EVOLUTION OF THE EARTH

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The terrestrial planets, as well as the Earth's Moon and other rocky bodies in the asteroid belt, are differentiated rock and metal mixtures that have been depleted in volatile elements to varying degrees. Compositional models for these bodies assume chondritic proportions of the refractory elements (*e.g.*, Ca, Al, and some 40 trace elements), with no fixed constraint on their absolute concentrations. These bodies are primarily composed of Fe, Mg, Si and O [making up 95% of their mass, with no fixed, chondritic proportions]. Detailed planetary geodesy underpins modeling of the metal to rock ratio and dynamics of the interiors of these bodies. Crucial to modeling planetary compositions are the absolute abundances and the distribution of heat producing elements (*i.e.*, extinct, short-lived isotopes and K, Th and U), the elements that provide the heat that drives convection and volcanism. The early thermal and chemical evolution of the planets was strongly controlled by accretionary growth and post-accretion additions (*e.g.*, late veener). Planetary degassing and heat dissipation is recorded in the volcanic products of these bodies and, in the case of planets, the atmospheric composition. Knowledge gained from developing and constraining the Earth's compositional models provides important guiding principles that are essential for advancing compositional models for other planets and rocky solar system bodies.

Geoneutrinos, which are anti-neutrinos produced during beta-decay in the U and Th decay chains, have now been detected by neutrino detectors, and afford an independent means of estimating the Earth's heat producing element concentrations. Recent results from the KamLAND and Borexino geoneutrino experiments are coincident with geochemical models of Th and U in the Earth. These detectors continue to count and, thus, uncertainties will be reduced with time (at present 2 detectors are accumulating data, a 3rd is to come on-line). Geochemical models posit that ~ 40% of the heat producing elements are in the continental crust, with the remainder in the mantle. Although models of core formation allow for the incorporation of heat producing elements, the core contribution of radiogenic heating is considered negligible. The Mantle Urey (Ur) ratio is a measure of the radiogenic heat contribution to the total mantle heat flux and is estimated to be ~ 0.3 from chemical and isotopic data. Such a low mantle Urey ratio is at odds with most parameterized convection models (*i.e.*, Ur = 0.7) for the Earth and thus challenge geophysical models. The geo/cosmochemical and geoneutrino constraints demonstrate that there is a significant contribution to the Earth's heat budget from the secular cooling of the mantle.

THE CHALLENGE OF CLIMATE SCIENCE

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Climate has become one of the hottest issues today, moving from an obscure scientific dispute to the status of a global geopolitical issue, but the concept of climate itself is a sophisticated concept that is not the static, intuitive, idea that we may use in everyday life. The basic mechanisms of climate are regulated by global energy balances and they are the result of complex nonlinear interactions among the several systems participating in the shaping of the Earth climate. The intensity of the non linear interactions generates an intense variability in climate that makes very difficult the detection of small, secular trends. The increase of carbon dioxide and of surface temperatures is now being established as a fact, but the attribution of the temperature rise to carbon dioxide increases is a complex decision process. We cannot perform crucial experiments in climate science and we have to rely on a combination of numerical experiments and consensus among experts to reach provisional explanations. Nevertheless, this process results in the accumulation of knowledge and we will have to live with the idea that this is the way in which climate science progresses.

CRITICAL ISSUES IN THE MANAGEMENT OF VOLCANIC CRISIS

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Volcanic crisis of the past four decades have represented a major challenge to worldwide society. Volcanic events and unrest crisis (not followed by eruption), with some significant consequence on human society have occurred at a rate of several events per year at global scale. A significant part of them have occurred near settled areas either producing victims and or relevant economic losses. Impact of eruptions has been generally severe on inhabited areas located in the immediate surroundings of active volcanoes. However, mudflows and ash fall have severely hit human communities even at tens of kilometres from source volcanoes. A much broader impact has resulted both on air traffic and airport functionality from the injection in the atmosphere of volcanic gas, aerosols and ash. The latter problem has greatly expanded over the last four decades as a result of worldwide escalation of flight transportation. Volcanic crisis vary significantly depending on size and violence of volcanic events, duration of the crisis, impacts on society (*e.g.* casualties, damage to buildings and critical facilities, economic losses) and different degrees of preparedness to deal with emergencies by local people, civil protection and public authorities. Size and intensities of post-1980 volcanic events have spanned from trivial to very large. The largest volcanic eruption was that of June 15th, 1991 Pinatubo (Philippines), when pyroclastic flows, ash fall and lahars devastated a huge area around the volcano. However, the event with the highest intensity and destructive power was the lateral blast and plinian eruption of Mount St Helens on May 18th, 1980 (USA). The largest death tall (at least 23.000 casualties) was paid in 1985 when lahars generated by the syn-eruptive snow and ice melting of the Nevado del Ruiz glacier, devastated the town of Armero (Colombia) situated more than 60 km from the ice capped volcano. The eruption the Eyjafjallajokull (Iceland) has finally shown how a relatively low-intensity, weeks-lasting eruption has the potential of producing unexpected, huge consequences on flight transportation. Lessons learned from the past four decades of volcanic crisis have strongly enhanced the average capability of responding effectively to volcanic emergencies substantially lowering the number of potential victims. However, such a capability is variable in different countries and at different volcanic systems being largely dependent on the preparedness of the system to deal with emergencies. Preparedness is a comprehensive concept that includes different degrees of knowledge of a specific volcanic system and the reliability of the associated hazard assessment (volcanic hazard evaluation), presence and reliability of an instrumental volcano monitoring system (eruption forecasting capability), presence and effectiveness of a well organized management system of volcano emergency (crisis management capability) and finally information to population at risk (education and info management). There is a widespread perception that, in contrast to earthquakes, volcanic eruptions can be effectively forecasted (or will be soon successfully forecasted) thanks to the rapid technological advancements and expansion of instrumental networks. However, a revision of the volcanic events of the past four decades demonstrates that unrest volcanic signals are often difficult to separate from actual forecasting signals so that the risk of either false alarm or lack of alarm is still high. Perhaps the major challenge of third millennium relies on the capability to raise preparedness by better integrating the scientific and civil protection functions. The experience of the past four decades indicates that the scientific function is often considered as to fully surrogate the decision-making function. This is in several cases a major source of problems and conflicts with the population involved in mitigation actions. A stronger and more qualified role of civil protection authorities can greatly facilitate scientific and decision making integration eventually increasing the respond capability.

MICROANALYSIS AND INTERNAL STRUCTURE OF U-Pb MINERALS: FROM MELTING TO SUB-SOLIDUS RECRYSTALLIZATION

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The development of U,Th-Pb micro-geochronology has come with an increasing interest in the microstructure and chemistry of U-Th minerals. Minerals like zircon, monazite, allanite, titanite and rutile can preserve multiple age domains within single crystals that are commonly reflected in chemical zoning. Cathodoluminescence (for zircon) and back-scattered electron images allow for fast recognition of such internal zoning and often constitute the first step in micro-geochronology. Particularly for zircon, distinct zoning patterns can be indicative of different growth environments from magmatic to sub-solidus recrystallization. Multiple overgrowths in anatectic zircons indicate repeated melting within a single sample and attest to the chemical and physical robustness of this mineral. At the sub-solidus state, dissolution-precipitation is an efficient process to form metamorphic zircon at the expenses of pre-existing crystals. This process can act in zircons that have no significant metamictization provided that fluids are present. Dissolution-precipitation produced zircon with a characteristic zoning and composition. Monazite has a large variety of internal zoning patterns, some of which are characteristic of magmatic growth or fluid alteration. For other U,Th minerals like allanite and titanite, internal zoning, when present, is poorly understood.

Electron back-scattered diffraction (EBSD) has been successfully used to recognize deformation in zircon, which, in some conditions, can lead to Pb loss and chemical changes in the original crystal [1]. Transmission electron microscopy (TEM) is the ultimate tool to investigate zircon microstructure. The zoning observed in cathodoluminescence is elusive at TEM and it is not repeated at the nano-scale. TEM analysis of zircon domains reveals that, even after billions of years of radioactive decays and high-grade metamorphism, zircon can be remarkably low in structural defects. Zircon rims formed during metamorphic recrystallization may contain nano-scale pores and strain centre, but are perfectly aligned with the inherited core and relatively unstrained.

The trace element chemistry of specific domains is increasingly used to determine the environment in which U,Th mineral formed. Electron microprobe, laser ablation - ICPMS and ion microprobes can provide chemical data for most accessory U,Th minerals. Typical REE signatures generally reflect the coexisting assemblage and can be recognized in more than one U,Th mineral. HREE depletion is common in zircon, allanite and monazite that formed in a garnet-rich assemblage, as for example at eclogite or granulite-facies. Presence or absence of a negative Eu-anomaly in most accessory minerals is related to the abundance of feldspars, and can be a key for recognizing growth in eclogite-facies. Sr enrichment in high pressure monazite and allanite is taken to reflect the absence of feldspar.

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REMOVAL OF LITHOSPHERIC MANTLE BENEATH THE NORTH CHINA CRATON: WHEN, WHERE AND HOW?

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Cratons, by definition, are regions of prolonged stability (≥ 1 Ga) within the continents and are characterized by cold, thick lithosphere whose density is offset by its refractory composition, giving rise to chemical buoyancy (the "tectosphere" hypothesis of Tom Jordan [1]). The thick, chemically buoyant mantle keel beneath Archean cratons is considered to be mechanically strong, in part because it is likely to be anhydrous, and thus contributes significantly to the relative stability of cratons. However, the eastern block of the North China Craton is an exception.

Here, a thick lithospheric keel developed in the Archean and persisted at least through the Paleozoic, as Ordovician kimberlites carry cool, refractory Archean peridotites and diamonds. Beginning in the Mesozoic, the lithosphere of the eastern block of the craton became destabilized, as witnessed by the onset of voluminous Mesozoic magmatism. Late Jurassic high Mg andesites, dacites and adakites from the northern portion of the eastern North China Craton have unusual compositions that suggest they formed from melting of ancient, mafic lower crust from the North China Craton that foundered into the mantle [2].

Cretaceous high Mg basalts and picrites from the eastern North China Craton also have unusual compositions and contain jadeitic clinopyroxenes that suggest their derivation from a peridotitic mantle that was hybridized by silicic melts from foundered eclogite [3]. From studies of these lavas, as well as on-going Re-Os studies of mantle xenoliths entrained in Paleozoic through Cenozoic magmas, we are beginning to define when and where the lithosphere was removed. The question of how this was accomplished is still unanswered and will require multidisciplinary efforts to image the changing lithosphere through time.

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SESSION 1.1

From the Solar System to the Earth System

Convenors:

C. Bonadiman (*Univ. of Ferrara*)
M. D'Orazio (*Univ. of Pisa*)
A.M. Fioretti (*CNR, Padova*)

IN SITU GEOCHEMICAL CHARACTERISATION OF SILICATE PHASES FROM THE VIGARANO CHONDRITE

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The Vigarano meteorite is the progenitor meteorite that defines the chondrite group CV of the Carbonaceous Chondrites class (CCs). Fragments of the Vigarano meteorite, the Morandi block, have been extensively analysed since the late fifties, for mineralogical/petrographic, and to lesser extent geochemical, studies, thus allowing to define the features of the CV group [1]. This is characterized by the least altered material (petrologic type 3, showing abundant chondrules, low degrees of aqueous alteration and unequilibrated mineral assemblages), which is enriched in refractory elements (~ 1.3 × CI) and depleted in volatiles (~ 0.24 × CI). The chondrules are large (mm-sized) and many of them are surrounded by igneous rims, large refractory inclusions and abundant matrix (40 vol.%). The chondrites record a wide range of oxidation states that were probably established both as a combination of the local oxidation state of the nebula and during parent body processing. The largest variation of oxidation states occurs within the CV group, which includes oxidized and reduced subgroups. Whereas the CV3 Allende is oxidized subtype CV(O), the Vigarano (as Morandi block), classified to reduced subtype CV(R), is one of the most primitive solid material of the solar system, because it experienced very weak aqueous alteration in a primitive asteroid.

The Cariani fragments, with respect to the Morandi block [2, 3] is relatively rich in Al (~ 1.6 × CV-Morandi), Na (2.2 × CV-Morandi, comparable to CI-Chondrite Ivuna) and Cr (~ 1.2 × CV-Morandi), but clearly depleted in Ca (~ 0.5 × CV-Morandi). With respect to REE, the Cariani fragments result enriched in Sm and depleted in Eu-Lu, at comparable La contents. Among the calcophile and siderophile elements, the Cariani block is slightly enriched in Ag and Tl (at CI level) with respect to Morandi block.

This contribution reports new data of the Cariani blocks. *In situ* major and trace element compositions of silicate minerals (and glasses) and Fe-Ni matrix, as well as "whole rock" major and trace element data are obtained, in order to reconcile the geochemical characteristics of the Morandi fragments to the Cariani ones. Moreover, these data allow us to interpret the role of the refractory trace elements (*e.g.* REE) in the geochemical evolution of the silicate Earth. In particular, *in situ* trace elements compositions of olivines, ortho-and clino-pyroxenes, and rare melilites will contribute to list (gas/solid) partition coefficients for the most common Earth silicate minerals.

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HYDROGEN CONTENTS IN CLINOPYROXENE FROM MARTIAN METEORITES (NAKHLITES) USING ELASTIC RECOIL DETECTION ANALYSIS

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Water contents in Nominally Anhydrous Minerals (NAMs) have been recently quantified in some Martian meteorites [1, 2, 3]. These data were obtained with several methods (mainly SIMS and FTIR) and on a restricted number of SNC (Shergottite, Nakhlite, Chassignite) meteorites. We present here new, high precision data on total hydrogen in clinopyroxene crystals from three nakhlites, obtained by the Elastic Recoil Detection Analysis (ERDA) technique. ERDA has been recently greatly improved [4, 5] and is now a very powerful tool to analyse hydrogen in NAMs. We concentrated our study on nakhlites because: i) they are the least affected by shock metamorphism among the SNC meteorites and hence the most likely to preserve their original water contents [6], and ii) they consist mainly of clinopyroxene, whose crystalline structure can accommodate measurable amounts of hydrogen [7]. We chose MIL 03346, Nakhla and NWA 998 because they span of the entire spectrum of textural, mineralogical, petrological and geochemical features and cooling history reported for nahklites [6, 8, 9]. Five clinopyroxene single grains were carefully selected from each nakhlite and samples were prepared for ERDA following the protocol described in [5]. Electron microprobe analysis was carried out on the same single crystals to check for chemical homogeneity. Clinopyroxenes from the three investigated meteorites show similar chemical composition ($En_{37}Fs_{23}Wo_{40}$) and similar H contents. Our results strictly refer to the crystal core regions. Slightly increasing water contents are observed from MIL 03346 (170 to 276 ppm H_2O) to Nakhla (214 to 301 ppm H_2O) to NWA 998 (301 to 383 ppm H_2O). The relative mean uncertainty of H measurements is 15%. These values fall within the wide range of water contents previously reported for Martian clinopyroxene and for clinopyroxene from various geological environments of the Earth (*e.g.*, mantle xenoliths, basalts and eclogite) obtained by different methods. Based on modal compositions of the three nakhlites [6], the bulk water content calculated using our new H data ranges from 131 to 278 ppm H_2O, assuming water contents for olivine and orthopyroxene from the literature [3] and no water contribution from the mesostasis. These data are consistent with the low amount of structural water (221-305 ppm H_2O) released by Nakhla [10] for $T > 300°C$. The restricted and almost identical water contents of clinopyroxenes from the three investigated nakhlites supports their crystallization from the same parent magma.

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A REFINED REFERENCE MODEL FOR GEO-NEUTRINO IN BOREXINO

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Geo-neutrinos, the antineutrinos from the progenies of U, Th and ^{40}K decays in the Earth, bring to the surface information from the whole planet, concerning its content of natural radioactive elements. Their detection can provide important constraints about terrestrial heat flow, the present composition and the origin of the Earth [1, 2]. In 2005 KamLAND collaboration has published the first experimental results [3], showing that the technique for exploiting geo-neutrinos in the investigation of the Earth's interior is available. In 2010 Borexino collaboration claimed the first observation more than 3σ C.L. of geo-neutrinos [4].

A reference model for geo-neutrino production is a necessary starting point for interpretation of geo-neutrinos measurements. The most recent models [5, 6, 7] are based on Earth's crust divided into 2° × 2° horizontally homogeneous tiles: this is clearly a rough approximation for describing the region surrounding the detector. Considering Borexino, placed at the Gran Sasso National Laboratory (LNGS), about one half of the signal originates from an area surrounding the detector within a radius of 800 km [5]. The regional flux needs to be determined with an accuracy that is comparable to uncertainties from the contributions of the rest of the Earth. This highlights the need for a "Refined Reference Model" (RRM), which improves the accuracy of the reference model by adding more detailed information concerning the region where the detector is located.

The regional contribution to the geo-neutrino signal at LNGS was determined based on a detailed geological, geochemical and geophysical study of the region. U and Th abundances of the main lithotypes belonging to the Mesozoic and Cenozoic sedimentary cover were analyzed. Sedimentary rocks were grouped into four main "reservoirs" based on similar paleogeographic conditions and mineralogy, leading to comparable U and Th contents. Basement rocks do not outcrop in this area. Thus U and Th in the Upper and Lower Crust of Valsugana and Ivrea-Verbano areas were analyzed. Irrespective of magmatic or metamorphic origin lithotypes were subdivided into a mafic and an acid reservoir, with comparable U and Th abundances.

Based on geological and geophysical properties, relative abundances of the various reservoirs were calculated and used to obtain the weighted U and Th abundances for each of the three geological layers (Sedimentary Cover, Upper and Lower Crust). Using the available seismic profiles as well as the stratigraphic records from a number of exploration wells, a 3D model was developed over an area of 2° × 2°. This allowed to determine the volume of the various geological layers and eventually integrate the U and Th contents of the whole crust beneath LNGS.

On this base the local contribution to the geo-neutrino flux was calculated and added to the contribution given by the rest of the world [5], obtaining a RRM prediction for the geo-neutrino signal in the Borexino detector: S(U) = (28.7±3.9) TNU and S(Th) = (7.5±1.0) TNU. The resulting uncertainties from the regional area are comparable to those from the rest of the Earth.

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THE STEREO IMAGING CHANNEL OF SIMBIOSYS FOR THE BEPICOLOMBO ESA MISSION

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BepiColombo is the fifth Cornerstone mission of the European Space Agency (ESA) foreseen to be launched in August 2014 with the aim of studying in great detail Mercury, the innermost planet of the Solar System.

Mercury is very important from the point of view of testing and constraining the dynamical and compositional theories of planetary system formation. In fact, being in close proximity to the Sun, it has been subjected to the most extreme environmental conditions, such as high temperature and large diurnal variation, rotational state changes due to Sun induced tidal deformation, surface alteration during the cooling phase, and chemical surface composition modification by bombardment in early history. Mercury has been studied by the Mariner 10 spacecraft in 1974-75 [1], when less than half of the planetary surface has been imaged at low resolution (scale factor from few hundreds of meters to 1-2 km/px) and its magnetic field and exosphere have been discovered. Since then, the only other satellite reaching Mercury is the NASA MESSENGER, that has very recently realized three flybys with the planet; MESSENGER will be inserted in orbit around Mercury in March 2011.

The BepiColombo payload will consist of two modules: the Mercury Planet Orbiter (MPO), realized in Europe, carrying remote sensing and radio science experiments, and the Mercury Magnetospheric Orbiter (MMO), realized by JAXA in Japan, carrying field and particle science instrumentation. These two complementary packages will allow to map the entire surface of the planet, to study the geological evolution of the body and its inner structure, *i.e.* the main MPO tasks, and to study the magnetosphere and its relation with the surface, the exosphere and the interplanetary medium, *i.e.* MMO targets.

The imaging and spectroscopic capability of the MPO modulus will be exploited by the Spectrometers and Imagers for MPO BepiColombo Integrated Observatory SYStem (SIMBIOSYS), an integrated system for imaging and spectroscopic investigation of the Mercury surface [2]. SIMBIOSYS incorporates capabilities to perform 50-110 m spatial resolution global mapping in both stereo mode and color imaging, high spatial resolution imaging (5 m/px scale factor at periherm) in panchromatic and broad-band filters, and imaging spectroscopy in the 400-2200 nm spectral range. This global performance is reached using three channels: the STereoscopic imaging Channel, STC [3]; the High Resolution Imaging Channel, HRIC [4]; and the Visible and near-Infrared Hyperspectral Imager, VIHI.

STC main scientific objective is the global stereo mapping of the entire surface of Mercury that will permit the generation of a Digital Terrain Model (DTM) of Mercury's surface, improving the interpretation of morphological features at different scales and clarifying the stratigraphic relationships between different geological units.

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THE WIDE ANGLE CAMERA OF THE OSIRIS SYSTEM ONBOARD THE ROSETTA ESA MISSION

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Rosetta is one of the cornerstone missions of the European Space Agency (ESA) dedicated to the exploration of the periodic 67P/Churyumov-Gerasimenko comet. The main mission objective is to study the physical evolution of the nucleus of the comet and of its dust and gas environment from 3-4 AU to perihelion. The Rosetta spacecraft is experiencing a rather long interplanetary journey, about 10 years, with also one Mars and three Earth gravity assists, before reaching the comet in 2014. The spacecraft has also the chance to flyby two main belt asteroids: (2867) Steins in September 2008 and (21) Lutetia in July 2010.

The scientific payload of the mission consists of both remote and *in situ* instruments. One of the remote sensing instruments on board the satellite is OSIRIS, realized by a cooperation among several European institutes [1]. OSIRIS is a double camera comprising a narrow angle camera, NAC, and a wide angle camera, WAC. The NAC [2], having the higher spatial resolution, is able to study the comet nucleus surface properties in great detail; the WAC, thanks to its large field of view, is able to image the limb and the coma to study the evolution of weak coma structures near the bright nucleus, providing information on gas and dust outflow and jets directly above the comet nucleus surface [3].

The WAC camera adopts an all reflecting, unvignetted and unobstructed two mirrors configuration, which allows to cover a 12° × 12° Field of View with a F/5.6 aperture and a geometrical Ensquared Energy better than 80% inside approximately 20 arcsec. The WAC is equipped with 14 filters in the 230-720 nm wavelength range, they have been especially selected to study the gas and dust comet emissions.

The flight model of the WAC has been successfully integrated and tested in our laboratories and finally has been integrated on the Rosetta spacecraft.

The optimal performance of the camera has also been proved and exploited in-flight during the Mars swing-by (February 2007), Earth swing-bys in November 2007 and in November 2009, when impressive images of the red planet and of our Earth-Moon system have been successfully taken.

Many images had also been taken during the asteroids Steins flyby on the 5th of September 2008, enabling us to study the surface photometrical and structural properties, to date the asteroid starting from cratering history and also to derive a 3-dimensional model of the asteroid itself [4].

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GEOGRAPHIC VARIATIONS IN PETROGRAPHY AND COMPOSITION IN AUSTRALASIAN MICROTEKTITES: IMPLICATIONS FOR THEIR FORMATION AND PARENT CRATER LOCATION

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Mineral inclusions: We report the occurrence of microscopic inclusions of shocked quartz plus a Zr-phase and traces of Fe-oxide crystallites in Australasian microtektites recovered from deep-sea sediment cores within 2000 km of Indochina (see [1] for details). The shocked quartz and the Zr-phase are interpreted as relicts of the target. Furthermore, the petrographic heterogeneity of Australasian microtektites in terms of abundance of relict mineral inclusions, vesicles and schlieren decreases towards Indochina. This finding supports the current hypothesis that the source crater of the largest and youngest tektite strewn field on Earth is located in the Indochina region, as internal heterogeneity characterizes impact glass found in or near the source crater. The finding also indicates that the Australasian microtektites with the longest trajectories experienced the highest temperatures or were heated longer. Lastly, the definition of microtektites should include the possible occurrence of microscopic relict inclusions as an indication of proximity to the source crater.

Alkali loss: We studied the variations of the volatile major elements Na and K in Australasian microtektites with distance from the putative source crater location in Indochina (see [2] for details). The dataset includes 169 normal-type Australasian microtektites (101 from this study and 68 from the literature) from 24 deep-sea sediment cores up to 8000 km from Indochina, and 54 Transantarctic Mountain microtektites from northern Victoria Land, 11000 km due southeast of Indochina. Normal-type ($MgO < 5.5$ wt.% and $SiO_2 = 60\text{-}78$ wt.%) Transantarctic Mountain microtektites and Australasian microtektites share a common volatilization trend with Na and K contents and range in alkali contents decreasing with distance from Indochina. The average total alkali ($Na_2O + K_2O$) concentrations at distance ranges of 1000-2000 km, 2000-4000 km, 4000-8000 km and > 8000 km are 4.27±0.67 wt.% (n = 84), 3.20±1.21 wt.% (n = 50), 2.10±0.25 wt.% (n =35) and 1.25±0.25 wt.% (n = 54), respectively. The trend highlights a relationship between increasing loss of volatiles in microtektites with longer trajectories and higher temperature-time regimes which should be taken into account in microtektite formation modeling. The trend is consistent with a previous hypothesis that Transantarctic Mountain microtektites belong to the Australasian strewn field and that Indochina is the target region for the parent catastrophic impact. Possible and likely complementary volatilization mechanisms include the "bubble-stripping" model [3] and diffusive loss at high temperature during impact melting and hypervelocity flight.

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MINIMETEORITES FROM THE TRANSANTARCTIC MOUNTAINS

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Meteorites and micrometeorites are typically > 1 cm and < 1 mm in size, respectively, and are commonly believed to sample different parent bodies [1]. Here, we report the discovery of a large number of meteoritic particles with sizes ranging from 0.8 mm to 5 mm in the Transantarctic Mountain (TAM) micrometeorite traps [2]. We propose to name them minimeteorites. Minimeteorites will allow the study of the transition between micrometeorites and macroscopic meteorites for the first time, thereby bridging the gap between these two research fields, whose separation is most likely linked to the human eye *versus* microscope search scale, and has no proven fundamental reasons.

During the 2003 and 2006 Antarctic campaign of the Italian *Programma Nazionale delle Ricerche in Antartide* (PNRA) we discovered a large and virtually unbiased micrometeorite collection on the tops of the Victoria Land TAM [2]. Thousands of micrometeorites > 400 μm in diameter were found trapped within the fine-grained, local detritus accumulated within weathering pits and joints of glacially eroded granitic summits with exposure ages older than 2 Myrs [2]. These traps have been collecting micrometeorites over the last ~ 1 Myr, as testified by the ~ 0.8 Myr-old Australasian microtektites found therein [3]. The finding of unusual micrometeorites up to 2 mm in size prompted a more-thorough search for these "giant micrometeorites" during the 2009 PNRA expedition on the top of Miller Butte (72°42' S, 160°14' E). Extraction of extraterrestrial particles from about half a ton of detritus sieved in the 0.4-5 mm size fraction were carried out *in situ* using a portable magnetic separator. 320 fully melted minimeteorites in the 0.8 to 3.2 mm size range were identified with certainty. The exponent of the linear fit of the cumulative size distribution in a log-log diagram is -5.3, as observed in unbiased micrometeorite collections [4]. Several tens of unmelted (similar to meteorites) to partially melted particles up to 5 mm size were also extracted, although further laboratory work is required to confirm the extraterrestrial nature of some. The ratio of unmelted versus melted micrometeorites increases with increasing size, as theoretically expected for the micrometeorite to meteorite transition. Note that the number of minimeteorites from the TAM collection is two orders of magnitude larger than that previously found in other Antarctic collections (for instance, only 3 spherules > 0.8 mm in diameter are reported for the South Pole Water Well Collection [4]). A full week of dedicated field work could lead to gain another order of magnitude.

Our finding confirms that the TAM micrometeorite traps are an extraordinary source of new and valuable material for planetary scientists, like the meteorite traps found on the Antarctic ice sheet [5]. In particular, the discovery of minimeteorites is of great interest since it will allow multiple high-precision analyses (*e.g.*, oxygen isotope and cosmogenic nuclide analyses) of individual micrometeorites for the obtainment of a statistically representative information on their parent bodies for the first time.

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THE CRYSTAL CHEMISTRY OF CHROMITES FROM THE H6 KERNOUVÈ CHONDRITE AND DETRITAL L-CHONDRITES FROM SWEDEN

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Chromite is a minor but regular constituent of ordinary chondrites and its chemistry in meteorites has been studied since the 60s. Besides the main components FeO and Cr_2O_3, it contains minor amounts of MgO and Al_2O_3. It has been noticed that Fe and Mg content of chromites is related to that of the olivines in the H, L and LL groups of equilibrated chondrites.

The here studied chromites are from the Kernouvè H6 chondrite and from ~ 470 Ma old fossil micrometeorites, found in Ordovician limestone at Kinnekulle in Sweden and derived from the disruption of the L-chondrite parent body [1].

Despite the fact that their chemistry has been studied since about 40 years, to our knowledge no single crystal diffraction studies have been performed on extraterrestrial chromites. The cell edge in H6 chondrite ranges from 8.3480 (2) to 8.3501 (1) Å, while in L-chondrite it varies from 8.3347 (3) to 8.3463 (3). The oxygen positional parameter is comprised between 0.2627 (2) and 0.26291 (7) in H6 and between 0.2625 (1) and 0.26267 (9) in L. These values show that there are some little differences between the two chondritic typologies. By comparison with the structural parameters of chromites from terrestrial occurrences they are similar to those of chromites from komatiites and kimberlites [2, 3], and chromites included in diamonds [3].

Chemistry of the analysed chromites points out to a nearly pure end-member compositions with limited Al ↔ Cr (Al < 0.26 apfu) and Mg ↔ Fe^{2+} (Mg ≤ 0.15 apfu) substitutions. Fe^{3+} seems to be considered as nearly absent in all the analysed spinels. Limited amount of Fe^{3+} have to be considered, according to stoichiometry, only for some point analyses in H6 chromites, while all of the analysed detrital chromites have to been considered as non-stoichiometric, a common feature in meteoritic minerals. Minor elements are Ti (0.06-0.09 apfu) and V (about 0.020 apfu). Zinc is about 0.01 apfu. Among the detrital chromites at Kinnekulle, [4] found two different occurrences that, according to their TiO_2 content, have been assigned to L and LL chondrite (TiO_2 about 3 wt.%) or H chondrite (TiO_2 between 1.4-2.4 wt.%), respectively. All the Kinnekulle chromites here analysed have been assigned to L chondrite (TiO_2 in the range 2.9-3.3 wt.%).

Because meteoritic material on the Earth surface is rapidly altered or weathered away with the exception of chromite, different methodologies have been recently developed to recognise the extraterrestrial detrital chromitic material [4, 5]. This work demonstrates that a structural study can, as well, identify extraterrestrial from terrestrial material and also that structural parameter differentiate H and L chondritic chromites.

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FIRST REPORT OF Cr AND Ti SULFIDES IN E3 CHONDRULE MESOSTASIS BY TEM INVESTIGATIONS

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Enstatite chondrites are an enigmatic group of chondrites that formed under highly reducing conditions. Despite their high temperature origins, chondrules in enstatite chondrites contain mesostases that are often rich in volatile elements such as Na and Cl. To understand the origin of these volatile enrichment in enstatite chondrites, we have studied the mesostases of chondrules in two unequilibrated enstatite chondrites, SAH97072 (EH3), and EET90299 (EL3) using EMPA and TEM techniques [1, 2]. Both of these meteorites contain chondrules with heterogeneous mesostasis compositions, particularly with respect to Na and Cl.

TEM and STEM imaging of FIB-prepared samples show that that the chondrule mesostasis contains a surprisingly high abundance of submicron crystallites. The dominant crystalline phases are readily observable by dark field STEM and consist of euhedral to rounded Cr-Ti and Ti-Cr sulfides (Fig. 1) with grain sizes ranging from ~ 0.2 µm down to a few tens of nanometers. These crystals occur embedded within a Na-rich aluminosilicate glass and appear to be quench crystallites that grew during rapid cooling of the chondrules.

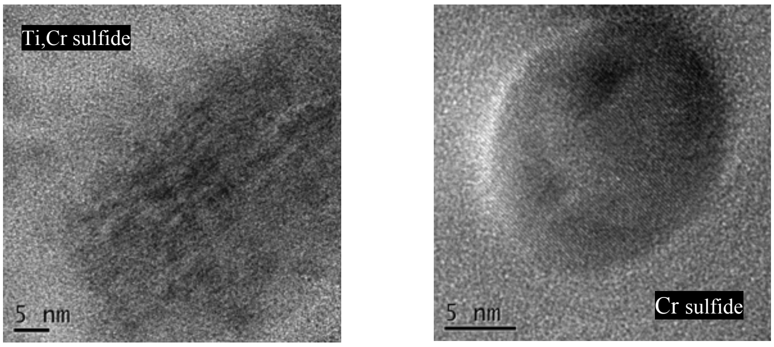

Fig. 1 (a, b).

Cr-rich sulfides have been reported previously in chondrules in enstatite chondrites [3, 4] and in SAH97159 (paired with SAH97072) [5]. Bendersky *et al.* [6] found Cr enrichments around olivine grain boundaries of ECs chondrules and interpreted them as result of Cr remobilization from olivine to sulfides and metals due to thermal metamorphic processes affecting enstatite chondrites. Due to the small size of the grains it was difficult to determine the Cr sulfide phase in the course of this work. Brezinaite (Cr_3S_4) is the only Cr-sulfide mineral identified by Bunch & Fuchs [7] in the Tucson iron meteorite and Petaev [8] in the Gibeon iron meteorite, so, the Cr-sulfide found in this work could be either brezinaite or a new mineral. Further investigations are in course to assess the mineralogical phase to these sulfides and to determine the relationships with the mesostasis.

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LOW-HIGH TEMPERATURE BEHAVIOUR OF OLIVINE: IMPLICATION FOR MERCURY SURFACE

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Under variable temperature conditions minerals may significantly change their crystal structure (*e.g.* change of the atomic positions) and consequently their spectral signatures. This could limit our capability of inferring compositions and rheological properties of geological materials from remote sensing acquisition of extraterrestrial surfaces. When (a) the temperature conditions are not well constrained, and (b) the properties of the material as a function of temperature are not characterized there is actually a high probability of misinterpreting the acquired data. In particular, MESSENGER (NASA) and Bepi-Colombo (ESA) missions will record spectral images of the Mercury surface, which experiences extreme temperature variations ($85 < T < 700$ K) due to its long rotational period, small heliocentric distance and eccentric orbit. Within such a wide range of temperatures the minerals constituting the surface of Mercury could undergo marked structural changes due to processes which are totally reversible (thermal expansion effects, polymorphic phase transformations) but would strongly affect the resulting spectral signatures. This could make the spectral interpretation very complex and could potentially lead to erroneous geological interpretations. In this work we investigated the low-high temperature evolution of the crystal structure of a natural olivine (solid solution between forsterite Mg_2SiO_4 and fayalite Fe_2SiO_4 end-members) extracted from a meteorite. Olivine is in fact one of the hypothesized constituents of Mercury crust. In order to determine its thermal expansion and possible phase transformations X-ray diffraction data will be collected on olivine between 80 and 700 K, the temperature range of the Mercury surface. This work wants to be the starting point in understanding which kind of change we could expect in the spectral signatures.

HISTORY OF THE VIGARANO METEORITE (EMILIA-ROMAGNA, ITALIA) AND RECOVERY OF AN IMPORTANT PART OF THE MAIN MASS

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The Vigarano meteorite fell to Earth on the 22nd of January 1910 at approximately 9:30 PM, near Vigarano Pieve, about 9 km W-NW of Ferrara (Emilia-Romagna region, Northern Italy). The main mass weighed 11.5 kg and was found immediately (Fig. 1), whilst a second part of 4.5 kg was recovered weeks later, a few hundred metres from the main mass [1, 2].

The Vigarano meteorite has been classified as a type 3 carbonaceous chondrite (CV3.3) with shock stage S1-S2.

Until recently, only 4 to 5 kg of the original mass were preserved in different museums around the world.

The rediscovery of 7 kg of material belonging to the Cariani mass increased the total known mass of the Vigarano meteorite to 12 kg.

From 1910 to the present day the Cariani mass have not been preserved in suitable conditions. These storage conditions led to the disintegration of the mass into small sharp fragments weighing only a few grams (Fig. 2).

Fig. 1. The Cariani mass (11.5 kg) just after impact in a postal card issued in 1911.

Fig. 2. What the main mass of the Vigarano looks like today.

The Natural History Museum of Ferrara is now in charge of 1425 g of the main Vigarano mass ("Cariani mass"), which are kept in low pressure and low humidity conditions in order to stop or at least slow down the disintegrating process.

From this collection, a 4.3 g sample was given to the Earth Sciences Department of the University of Ferrara for preliminary analyses [3, 4].

The discovery of approximately 7 kg of the Vigarano meteorite's main mass ("Cariani mass") and an extensive documental research allowed:

- a substantial development of the history of this important carbonaceous chondrite;
- the exact location of the impact site to be identified;
- the identification of fake pieces of the meteorite;
- the locations of the Vigarano samples in the world to be updated.

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SESSION 1.2

The deep Earth through experiments and theoretical models

Convenors:

P. Fumagalli (*Univ. of Milano*)
M. Merli (*Univ. of Palermo*)
M. Merlini (*Univ. of Milano*)

ELASTIC BEHAVIOUR OF ZOISITES AND THEIR GEOLOGICAL IMPLICATIONS

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The relationships between arc volcanism-earthquakes and subduction zones have been systematically observed and investigated around the globe ([1], and references therein).

Several authors [1, 2, 3] have argued that the correct model for explaining the generation of many volcanic arc and intermediate earthquakes in the subduction zones involves the progressive dehydration of the subducting slab through a series of reactions that release H_2O into the mantle wedge. These fluids released from subducting slabs could trigger hydration-driven partial melting reactions, inducing partial melting of the mantle wedge above the slab, which in turn is considered responsible for the intermediate earthquakes [2, 3], as well as for arc volcanism [1] in the subduction zones. A key role in these dehydration reactions is played by the hydrous mineral phases that are mainly contained on the subducting slab. Therefore a detailed study of the properties of the hydrous phases, and especially the thermo-elastic behaviour, will be an important requirement for understanding mantle properties and processes within the subduction zones, in particular for constraining their stability and the position of the related dehydration reactions in which they are involved as a function of pressure and temperature [4, 5].

In order to evaluate the effect of these dehydration reactions at the structural scale, we focused our work on a natural zoisite sample (Fe-free end member), from Merelani Hills in the Arusha Region, United Republic of Tanzania. It is a hydrous mineral containing 2 wt.% of water, which belongs to epidote group of minerals, with ideal formula $Ca_2Al_2Si_3O_{12}OH$. Zoisite occurs in high and ultrahigh-pressure metamorphic rocks from a wide variety of geological settings, including continental collisions and subduction zones [4, 5, 6]. Minerals of the epidotes group are part of numerous phase equilibria, which need to be accurately evaluated in order to understand several geological processes. Many authors have investigated minerals of the epidotes group at high pressures with different techniques obtaining different results [5, 7]. In order to clarify the discrepancies we investigated the sample at high-pressure (up to 6.5 GPa) by means of single crystal X-ray diffraction, We determined the unit-cell parameters in order to calculate the Equation of State and measured intensity data to follow the evolution of the structure with pressure.

Preliminary results using a Birch-Murnhagan EoS yield a Bulk modulus (K_{T0}) of 122(1) GPa with a $K' = 6.9(4)$ and $V_0 = 903.43(7)$ Å^3, not in very good agreement with data by [7] on a Fe-rich sample (0.1 apfu), probably because of their limited pressure range, but in very good agreement with the more recent Brillouin data [5] on a Fe-free sample. As shown by the *Ff* plot and confirmed by the evolution of some geometrical parameters there is a change in the structural evolution at about 2 GPa. In order to fully understand the cause of this change, which probably involves the OH group, further data collection and analysis is under way and new spectroscopic measurements will be required.

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HIGH-PRESSURE BEHAVIOUR OF $YCrO_3$ PEROVSKITE

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Perovskites, ternary compounds with general formula $^{[XII]}A^{[VI]}BO_3$, are of great interest in both Earth sciences because, at the high pressure and temperature conditions of the Earth's lower mantle, the pyroxene enstatite, $MgSiO_3$, transforms into a denser perovskite-structured polymorph [1], and technological applications due to their peculiar electric, magnetic, piezoelectric and optical properties. In particular, $YCrO_3$, a $GdFeO_3$-type perovskite, has become an attracting material due to its multifunctional biferroic behaviour [2], and to its recent use as interconnection for the SOFC's [3]. Contrasting to what expected by its lattice flexibility, a recent work revealed that the $YAlO_3$-$YCrO_3$ system exhibits the lowest structural relaxation, if compared with other structures hosting Cr^{3+} in octahedral coordination [4]. Possible explanations involved the role of covalency in Cr-O bonds or the different elastic properties of the two end-members. In the last two decades, many studies have been devoted to assess the high pressure behaviour of orthorhombic perovskites, but no data are reported for $YCrO_3$.

For these reasons, we determined the elastic properties of the orthochromate perovskite (space group *Pbnm*) using synchrotron powder diffraction, up to 60 GPa, comparing our results with the high pressure behavior of orthoaluminate trying to understand the low relaxation around Cr^{3+} in the $YAlO_3$-$YCrO_3$ perovskite system.

Each data fitting were obtained by using a third-order Birch-Murnagham equation of state. The P-V data gave a V_0 = 218.23(4) Å^3, and a bulk modulus K_{T0} = 208.4(5) GPa, with a K'_0 = 3.7(1). The elastic moduli of the individual crystallographic axes showed that the *b*-axis is appreciably less compressible than both *a*- and *c*-axis (K_{a0} = 195(5) GPa, K_{b0} = 223(7) GPa, and K_{c0} = 200(6) GPa, respectively), implying a distortion increasing with pressure. The polyhedral bulk moduli for YO_{12} and CrO_6 polyhedra led to: $V_{0,poly}$, K_{p0}: 46.09(2) Å^3, 254(2) GPa for YO_{12}, and 10.40(1) Å^3, 251(5) GPa for CrO_6. The volume compressibilities of the YO_{12} and CrO_6 sites are therefore equivalent.

Those results are different to those previously reported for the orthorhombic $YAlO_3$ perovskite in which the *b*-axis is significantly more compressible than both *c* and *a* [5]. Considering the elastic moduli of both $YCrO_3$ and $YAlO_3$, the two structures under pressure show a different anisotropic behaviour along [101] and [010]. Furthermore, for the $YAlO_3$ perovskite the compressibility of the A site is ~ 15% less than that of the AlO_6 octahedron. Such contrasting trends can be explained by the stronger confinement of Y ions in $YAlO_3$ due to the smaller size of octahedral network in the orthoaluminate compared to the orthochromate.

As known from previous work [4], the decrease of mean octahedral bond distance, <B–O>, from $YCrO_3$ to $YAlO_3$ is accompanied by shortening of the average <A–O> distance and decreasing of interpolyhedral tilting. The associated strong confinement of Y cation in $YAlO_3$ does not occur in $YCrO_3$. Here the A site is easier to compress and does not hamper the enhance of octahedral tilting and rotation expected at high pressure conditions.

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AB INITIO QUANTUM-MECHANICAL CALCULATION OF THERMODYNAMICAL PROPERTIES OF MAGNESIUM PEROVSKITE AND POST-PEROVSKITE AT EXTREME CONDITIONS OF TEMPERATURE AND PRESSURE

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Magnesium perovskite ($MgSiO_3$) is supposed to be the most abundant mineral in the lower mantle of Earth, thus contributing mainly into seismic, rheologic and other geophysical properties of this layer. It is stable within a wide range of pressures and temperatures and till recent time it was believed to preserve its structure at the extreme conditions of the Earth's lower mantle shell. However, the recently discovered new post-perovskite phase of $MgSiO_3$, which is stable about the thermodynamic regime of the seismic discontinuity at the Earth D" layer, was rapidly taken into consideration within consistent models accounting for the anomalies met at the indicated shell.

Only recently, the experimental means to reach the extreme conditions of the Earth's mantle became accessible, but unfortunately the results are still subjected to considerable inaccuracy due to technical constraints. Therewith, theoretical *ab initio* simulations provide for reliable data on the subject of interest.

In our work we present results on *ab initio* quantum-mechanical simulations of magnesium perovskite and post-perovskite phases performed by using the so called B3LYP Hamiltonian, which is widely acknowledged for providing reliable and accurate structural and elastic data for minerals, in comparison to other available DFT and Hybrid HF/DFT approaches. The calculations are elaborated with the CRYSTAL06 [1] software package, through the evaluation of the vibrational modes' frequencies for crystallographic unit cells and super cells of the modelled structures. This makes it possible the prediction of the thermal dependence of the structural and elastic properties, and to connect the results of the simulations to thermodynamic quantities in the frame of quasi-harmonic approach.

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EVALUATION OF OVERPRESSURE INSIDE THE EARTH CAUSED BY PHASE TRANSITIONS

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For research of the dynamic processes at great depths it is necessary to start with that physical state in which exists a substance of the Earth. The substance of the mantle of the Earth is in a solid state, however as a result of changing of thermodynamic conditions it can transform from one solid state in another, changing the physical properties (phase transitions of the first sort). These transitions invoces the internal strains, which show a cause of the geodynamic phenomena. As a result, the volume phase transition, and hence the matter density changes abruptly, so it is clear that for the mathematical modeling of phase transitions is necessary to consider this matter as the thermoelastic material with nonclassical properties. In this paper two cases of phase transitions that occur in the mantle are considered: a partial melting in the asthenosphere, and the discontinuity of physical properties at depths of 400 and 600 km.

1. Fluctuations of strains in stochastic inhomogeneous partially melted astenosphere. The substance of the mantle is considered as a random inhomogeneous thermoelastic media, for which the law of Duhamel-Neuman is true: $\sigma(r) = C(r)\varepsilon(r) - \beta(r)\theta$. Here θ is a temperature changing. At even heating and at absence of external stresses average strain will be equal in such medium to zero. However fluctuation of strain is not equal to zero due to different coefficients of expansion of the solid phase and partial melt [1]. These fluctuations will be equal to $\langle\sigma^2\rangle = M_\beta\theta^2$, where M_β is the factor depending on a difference of thermoelastic parameters in solid and liquid phases. Estimations show that these pressures are comparable with hydrostatic pressure upon considered depth and consequently they can cause volcanic activity.

2. The strains invoked by transition solid - solid. Earth seen as spherical thermoelastic body with uneven heating and density, which has a discontinuity at some temperature T_f. Temperature distribution with depth is known, in the mantle is increased quasi linearly. So, if $T < T_f$ it is $\rho = \rho_1$, and if $T > T_f$ it is $\rho = \rho_2$, that is there exists a border, depended on temperature. In this system temperature increases by only a few degrees leads to the material with a phase of greater density will be striving to move into a phase with less density, increasing its volume. But that inside the Earth is no place to increase the volume, the shapes will occur a material breach of crystal structure, *i.e.* dislocations, which leads to internal strains. To describe this state should be using equations of incompatibility $Rot\varepsilon = -\eta$. Here η is the incompatible tensor, this tensor depends on the dislocation density. Thus, knowing the dislocation density, we can determine the internal strains, that arise. This situation occurs at depths of 400 and 600 km. Internal tensions that arise at these depths may be causing the Earth's tectonic activity.

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THE HIGH-PRESSURE STABILITY OF CHLORITE AND A NEW HYDROUS SILICATE IN THE SYSTEM $MgO-(Al,Cr)_2O_3-SiO_2-H_2O$

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The chemical system $MgO-Al_2O_3-SiO_2-H_2O$ (MASH) is well known to be a simplified model composition space for the study of water transport and recycling into the Earth's mantle *via* subduction processes. In order to understand the influence of chromium on phase relationships, we experimentally investigated the stability of chlorite, assuming that Cr is substituting for Al in the octahedral site. Three different bulk compositions A, B and C with Cr/(Cr+Al) = 0.15, 0.5 and 1.0 have been considered. Gels have been used as starting materials and run between 1.5-6.5 GPa, 650-900°C in piston cylinder and multi anvil apparatus. All experiments were fluid saturated. All run products have been inspected by SE/BSE images and were analyzed by EMPA.

Cr-chlorite was found only in bulk A. It coexists with enstatite up to 3.5 GPa, 800°C; at 5.0 GPa, 750°C it coexists with forsterite, pyrope and spinel. At 900°C, 3.5 GPa, the anhydrous phase assemblage pyrope, forsterite and spinel has been found. At 6.0 GPa, 650°C Mg-sursassite was observed. Bulk B and C show a chromite, enstatite and forsterite phase assemblage; no pyrope was detected up to 6.5 GPa, 700°C. Chromium strongly partitions into spinel ($X_{Cr} = 0.8806$), followed by orthopyroxene ($X_{Cr} = 0.1428$), Cr-chlorite ($X_{Cr} = 0.0815$) and garnet ($X_{Cr} = 0.0339$). Cr affects the stability of chlorite by shifting its breakdown reactions towards higher T and P, but Cr solubility at high P results to be reduced as compared with low P occurrence in hydrothermal environments.

A new hydrous phase have been discovered in the P,T range of 5.2-5.5 GPa and 680-720°C and it has been reproduced in the pure MASH model system. It is monoclinic with space group *C*2/*c* and unit cell parameters $a = 9.882(1)$, $b = 11.623(1)$, $c = 5.081(1)$ Å, $\beta = 11.1(1)°$. This new phase has been identified with conventional electron diffraction. Its structure has been solved using the automated electron diffraction technique [1], a new technique that allows a single crystal electron diffraction experiment on crystals of less than 1 mm, obtaining *quasi* kinematical intensities suitable for a conventional direct methods structure solution attempt. It has chemical composition of $Mg_{2.1}Al_{1.8}Si_{1.1}O_6(OH)_2$, and has a pyroxene like structure with 3 cations instead of 2 in the octahedral layer, which force the tetrahedral chains to be more separate. The two anion sites of the extra octahedral cation, that are not shared with tetrahedra, are occupied by an hydroxyl. A Rietveld refinement on the data taken on this sample, and image simulation of high resolution electron microscopy images further confirm this structural model.

The coexistence of this new phase with forsterite and pyrope beyond the chlorite stability field largely expands the depth of hydrated assemblages in subducted oceanic lithosphere and further promotes H_2O recycling in the mantle.

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SUBSOLIDUS PHASE RELATIONS IN THE CARBONATE TERNARY $CaCO_3$-$MgCO_3$-$FeCO_3$ AT PRESSURES TO 6 GPA: AN EXPERIMENTAL STUDY AND THERMODYNAMIC MODELING INCLUDING ORDER/DISORDER

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Subduction carries atmospheric and crustal carbon hosted in the altered oceanic crystalline basement and in pelagic sediments back into the mantle. Reactions involving complex carbonate solid solutions(s) will lead to the transfer of carbon into the mantle, where it may be stored as graphite/diamond, in fluids or melts, or in carbonates. To constrain the thermodynamics and thus reactions of the ternary Ca-Mg-Fe carbonate solid solution, piston cylinder experiments have been performed in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ at pressure of 3.5 GPa and temperatures of 900-1100°C. At 900°C the system has two miscibility gaps: the *solvus* dolomite-calcite, which closes at $X_{MgCO3} \sim 0.7$, and the *solvus* dolomite-magnesite, which ranges from the Mg- to the Fe-side of the ternary. With increasing temperature, the two miscibility gaps become narrower until complete solid solutions between $CaCO_3$-$Ca_{0.5}Mg_{0.5}CO_3$ is reached at 1100°C and between $CaCO_3$-$FeCO_3$ at 1000°C. The *solvi* are characterized by strong compositional asymmetry and by an order-disorder mechanism, quantified by the long range order parameter.

Temperature and composition dependence of the long range order parameter in Fe-bearing dolomite have been investigated with *in situ* techniques, in order to avoid quench effects. Powder XRD synchrotron experiments were performed at the high-pressure and temperature, at the beamline ID27 of the European Synchrotron Radiation Facility. The order parameter is independent to the pressure in the range of P investigated, between 2.5 and 4.2 GPa, and it decreases with the increasing of temperature and X_{Fe} in dolomite. The disorder process has been modeled fitting our experimental data with a phenomenological approach intermediate between the Landau theory and the Bragg-Williams model, estimating the complete disordering of dolomite at 1246 K. Our model excludes also the stability of ordered ankerite at geological conditions, confirming natural and experimental evidences. This study provides also additional information to the understanding of the disputed breakdown reactions of dolomite into aragonite + magnesite at high pressure. Our results suggest the stability of the assemblage aragonite + magnesite at low pressure and at very low temperature, contradicting the curvature and the flattening of the reaction boundary at 5-6 GPa [1].

Gathering together all the experimental data, a solid solution model based on the van Laar macroscopic formalism has been calculated for ternary carbonates. This thermodynamic solid solution model is able to reproduce the experimentally constrained phase relations in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ in a broad P-T range and to predict the disordering temperature of dolomite in accordance with the results of *in situ* experiments.

To test our model, calculated phase equilibria have been compared with experiments performed in carbonated mafic protolithes, demonstrating the reliability of our solid solution model at pressures up to 6 GPa in complex systems.

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BEHAVIOUR OF TRIGONAL KALSILITE AT HIGH PRESSURE AND LOW TEMPERATURE

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Kalsilite (ideal formula $KAlSiO_4$) is an open-framework silicate belonging to the "feldspathoid group". It occurs mainly in K-rich and silica under-saturated volcanic rocks and is usually associated with olivine, melilite, clinopyroxene, phlogopite, nepheline, and leucite. Kalsilite also occurs in metamorphic rocks. The tetrahedral framework of kalsilite is isotypic (or homeotypic) with tridymite and has topological symmetry $P6_3/mmc$, whereas the topochemical symmetry of kalsilite is $P6_3mc$ as a result of Al/Si ordering within the tetrahedra. The tetrahedral framework consists of (0001) sheets of (ordered) AlO_4 and SiO_4 tetrahedra forming six-membered rings (hereafter 6mR), pointing alternately up and down [*i.e.* 6mR // (0001): UDUDUD]. The sheets are stacked along the *c*-axis and joined through the apical O1 atoms, which formally occupy special positions on the 3-fold axis. In the structural model described in space group $P31c$, the bridging oxygen between the sheets lies on the triad axis, giving an unusual Si-O-Al angle of 180°. The K-site lies in the 6mR-channel running along [0001], with a coordination shell of nine framework oxygens, with three independent groups of bond-distances [with $\Delta(\text{K-O})_{\text{max}} = 0.04$ Å at room-conditions].

The thermo-elastic behaviour and the structural evolution of a natural metamorphic kalsilite from the Punalur district in Kerala (southern India), with $P31c$ symmetry and a K/Na molar ratio of ~ 350, were investigated by *in situ* single-crystal X-ray diffraction up to 7 GPa and down to 100 K. At low temperature, the variations of the unit-cell parameters are continuous, and show no evidence of any phase transitions in this temperature range. An expansion is observed along [0001] with decreasing temperature. The axial and volume thermal expansion coefficients between 298 and 100 K, calculated by weighted linear regression through the data points, are $\alpha(a) = \alpha(b) = 1.30(6)\cdot10^{-5}$, $\alpha(c) = -1.5(1)\cdot10^{-5}$, $\alpha(V) = 1.1(2)\cdot10^{-5}$ K^{-1}. The main structural change on decreasing temperature is a cooperative anti-rotation of tetrahedra forming the 6-membered rings lying parallel to (0001). This tetrahedral rotation is coupled with a change in the distances between the extra-framework cations and the framework oxygens. A small decrease in the tetrahedra tilts perpendicular to [0001] is responsible for the negative thermal expansion along [0001].

At high-pressure, an iso-symmetric first-order phase-transition is observed at about 3.5 GPa. The elastic behaviour of both the polymorphs was described with a 3rd-order Birch-Murnaghan Equations-of-State with: $V_0 = 201.17(1)$ Å^3, $K_{T0} = 59.7(5)$ GPa, $K' = 3.5(3)$ for the low-P polymorph, and $V_0 = 200.1(13)$ Å^3, $K_{T0} = 44(8)$ GPa, $K' = 6.4(20)$ for the high-P polymorph. The pressure-induced structural evolution in kalsilite up to 7 GPa appears to be completely reversible. In the high-P polymorph, the K-polyhedron is significantly more distorted than that observed in the low-P polymorph [$\Delta(\text{K-O})_{\text{max}} = 0.39$ Å at 4.6 GPa].

EQUATION OF STATE AND STRUCTURAL EVOLUTION OF A NATURAL ORDERED OMPHACITE

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Omphacite is a clinopyroxene with chemical composition intermediate within the diopside - jadeite solid solution. Its nominal composition corresponds to the 50:50 term (*i.e.* $(Ca_{0.5}Na_{0.5})(Mg_{0.5}Al_{0.5})Si_2O_6$). An ordered omphacite has a $P2/n$ space group and its structural setting includes two tetrahedral sites (T1 and T2) which accommodate Si, two octahedral sites (M1 and M11) that host Mg and Al, and two eight-fold coordinated sites (M2 and M21) over which Ca and Na distribute. Omphacite is one of the main mineralogical species in high pressure rocks as eclogites and thus plays an important role in petrological processes taking place at deep environments. The elastic behaviour of $(Ca_{0.5}Na_{0.5})(Mg_{0.5}Al_{0.5})Si_2O_6$ omphacite has been investigated so far only for an ordered sample [1] using synchrotron X-ray powder diffraction method. In such study the authors used a Birch-Murnaghan equation of state to fit the pressure volume data obtaining the following coefficients: K_0 = 117(3) and K'_0 = 6.0(6). Concerning the structure evolution of omphacite as a function of pressure no data are so far available.

In this work we have determined the pressure volume equation of state and performed a high-pressure structural study on a natural omphacite sample (from the Münchberg Mass eclogites, Germany, [2]) with composition $(Ca_{0.49}Na_{0.51})(Al_{0.54}Mg_{0.39}Fe^{2+}_{0.07})Si_2O_6$. The sample was characterized at room-P by means of single-crystal X-ray diffraction in order to determine the order degree of Al/Mg and Ca/Na in the M1/M11 and M2/M21 sites. We obtained the following order parameters Q_{M1} = 0.900 and Q_{M2} = 0.440, in agreement with [2], indicating a strong ordering. The evolution with P at room temperature was investigated using a diamond anvil cell (the lattice parameters were measured at 13 different pressures for EoS determination and 5 complete intensity data collections for structural refinement) up to *ca*. 7.5 GPa. Fitting the pressure volume data by a third-order Birch-Murnaghan EoS and refining simultaneously V_0, K_0 and its first pressure derivative K' we obtained the following coefficients: V_0 = 421.42(4) Å^3, K_0 = 122(1) GPa and K'=5.1(3).

The structural evolution with P shows that the volumes of M1 and M11 polyhedra decrease by 5.1 and 5.5% respectively, and those of M2 and M21 decrease by 6.7 and 7.0%, respectively. The tetrahedral volumes, as expected for clinopyroxenes, do not show significant variations throughout the pressure range investigated. The single chain of tetrahedra shrinks with pressure, as expressed by the variation of the kinking angle (O32-O31-O32), which changes from 168.52 to 166.09°. The two tetrahedral become less tilted with P, with a reduction of their tilt angles from 4.14 to 3.14° and from 2.37 to 1.30°, for T1 and T2, respectively.

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AB INITIO COMPUTATIONAL METHODS FOR THE PREDICTION OF STABILITY, STRUCTURE AND PROPERTIES OF MINERALS AT HIGH PRESSURE AND HIGH TEMPERATURE CONDITIONS

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In the last decade, the reliability of *ab initio* computational methods for the prediction of structure and properties of minerals, and for their interpretation on a sound physical basis, from *first principles*, has definitely been proven. Indeed, the quantum-mechanical approach has been applied to predict structure, its evolution with pressure, and the equation of state of a very large number of rock forming minerals having ideal composition, at the *static limit* ($T = 0$ K, together with the neglection of *zero point effects*). Results were generally in close agreement with low temperature experimental data, especially if hybrid HF/DFT Hamiltonians containing an *exact*, *non local* Hartree-Fock contribution to the electronic exchange were employed [1, 2, 3].

Recently, the availability of powerful computational resources at a relatively low cost, allowed for the calculation of vibrational frequencies and their dependence upon the pressure (mode-γ Grüneisen's parameters). Such results can be directly compared with those from experimental infrared and Raman spectra, at room pressure, as an aid to the correct assignment of the relevant spectroscopic signals [4, 5], but most importantly, through a statistical-mechanical approach within the limit of the *quasi-harmonic* approximation, they can be used for the prediction of the thermal dependence of the structure and of the elastic properties of minerals [6, 7, 8].

The key role played by such computational techniques is particularly evident in the cases of very high pressure and temperature conditions, which are those typical of the Earth's lower mantle, where the experimental measurements are of difficult execution, and thermo-elastic data are generally affected by large uncertainties. The computed elastic properties of the mineral phases, which are supposed to exist in the lower mantle, can confidently be used for the validation of Earth's lower mantle models, derived from different grounds.

A discussion of the key points to be considered when performing a quantum-mechanical calculation, or simply judging results from literature, will be presented.

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CARBON AND CARBONATES IN THE EARTH'S MANTLE AND IMPLICATIONS FOR REDOX MELTING BENEATH MID-OCEAN RIDGES

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The mantle is the largest identified reservoir for carbon on Earth but the residence time of carbon in the mantle and its flux out of the mantle will depend crucially on the conditions under which it is stable within melts (carbonatites and kimberlites) or fluids, compared with conditions under which it forms solid phases, such as graphite or diamond, that linger in the convective mantle. It is possible that small degree carbonate-rich melts are the first liquids produced during adiabatic mantle up-welling beneath mid-ocean ridges [1]. Several lines of geophysical evidence support the presence of melts at depths between 150 and 300 km beneath ridges based on seismic anisotropy and electrical conductivity measurements near ridge axes [2].

The strong partitioning of incompatible trace elements into these small degree melts may scavenge trace elements from deeper, and therefore larger, portions of the mantle than are affected by the main phase of basalt-genesis and this may influence the trace element signature in erupted MORB. Numerous studies have been performed to understand decarbonation and the on-set of melting in CO_2-bearing mantle systems but very little attention has been paid to the stability of carbonate minerals and melts with respect to diamond and graphite as function of the oxygen fugacity.

In this study, the oxygen fugacity buffered by equilibria involving both elemental carbon (graphite or diamond) and carbonate (minerals or melts) were determined in a simplified Fe-Ca-Mg-Si-O-C model peridotite composition at pressures between 2.5 and 11 GPa and temperatures at and above the carbonated peridotite solidus (1100-1600°C). Oxygen fugacities were experimentally measured using iridium-iron alloy as a sliding redox sensor. Above the carbonate peridotite solidus the silicate component of the melt increases with increasing temperature. The results show that this dilution of the carbonate melt with increasing temperature drives the equilibrium oxygen fugacity down compared to the extrapolation of carbon/carbonate equilibrium from previous studies [3]. In addition, experiments have been performed in the Fe-Ca-Mg-Al-Si-O-C system to determine the ferric iron content of garnets at an oxygen fugacity buffered by the carbon-carbonate equilibria in a peridotite assemblage. The ferric iron contents of the garnet in the run products were determined by ^{57}Moessbauer spectroscopy.

The results from these experiments allow the redox conditions of carbon and carbonate stability to be compared directly to the expected Fe^{3+}/Fe_{tot} ratios along the decompression path in convective mantle.

Futher, our results imply that in up-welling mantle beneath mid-ocean ridges, the relative oxygen fugacity of peridotitic rocks will increase on decompression. Diamond and then graphite are the dominant C-bearing phases at depth, but become oxidized by ferric iron in garnet as a result of decompression. Only once graphite is oxidized, which will occur at relatively shallow depths, can small degree carbonate-rich melts form.

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CARBONATES IN THE LOWER MANTLE AND TRANSITION ZONE AS FUNCTION OF THE OXYGEN FUGACITY

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The stability of carbonate in the mantle relative to diamond depends on oxygen fugacity.

In the Earth's lower mantle it is likely that the oxygen fugacity is sufficiently low enough for Fe-Ni metal to be stable, however, high pressure and temperature experiments are required in order to test whether this means diamond is the only form of carbon present in the lower mantle.

In this study, the oxygen fugacity buffered by equilibria involving both elemental carbon (graphite or diamond) and carbonate (minerals or melts) were determined in a simplified Fe-Al-Ca-Mg-Si-O-C model peridotite composition at pressures between 16 and 50 GPa (~ 1100 km) and temperatures of 1500-1700°C. Oxygen fugacities were measured using iridium-iron alloy as a sliding redox sensor.

Experiments at 16-25 GPa were performed in 1000 and 1500 ton Kawai-type press.

Experiments at 50 GPa were performed using the MADONNA D-DIA (1500 tons) apparatus with sintered diamond anvils installed at the Geodynamics Research Center, Ehime University in Japan. The advantage of the MADONNA press is that the displacements of all the six anvils can be measured and the differential rams pressures can be controlled with the main ram load. High-pressure cell assemblies have been optimized for use with SD anvils. High temperatures were reached using a cylindrical $LaCrO_3$ furnace [1]. Pressure was accurately determined using a calibration based on using the same assembly at the SPEED-Mk.II multianvil press installed at BL04B1 beam line in SPring-8. *In situ* X-ray diffraction (XRD) measurements with synchrotron radiation were carried out using Au as an internal pressure standard.

Experiments in the wadsleyite stability field were also carried out in order to determine the Fe^{3+} content at an oxygen fugacity buffered by the carbon-carbonate equilibria.

The ferric iron content of the wadsleyite layer in the run products was determined by ^{57}Mössbauer spectroscopy at room temperature and pressure.

Such runs allowed us to estimate the likely redox conditions occurring in the lower mantle at which elemental carbon (diamond) might be equilibrated with carbonate, ferropericlase, Al-bearing perovskite and a metal phase.

Our results imply that: (1) wadsleyite $Fe^{3+}/\Sigma Fe$ ratios from experiments buffered at similar levels are low compared to values measured at IW, implying that high levels of ferric iron may not be necessary for the development of carbonate bearing assemblages in the transition zone; (2) the effect of pressure on the carbonate/carbon buffer indicates that the diamond stability field may not persist deep into the lower mantle, with carbonates being the stable host for carbon, probably in equilibrium with Fe-Ni carbide.

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AB INITIO STUDY OF DOLOMITE CATION DISORDERING. FURTHER DETAILS

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Studies on chemical-physical properties of dolomite mineral are directly related to different research fields, *i.e.* Earth's global carbon cycle, CO_2 sequestration, fluid reservoir properties, fault weakening. Since cation distribution, in dolomite, over crystallographic sites strongly influences thermodynamic and kinetic properties of dissolution-precipitation reactions, we applied first principles calculation methods in order to better understand thermodynamic stability of different disordered dolomite structures. Preliminary *ab initio* results concerning total-energy calculations of stoichiometric dolomite structures allowed us to observe both polymorphic and polytypic defects in cation distribution. By taking into account the equipartition law, we calculated, as a first approximation, characteristic disordering temperatures (T_{cd}). We found a temperature range of about 800-2000 K [1]. Thus, defects in cation distribution seem energetically stable only at relatively high temperature conditions. *Ab initio* calculations were performed at the hybrid Hartree-Fock/Density Functional Theory (HF/DFT) level [2, 3] by using a development version of the CRYSTAL program [4]. Calculations were performed by using the WC1LYP Hamiltonian which includes a *non local exact* Hartree-Fock exchange contribution.

The aim of the present study is the processing of the previous data by using statistical thermodynamics. Among the entire set of calculations, for the first time we chose configurations simulated over conventional 1×1×1 cells. It means 3 formula units per cell and 20 configurations divided in 14 inequivalent classes, and just 3 inequivalent polytypic structures (Fig. 1).

Thermodynamic properties calculation allowed us to trace the real characteristic disordering temperatures for the simulated structures. In this way we found a T_{cd} range wider than the previously estimated one [1]. It led us to hypothesize defects in cation stacking sequence even at relatively low temperatures.

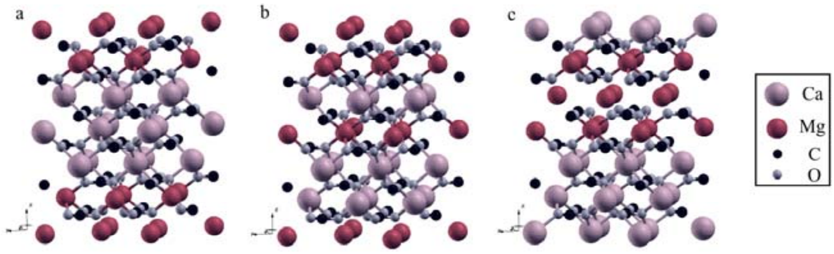

Fig. 1. Inequivalent calculated polytypic structures over conventional cells 1×1×1.

Future works are planned to use experimental approaches for studying disordering as well as crystalline size in dolomites. Together with disorder, crystalline size is one of the most important parameters which have to be taken into account in dissolution studies because of their strong influence on kinetics of the involved reactions. Furthermore, we are going to apply the same statistical thermodynamics method on structures calculated with non-conventional supercells 2×2×2. Due to the greater number of formula units per cell, the possibility for inequivalent polymorphic/polytypic structures will increase. Moreover, the effect of pressure and temperature on cationic disordering will be investigated by first principles calculation to better understand the natural environmental disordering conditions.

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SESSION 1.3

From the mantle to oceanic and continental crust (session in memory of Giorgio Rivalenti)

Convenors:

M. Mazzucchelli (*Univ. of Modena and Reggio Emilia*)
R. Petrini (*Univ. of Trieste*)
G.B. Piccardo (*Univ. of Genova*)

CLINPYPYROXENE AS A KEY TO UNDERSTAND THE EVOLUTION OF THE SUBCONTINENTAL LITHOSPHERIC MANTLE

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In order to better understand the original formation and evolution of the Earth's mantle it is compulsory to model the very early fractionation of the silicate portion from the core of our planet. This is the most traumatic process suffered by our planet and it occurred before the end of the Hadean (3.8 Ga, following [1]). At that time the largely molten mantle would probably have been convecting too rapidly to permit extensive segregation of liquidus phases. As crystallization progressed, convection would have slowed down as the remaining crystal-magma mixture became more viscous. The later differentiation of the silicate phases containing relatively high volatile (less refractories) elements (*i.e.* Fe) from the residua containing relatively highly refractories (*i.e.* Mg, Ca, and REE) occurred. The early mantle should reflect a solid/liquid mineral formation in the magma ocean stage of the Earth, in a crystallization sequence that in a self-sustained oxidizing regime [2] rapidly crystallised (F ~ 75%) Mg-Pvsk + Fe-Prvsk + Ca-Prvsk (the primordial lower mantle), leaving a residua that soon after solidified, forming Ringwoodite, Majorite and Ca-Perovskite (primordial lower-upper mantle transition zone) and finally the primordial upper mantle peridotite, with cpx estimated < 5% [3]. Peridotites from modern environments have nearly constant Fe content (FeO *ca.* 8%), even at the highest degree of depletion (*e.g.* [4]). This is primary due to the melting behaviour of pyroxenes (rather than olivine) in a peridotite system. Fe is buffered in opx/melt and cpx/melt system and, varies from the most fertile lherzolites to the most residual harzburgite/dunites of only 0.8 wt.% and 0.5 wt.% in opx and cpx respectively. On the other hand, olivine looses easily iron passing from ~ 10.0-10.5 wt.% in the most fertile to ~ 7.0 wt.% in the most depleted modern peridotites. If these processes have records in the Earth's evolutions, the place where we have to investigate it is the subcontinental lithospheric mantle (SCLM). One of the most intriguing hypotheses is that the "primary" cpx (and garnet) in the SCLM does not, in fact, derive from the segregation as liquidus phase during the early stages of cooling of the magma ocean (*e.g.* [3, 5]): it is, probably, a metasomatic product of a subsequent enrichment of the lithospheric mantle due to the efficient recycling of the very early crust (or, alternatively, by the circulation of ultra-hot mantle plumes). Data from a very large data set of mantle-derived Cr-pyrope indicate that the SCLM has undergone a secular evolution from highly depleted mantle in the Archean to more fertile in Phanerozoic time, reflecting both refertilisation and changes in the processes that generate SCLM (*e.g.* [5]). With this contribution we extend the search for geochemical fingerprints in the SCLM using clinopyroxene, which can provide a wider sampling of the SCLM than garnets alone. Cr-diopside is the only mantle phase stable from the lower part of the upper mantle (550 km) to the Moho discontinuity. It represents one of the best tools for recording SCLM compositional variations related to depletion and enrichment processes over a large time span. A large data set of cpx from Archean to Phanerozoic mantle are thus reported and compared, aiming at highlight the compositional variations of this important phase in the mantle over time.

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THE COMPOSITION OF PLAGIOCLASE AS PRESSURE MARKER OF THE LOW-P LITHOSPHERIC MANTLE EXHUMATION: A NEW EMPIRICAL GEOBAROMETER

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The crystallization of plagioclase-bearing equilibrium assemblages in mantle peridotites is indicative of lithospheric mantle exhumation at relatively low-P conditions. Recently, subsolidus experimental data in Ti-Cr-Na-Fe-CMAS system on depleted and fertile lherzolite compositions [1] confirmed that the spinel- to plagioclase-lherzolite transition is governed by a continuous reaction, resulting in systematic compositional variations in coexisting minerals at decreasing P within the plagioclase stability field, similar to what observed in natural plagioclase peridotites [*e.g.* 2, 3, 4, 5]. Experimental results also indicated that plagioclase records a marked anorthite content (An) variation within a rather narrow range of P. This suggests that plagioclase composition represents a potential geobarometric marker for the low-P evolution of lithospheric mantle. Multiple least-squares regression analysis of experimental data at P ranging from 0.31 to 0.8 GPa and temperature from 1000-1150°C on a fertile lherzolite (FLZ) provided an empirical expression for P in terms of plagioclase composition and T. Evidence that the chemistry of plagioclase is not affected by the X_{Cr} value of peridotite bulk [1] makes the proposed An-in-plagioclase barometer applicable to a rather wide range of mantle rocks. Moreover, experiments on a modified Na-rich FLZ are in progress to test the existence of a correlation between plagioclase chemistry and bulk Na_2O/CaO ratio. Preliminary results on first experiments (0.8-0.9 GPa, at 1100°C) show that bulk Na_2O/CaO influences the high pressure stability of plagioclase lherzolite assemblage, but it seems to have a minor effect on plagioclase chemistry at fixed P-T conditions. If confirmed, this would extend the applicability of the new geobarometer to a wide range of mantle rocks.

In this work, the An-in-plagioclase barometer has been applied to plagioclase lherzolites from the External Liguride ophiolitic Unit (Northern Apennine, Italy); these peridotites have bulk composition analogous to experimental lherzolite FLZ, and show textural evidence and mineral compositional variations indicative of plagioclase-facies recrystallization [2]. Detailed microstructural analyses have revealed systematic chemical zoning in plagioclase and pyroxene neoblasts from the plagioclase-bearing assemblage. An-reverse zoning in plagioclase is coupled to Al, Na and Ca content core-rim variations in texturally associated pyroxenes. Geothermometric investigations yielded temperature ranging 950-870°C, with a progressive cooling recorded by core-rim traverses in pyroxene neoblasts. The new empirical barometer leads equilibrium P of 0.73 and 0.31 GPa in plagioclase cores and rims, respectively, indicative of the exhumation from about 22 to 9 km depth of this lithospheric mantle sector. Experimentally-derived Na-Ca partitioning between plagioclase and clinopyroxene can be used to test the attainment of chemical equilibrium in neoblastic plagioclase-bearing assemblages from natural mantle peridotites, thus enlarging the applicability of the An-in-plagioclase barometer in equilibrated plagioclase peridotites of different origins (subsolidus *vs*. melt impregnation). The proposed empirical equation, coupled to detailed microanalytical investigations on plagioclase-bearing granoblastic assemblage allow to trace the progressive decompressional evolution of the lithospheric mantle through the plagioclase-stability field up to very low-P.

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MANTLE HETEROGENEITIES BENEATH THE EASTERN SWIR

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The eastern termination of the South West Indian Ridge (SWIR) is characterized by very slow spreading rates, reduced magma production and a peculiar accretionary tectonics [1]. Oblique spreading sectors separate orthogonal segments characterized by an anomalous abundance of variably extended core complexes that accommodate spreading through low-angle, long-lived, detachment faulting. High axial depths, along with abundant mantle exposures at the seafloor and reduced crustal thickness suggest mantle temperatures to be the lowest of the entire South West Indian Ridge and/or the presence of a more refractory mantle underneath [2, 3]. This region is bounded by the Gazelle fracture zone (FZ) to the west and divided in two domains by the Melville FZ. Based on basalt chemical and isotopic fingerprint it appears that this fracture zone represents a major thermal and compositional boundary [4, 5]. We have carried out a detailed major and trace element study of mantle residua from the two domains east and west of the Melville FZ recognizing different compositional domains in the mantle underlying this region along with different melting styles. The western domain reflects a high degree of depletion. By contrast the domain East of the Melville fracture zone is characterized by mantle that underwent low degrees of partial melting mirrored by the overall lower crustal thickness. East of Melville FZ the abyssal peridotites show a large interaction with variably aggregated melts, locally leading to near-complete equilibrium with the associated basalts. In one dredge the peridotite is equilibrated with a melt strongly enriched in LREE and depleted in HREE interpreted as a garnet-derived melts. Spatially associated basalts with compositions similar to the calculated melt were not collected in the region. However, basalts from a nearby dredge are characterized by REE patterns distinctly depleted in HREE in association with the enriched-most isotopic signature. This suggests that melting of isotopically enriched heterogeneities and garnet signature are two aspects of the same process. However the chemically depleted character of these basalts requires they have been generated by large extent of melting of the source lithology and variably mixed with depleted melts from the surrounding mantle. Fertile lherzolites are also spatially associated with more depleted domains that appear to have undergone significant (~ 5% of DMM) partial melting in the garnet stability field. The scattered presence of mantle rocks too depleted for resulting from the melting process beneath the region east of Melville confirms the presence of relict domains of ancient depletions. The entire range of basalt compositions from this stretch of SWIR overlaps the calculated range of the melts in (partial) equilibrium with the peridotites strongly suggesting that the variability of the mantle composition is likely similar at local (dredge) and regional scales.

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THE TRANSITION FROM ULTRAPOTASSIC TO SHOSHONITIC AND HIGH-K CALC-ALKALINE MAGMATISM IN POST-OROGENIC SETTING: A KEY Sr-Nd-Pb STUDY OF THE RADICOFANI MONOGENETIC VOLCANO, TUSCANY, CENTRAL ITALY

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The Radicofani Volcano is a small monogenetic volcano characterised by few lava flows, a cinder cone and a denudated neck, representing a Pleistocenic magmatic event in the frame of the ultrapotassic (lamproitic) to calc-alkaline volcanic association of the Tuscan Magmatic Province. In spite of the short time span of activity a large chemical and isotopic variability is observed along the rocks of the neck and at a minor extent win the lava flows and scoriae. Most of the rocks of the Radicofani volcano are shoshonitic with minor high-K calc-alkaline terms, and variable K_2O contents linearly correlated with trace element and isotopic variations. Shoshonitic and high-K calc-alkaline rocks of the Radicofani volcano are significantly different from other shoshonites associated with the leucite-bearing ultrapotassic rocks of the Roman Magmatic Province. The studied rocks are characterised by high, but variable, levels of incompatible trace elements with a clear orogenic signature showing negative anomalies of Ba, Ta, Nb, and Ti, and peaks at Cs, K, Th, U, and Pb. Initial values of $^{87}Sr/^{86}Sr$ increase along with incompatible trace elements contents and selected trace element ratios (*e.g.* Th/La), whilst the opposite is true for $^{143}Nd/^{144}Nd$. High-K shoshonites show the highest incompatible trace element contents coupled to highest $^{87}Sr/^{86}Sr$ and lowest $^{143}Nd/^{144}Nd$. On the basis of geochemical and isotopic signatures it is argued that magmas were generated in a modified lithospheric mantle source after CO_2-poor crustal-derived metasomatism. One of the most intriguing features of Radicofani rocks is their distribution in a Th/La *vs*. Sm/La diagram. In the same way as Tethyan Lamproites, Radicofani rocks define a positive correlation. This constitutes a paradox [1] with respect to all subduction related magmas worldwide, which instead display ubiquitous negative correlation [2]. This has to be interpreted as related to the special geodynamic and thus metamorphic condition responsible for the chemical composition of lamproitic magmas.

Interaction between the metasomatic agent and lithospheric upper mantle produced a low-melting point metasomatised veined network. The partial melting of the vein's mineralogy produced leucite-free ultrapotassic magmas (*i.e.*, lamproite). Partial melting was triggered by re-equilibration of isotherms after orogenic front migrated eastward. Further upraise of the isotherms induced larger degrees of partial melting in both vein's mineralogy and surrounding mantle.

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U-Pb ZIRCON GEOCHRONOLOGY OF GABBROIC SEQUENCES FROM LIGURIAN OPHIOLITES (NORTHERN APENNINE, ITALY)

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Jurassic ophiolites from Eastern Liguria are lithosphere fragments of the Ligurian-Piedmontese ocean. The association of ophiolites and continental crust material from External Ligurian units is considered an ocean-continent transition towards the Adria margin, similar to the modern ocean-continent transition of Western Iberia margin [1]. The ophiolites from Internal Ligurian units most likely represent a distal portion of the Ligurian-Piedmontese basin and show structural and compositional features similar to those of modern (ultra-)slow spreading ridges [2]. The Ligurian ophiolites are characterised by a basement made up of gabbroic plutons intruded into mantle peridotites. This basement records a polyphase tectonic evolution in shear zones, from near solidus ductile conditions to a low temperature brittle regime, associated with its exhumation at the seafloor through detachment faulting [3, 4]. The high temperature ductile structures are crosscut by dykes showing sharp planar boundaries against host rocks and displaying basaltic or albitite/plagiogranite compositions [5]. To yield new geochronological constraints for the rifting process that led to the opening of the Ligurian-Piedmontese basin, we carried out systematic U-Pb zircon datings of External and Internal Ligurian gabbroic sequences by laser ablation ICP-MS. In particular, zircons were collected from gabbros and crosscutting albitite/plagiogranite dykes. We recognised three distinct intrusive pulses, which cover a time interval of about 20 Ma (from the Middle to Upper Jurassic). In addition, a few gabbroic bodies yielded uncertain geochronological determinations, which suggested the occurrence of slightly older intrusive events. We found a long time interval (Ma-scale) between intrusion of the gabbros and injection of albitite/plagiogranite dykes, thus implying a very slow exhumation rate for the gabbro bodies. Taken as a whole, the data obtained are consistent with a geodynamic model in which some of the gabbro bodies were intruded into the extending continental lithosphere and an embryonic oceanisation occurred in the Upper Jurassic.

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GENESIS AND EVOLUTION OF MAFIC AND FELSIC MAGMAS OF THE GEDEMSA AND FANTALE VOLCANOES (MAIN ETHIOPIAN RIFT)

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The Gedemsa volcano is located in the central part of the Ethiopian Rift, about 100 km SE of Addis Ababa. Its maximum elevation is 300 m above rift floor and is characterized by a wide central caldera, about 8 km in diameter. The general stratigrafic sequence in the area includes, from base upwards, rift-floor ignimbrites (1.7 Ma), basaltic rocks, pantelleritic and subordinate trachytic pyroclastic deposits and lava flows and domes, and widespread basaltic deposits. The Fantale volcanic complex is located in the northern part of the Main Ethiopian Rift, where Afar depression begins. Its maximum elevation is 1644 m above rift floor and the volcanic structure is characterised by a summit central caldera whose diameter is about 4 km. The eruptive activity of this volcano is represented by trachytic and rhyolitic lavas, while the most diffuse unit is an ignimbrite related to the caldera collapse. Explosive activity has occurred inside and outside the caldera, forming tuff cones and thick pumice fall out deposits. The only mafic unit is represented by a basaltic eruption occurred in 1870 AD. Historical eruptions and intense fumarolic activity are evidence of the persistence activity of the Fantale in this part of the Main Ethiopian Rift.

Products of the two volcanoes show a typical mafic-felsic bimodal distribution with few intermediate terms. New mineralogical, geochemical and isotopic (Sr, Nd, Pb) data of selected products of the Gedemsa and Fantale volcanoes will be presented and used to discuss the genesis of the silicic and basaltic magmas, the contribution of the Afar plume, the interaction between mantle derived magmas and the Pan-African crust, and the relationships between magmatism and tectonism.

PETROGENETIC ASPECTS OF THE CONTAMINATION PROCESSES IN THE MAFIC-ULTRAMAFIC COMPLEX OF NIQUELANDIA (GOIÀS, BRAZIL)

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The mafic-ultramafic complex of Niquelandia is one of the three major layered intrusions occurring in the Goiàs State, Central Brazil.

Previous studies on this complex [1] have revealed that the parent melts of the complex have suffered a significant crustal contamination.

In a recent field work several lenses or septa of exotic metamorphic rocks were found striking parallel or sub-parallel to the complex layering: the total amount of these rocks has been estimated to represent the 13% of the volume of the whole complex.

These lenses or septa were found starting from the intermediate portion of the Layered Gabbro Zone (LGZ) unit upwards; however, they are mainly concentrated at the contact between Lower Sequence (LS) and the Upper Sequence (US).

They can be divided in three major lithotypes: quartzites, gneisses and calc-silicate rocks derived from sandstones, pelites and marls, respectively.

The petrological and geochemical investigation of transects perpendicular to the complex layering provided the evidences that these rocks are the crustal contaminants of the complex parent melts: as the matter of fact they produced an enrichment in the hybrid melts of incompatible elements (*i.e.*: LREE, K, Ba, and Rb).

On the basis of their petrographic and geochemical characters, the contaminants are supposed to belong to the upper stratigraphic unit of the volcano-sedimentary sequence of Indaianopolis.

This is also in agreement with geochronological data. In fact Pimentel and co-workers [2] dated one of the septa of contaminants occurring in US with the U/Pb method on zircons: they obtained an age of 1248±23 Ma and suggested that this age is referred as the US intrusion age, proposing that US and LS (their estimate of LS intrusion age is 797±10 Ma) were not coeval.

This model is incongruent with the robust evidences that US and LS are cogenetic, as for instance the similar LILE patterns found in rocks of the two different units or the outcropping, in LS, of cumulus rocks similar to the US ones.

We present a simplified model of assimilation and fractional crystallization which tentatively supports the hypothesis that LS and US are genetically kindred.

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INSIGHTS INTO THE TRIASSIC GEODYNAMIC EVOLUTION OF THE ADRIA PLATE: THE STUDY CASE OF THE MAFIC-ULTRAMAFIC SEQUENCE OF FINERO

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A strategic lithologic sequence for the study of the Middle-Upper Trias magmatic events in the South-Alpine domain (Adria plate) is outcropping in the Finero area, located in the north-easternmost sector of the Ivrea-Verbano Zone (Western Alps). Such a sequence is located along the Insubric line and is formed by a strongly-metasomatised mantle body, surrounded by a mafic-ultramafic intrusive sequence [1, 2, 3], which documents the alternation of mantle and crustal rocks placed at the bottom of the Adria plate before the opening of Ligurian-Piedmontese branch of the Jurassic Tethys.

Unlike the intrusive sequences of the central and southern sectors of the Ivrea-Verbano Zone, characterised by Permo-Carboniferous emplacement ages, the Finero massif shows abundant radiometric evidence of intrusion of basic melts at the bottom of the continental crust during Trias, which formed the cumulitic sequences of the so-called Basic Complex of Finero. Besides, in Triassic times, the mantle sequence of Finero suffered a virtually complete metasomatic recrystallisation triggered by several episodes of pervasive to channelled porous flow migration of (mostly hydrous) melts. Later on, but yet in Triassic time, the mantle sequence experienced the intrusion of basic veins-dykes (locally characterised by the presence of sapphirine), which discordantly cut the mantle foliation. Thus, the mafic-ultramafic Finero sequence represents a unique opportunity to characterise the composition of Triassic melts migrating through the Adria realm escaping significant interaction with the continental crust. Notwithstanding that several papers have been devoted to the petrologic investigation of the mafic-ultramafic Finero sequence since the beginning of the seventies, its petrochemical and geodynamic evolution is presently very poorly constrained. Crucial issues still debated are: 1) the sources of the liquids that percolated the mantle sequence, the timing and geodynamic setting of the mantle metasomatism; 2) the age of accretion of the mantle sequence to the bottom of the continental crust; 3) the geochemical composition of the parent melts of the Basic Complex, their differentiation processes, the timing of the different melt injections and their potential relationships with the melt-related events recorded by the associated mantle sequence. In the frame of this contribution, new data about the major and trace mineral chemistry of the three main units of the Basic Complex (*i.e.* Internal Gabbro, Amphibole Peridotite, External Gabbro) and of the various peridotitic (*e.g.* phlogopite harzburgites, dolomite-apatite-bearing wehrlites, dunites with chromitites bands and/or pyroxenite-hornblendite veins), pyroxenitic (*e.g.* phlogopite-bearing websterite, orthopyroxenites, clinopyroxenites) and femic (*e.g.* sapphirine-bearing amphibole gabbros) lithologies of the mantle sequence will be provided, in order to constrain the geodynamic setting of the melt-related processes.

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SAPPHIRINE-BEARING AMPHIBOLE GABBRO FROM THE MANTLE SEQUENCE OF FINERO (SOUTHERN ALPS): PETROGRAPHY, GEOCHEMISTRY AND GEODYNAMIC CONTEXT

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A late swarm of sapphirine-bearing amphibole gabbroic veins discordantly crosscut the main layering of the Finero phlogopite-peridotite massif, Western Italian Alps. Sapphirine locally occurs in a melanocratic zone placed between a leucocratic gabbroic band, forming the central part of the intrusion, and the host peridotite. The melanocratic zones are observed on both sides of the leucocratic gabbroic vein and consist of (i) an outer orthopyroxene-rich zone along the host peridotite, and (ii) an inner amphibole-rich zone placed along the leucocratic gabbroic band side. Sapphirine either overgrows spinel or occurs as isolated inclusion within large amphiboles in the amphibole-rich melanocratic zone. Spinels without sapphirine envelopes also microtexturally co-exist with independent sapphirine grains. EMPA and LA-ICP-MS analyses of minerals from the melanocratic and leucocratic bands evidence significant differences in terms of both major and trace elements in the composition of the parent melts. In particular, the amphiboles in the melanocratic zones show higher TiO_2, Na_2O and K_2O, M-HREE and HFSE than those in the leucocratic ones. The Al_2O_3 content of amphibole and the Fo in olivine of the host peridotite are significantly higher and lower, respectively, than those in other Finero peridotites far from the amphibole gabbroic veins. Moreover, amphiboles from the host peridotite are characterised by LREE-enriched convex-upward patterns significantly different with respect to those documented in literature for the Finero phlogopite-peridotites [1]. Mineral assemblages and mineral chemistry in both the melanocratic zone and the host peridotites are interpreted as the result of different stages of melt migration associated with melt-rock interaction. In particular, the major and trace element compositions of the amphiboles from the wall peridotite suggest that during an early stage, possibly before the opening of the conduits, the peridotite suffered porous flow migration of a melt more enriched in REE with respect to those forming the gabbroic bands. The crystallisation of the melanocratic bands is related to a second stage, in which the precipitation of large amphiboles was accompanied by a strong reaction between host peridotite and melt flowing into the conduit that determined the complete substitution of peridotite olivine with orthopyroxene at the peridotite-vein contact. A third stage was characterised by with the precipitation of the leucocratic band, associated to a further enlargement of the vein. Petrographic survey highlights that parent melt of leucocratic zone reacted with the minerals of the melanocratic one, inducing sapphirine growth around spinels. The genetic relationships occurring between the parent melts of the melanocratic and leucocratic zones must be yet established. Working hypotheses consider the parent melt of the leucocratic zone either related to a late injection or a residual differentiate after precipitation of melanocratic band in the frame of flow differentiation process. Quantitative considerations suggest that the selective addition of Al-rich phases, like amphiboles and micas, to a basalt can determine the large Al/Si ratios required for sapphirine precipitation. Modelling results indicate that the eutectic T of Finero phlogopite-peridotite is < 1000°C and that the first partial melts are saturated in corundum. Thus, it is proposed that injection of basaltic melts triggered the partial melting of limited volumes of phlogopite peridotite producing Al-rich melts: the mixing of such Al-rich components with the migrating basalt is believed to have played a fundamental role in favouring the precipitation of sapphirine.

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INDIAN RIDGES, HOTSPOTS AND INTERACTIONS: RÉUNION-CIR AND AMSTERSDAM-ST PAUL-SEIR CASES

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Recent studies on regions of the Indian Ocean where hotspots interact with spreading ridges show a variety of situations corresponding to the various phases of the interaction. New results on the Reunion hotspot - Central Indian Ridge and St Paul-Amsterdam hotspot - Southeast Indian ridge interactions shed a new light on these various phases.

In this frame trace element and isotope data help us to decipher within the mantle components, which contribute to the active magmatism of these areas.

In the case of Reunion-CIR interaction, He data support a flux of ^{3}He enriched material through the off axis ridges Three Magi and Gasitao toward the southern end of the CIR involved segment [1]. Radiogenic isotopes reveal that this material derives from the heterogeneous Reunion plume and travelled from the present position of the plume until the spreading axis. Witnesses of this transfer are the off axis ridges produced by melting of the underlying mantle through tension cracks in the lithosphere and may be also the island of Rodrigues.

In the case of the St Paul-Amsterdam plateau, investigation of the on axis plateau lavas [2] pointed out the complexity of the interaction between the ASP plume and the SEIR. New radiogenic isotope data establish a link between the seamount chain, the plateau and the islands. Subtle changes in composition are due to the two stages construction process of the plateau and seamounts. Some of them, highly alkaline, derive from lithospheric melting along tension cracks during a last phase of off axis magmatism on the Australian plate.

In both locations, it appears that the construction of plateau and/or off axis ridges/seamounts is related to the level of activity of the plume that pulses with time.

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IRON OXIDATION STATE OF GARNET FROM UPPER MANTLE XENOLITHS IN THE GIBEON KIMBERLITE PROVINCE (NAMIBIA) AND IMPLICATIONS FOR GEOTHERMOBAROMETRY

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The Gibeon Kimberlite Province of southern Namibia is located between Keetmanshoop and Mariental, comprising more than 75 group-1 kimberlites. Such "off-craton" kimberlites are non-diamondiferous, unlike many of the older "on-craton" kimberlites of the adjacent Kaapvaal craton. P-T conditions of crystallization [1] indicate a restricted pressure range (3.8-4.6 GPa), corresponding to a depth of origin between 100 and 140 km. A temperature gradient has been recognized between samples coming from similar depths, which reflects the transition between low-T, coarse equant xenoliths to high-T mosaic-porphyroclastic xenoliths.

In order to study P-T-fO_2 relationships in this off-craton mantle setting, we have measured $Fe^{3+}/\Sigma Fe$ ratios in nineteen garnets in thirteen peridotite xenoliths from the Gibeon Townsland 1 kimberlite pipe, using the electron microprobe (flank method; [2]). The selected xenoliths are representative of the three main texture types (coarse equant, porphyroclastic and mosaic-porphyroclastic). Results show a total variation of $Fe^{3+}/\Sigma Fe$ from 2.9 to 11% among all samples. No apparent correlation is identified between xenolith texture and Fe oxidation state. Overall, $Fe^{3+}/\Sigma Fe$ ratios are comparable to those in xenolithic garnets from Kaapvaal kimberlites [3]. Two of the analyzed garnets are zoned in terms of $Fe^{3+}/\Sigma Fe$ ratios. Sample KGG-Y1-55 (porphyroclastic) shows a rimward decrease of $Fe^{3+}/\Sigma Fe$, which is associated with a decrease of total Fe and can thus reflect partial reequilibration during heating processes. Sample KGG-Y1-62a (mosaic-porphyroclastic) shows a rimward increase in $Fe^{3+}/\Sigma Fe$, suggesting oxidation.

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THE ROLE OF ECLOGITE IN THE RIFT-RELATED METASOMATISM AND CENOZOIC MAGMATISM OF NORTHERN VICTORIA LAND

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Isotopic analyses (Sr, Nd, Hf on separated clinopyroxenes and *in situ* Re-Os on sulphides) were performed in mantle-peridotite xenoliths from Baker Rocks (BR) and Greene Point (GP), two localities of Northern Victoria Land (NVL, Antarctica), less than 100 km apart and separated by the Tinker Campbell Discontinuity (TCD). At BR amphibole-bearing and anhydrous lherzolites, with minor harzburgites and pyroxenites are present, while only anhydrous lherzolites and harzburgites are found at GP. Both suites are characterized by pyrometamorphic textures superimposed on typical protogranular to porphyroclastic textures. Previous major and trace element studies evidenced two different metasomatizing agents which percolate different lithospheric mantle domains under the Ross Sea region. At BR a TiO_2-rich nephelinite mainly reacted with primary clinopyroxene transforming it into amphibole. At GP metasomatism is caused by a K-rich, Ti-poor melt reacting mainly with opx and giving secondary cpx and a SiO_2-rich glass. These glasses are also characterized by very low Nb and high Zr contents.

Most of the BR sulphides have radiogenic $^{187}Os/^{188}Os$ (0.1318-0.379 with $^{187}Re/^{188}Os$ ratios between 0.46 and 3.3), while unradiogenic $^{187}Os/^{188}Os$ characterizes the GP suite (0.1068-0.1279 with $^{187}Re/^{188}Os$ ratios from 0.0002 to 0.045). At BR $^{87}Sr/^{86}Sr$ in silicates varies between 0.70296 and 0.70488, $^{143}Nd/^{144}Nd$ lies within a narrow range (0.51271-0.51296), and $^{176}Hf/^{177}Hf$ ranges from 0.28300 to 0.28337. Cpx from GP have similar $^{87}Sr/^{86}Sr$ (0.70277-0.70434), $^{143}Nd/^{144}Nd$ (0.51261-0.51347), and $^{176}Hf/^{177}Hf$ (0.28332-0.28519).

Notwithstanding the rather limited number of Os-rich sulphides in the GP suite, Os model ages for BR and GP largely overlap. A histogram of T_{RD} (Time of Rhenium Depletion) model ages shows peaks at 3.0-3.3 Ga, 2.3 Ga, 1.3-1.4 Ga, 0.9-1.1 Ga, 580-620 Ma and 120 Ma (the youngest being recorded only at BR).

The highly radiogenic Os found in the BR xenoliths cannot be explained by contamination from the host basalts, unless they were derived from a source which was enriched in Re far in the past. Alternatively they can be explained through mixing with an eclogitic lithotype. Oceanic crust may have been introduced into the sublithospheric NVL mantle, transformed in eclogites during the Ross Orogeny (550 Ma) and reactivated during the opening of the West Antarctic Rift System. In this case up to 60% of recycled material would be required to explain the most radiogenic Os-isotope values. Alternatively if older (up to Archean) eclogitic rocks, generated by previous subduction events or by cumulitic processes, were already present in the lithospheric mantle the percentage of mixed material can be reduced to about 15%.

Based on Hf systematics the most radiogenic GP cpx could also be explained by adding an eclogite percentage varying between 35 and 20%. However in this locality the possible presence of garnet in the source and successive equilibration in the spinel stability field, could also account for the highly radiogenic cpx values.

METASOMATISM IN THE LITHOSPHERIC MANTLE BENEATH SARDINIA: NEW EVIDENCE FROM WEHRLITE AND HARZBURGITE XENOLITHS

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The Plio-Quaternary alkaline volcanics from Sardinia include abundant mantle xenoliths [1, 2, 3] and rare lower crustal mafic granulite xenoliths [4]. The ultramafic xenoliths mainly consist of four-phase anhydrous spinel harzburgite and cpx-poor lherzolites representing the uppermost levels of the Sardinia lithospheric mantle [2, 3]. They are variably depleted rocks generally affected by criptic metasomatism related to highly alkaline mafic melts [3].

The xenoliths from the Montiferro Volcanic Complex and some Logudoro eruptive centres also include minor anhydrous pyroxenites (spinel clinopyroxenites, ol-bearing and ol-free websterites), phlogopite- amphibole-bearing clinopyroxenites with cumulate texture, clinopyroxene and mica megacrysts. In this work we present some preliminary data and observations on newly discovered metasomatised xenoliths, *i.e.* wehrlites and phlogopite harzburgite hosted in basanites from the Montiferro Volcanic Complex.

The wehrlites occur as mm- to cm-thick bands cutting previous spinel harzburgites. The contact is sharp and irregular. They are composed of clinopyroxene (40-50 vol.%) + olivine (45-55 vol.%) + orthopyroxene ($\leq$ 5 vol.%) + spinel ($\leq$ 3 vol.%) and have protogranular to granoblastic textures. One of these xenoliths contains apatite and preserves evidence of replacement of a previous harzburgite assemblage, *i.e.* clinopyroxene + olivine coronas developed around orthopyroxene and relics of deformed olivine in the secondary clinopyroxene. Temperature inferred for the lithospheric equilibration of the harzburgite protholith based on the CaO content of the relic orthopyroxene [5] is ~ 1000°C, in agreement with the estimates reported in [3]. The wehrlite assemblage is composed of clinopyroxene with highly variable Cr_2O_3 (0.8-2.6 wt.%) and Na_2O (0.6-1.9 wt.%) contents, Mg-rich olivine (Fo_{91-92}), euhedral, highly chromian spinel (Cr# = 0.57-0.62) included in clinopyroxene and interstitial Cl-rich apatite. As a whole, the observed reactions and the mineral assemblage of this wehrlite bear similarities to those attributed to carbonatite metasomatism in xenoliths from continental [6, 7, 8] and oceanic [9, 10] upper mantle.

The phlogopite-bearing harzburgite is a spinel-free porphyroclastic rock characterized by relatively Fe-rich olivine (Fo_{87-88}) and orthopyroxene (Mg# ~ 0.88) deformed porphyroclasts mantled by fine grained neoblastic ol + opx with interstitial clinopyroxene (Al_2O_3 = 6.2-7.4 wt.%, Cr_2O_3 = 1.0-1.6 wt.%, Na_2O = 0.6-1.4 wt.%). Dark brown phlogopite (Mg# = 0.84) occurs as a disseminated phase characterized by remarkable TiO_2 (7.0-7.5 wt.%) and BaO (0.6 wt.%) contents which may reach unusually high values in the crystal rims (12.9-15.0 and 1.6-4.0 wt.%, respectively). TiO_2 abundance of the phlogopite cores are comparable to those of the mica megacrysts entrained in the same lava flows, although the megacrysts are characterized by distinctly lower Mg# values (~ 0.77). Relatively high temperatures of equilibration (1100-1150°C) have been calculated for the porhyroclastic and neoblastic assemblage of this strongly metasomatised rock.

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REFERTILIZATION EVENTS RECORDED BY THE SUBCONTINENTAL MANTLE: THE EXTERNAL LIGURIDE PERIDOTITES (NORTHERN APENNINES)

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The External Liguride mantle represents subcontinental litosphere exhumed in Jurassic times at an ocean-continent transition [1, 2]. These mantle rocks include (i) porphyroclastic spinel tectonites showing incipient re-equilibration in the plagioclase facies [1]; (ii) plagioclase-facies peridotite mylonites with spinel tectonite relics and pyroxenite layers recording an early equilibration stage at T ~ 1150°C and P ~ 2.8 GPa: [2]; (iii) coarse granular peridotites enriched in plagioclase [3]. The spinel-facies assemblage of the peridotites is characterized by Na_2O and Al_2O_3-rich clinopyroxene with slight LREE depletion, spinel with low Cr# and disseminated Ti-rich amphibole. The peridotites (i) locally preserve highly depleted Nd-Sr isotopes coupled with Proterozoic Os model ages [1, 4]. As a whole, the External Liguride peridotites were considered to represent relatively fertile, MORB-type mantle accreted to the lithosphere in Proterozoic times [1]. However, the occurrence of different types of pyroxenites, the widespread amphibole formation and the evidence of interaction with asthenospheric melts during the shallow evolution [3], suggest that fertile nature of the External Liguride mantle bodies may be the result of multiple refertilization events during or before their emplacement. The peridotite plagioclase mylonites (ii) include garnet clinopyroxenites and opx-rich websterites layers showing Opx + Spl ± Cpx symplectites after Mg-rich garnet [1]. Major and trace element composition of minerals and bulk rocks indicate the garnet clinopyroxenites formed through recycling of plagioclase-bearing mafic protoliths that underwent variable degrees of partial melting in the garnet stability field or to high-pressure segregation from melts of recycled crust. Peridotite replacement by olivine-undersaturated melts (grt-pyroxenite-derived liquids and/or asthenospheric melts) through olivine consumption and pyroxene ± garnet forming reactions may be a viable process for the websterite formation. Reactions at lower melt/rock ratio may have also caused peridotite refertilization. A later infiltration of silica-undersaturated (alkaline) melts under spl-facies conditions is testified in both websterites and peridotites by opx-consuming reactions associated with crystallization of Ti-prg + Ol ± Cpx ± Ni-rich sulphides. Most pyroxenites have T_{DM}(Nd) and T_{DM}(Hf) younger than the exhumation age, thus arguing for fractionation of Sm/Nd and Lu/Hf ratios related to the Mesozoic rifting. Nd-Hf isotope compositions recalculated for the minimum age of fractionation vary in a wide range (ε_{Nd} = +4.3 to +12.6, ε_{Nd} = + 2.8 to + 31.5). Most samples, however, fall close or slightly below the mantle array. This isotope heterogeneity presumably reflects protoliths crystallized from MORB-type to slightly enriched melts. Local Hf-Nd decoupling in the pyroxenites may be attributed to an older fractionation event involving grt-bearing lithologies. The plagioclase-enriched peridotites (iii) are characterized by large plagioclase patches replacing spinel, Cpx porphyroclasts replaced by Opx + Pl, and gabbroic microgranular pods. They were eventually intruded by MORB-type gabbroic rocks and basalts. Clinopyroxenes from these peridotites have convex-upward REE patterns, Eu-Sr negative anomalies and significant REE and Zr enrichment with respect to the porphyroclastic clinopyroxenes of rocks unaffected by impregnation. Their geochemical features were most likely due to interaction with low-degree fractional melts of a MORB-type source [3].

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A SUBCONTINENTAL MANTLE-LOWER CRUST ASSOCIATION: NEW DATA ON THE VEINED MANTLE FROM SANTA LUCIA UNIT (CENTRAL CORSICA)

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The S. Lucia nappe belongs to the Alpine Corsica and consists of a pre-Alpine crystalline basement, overlain by a Middle Cretaceous detritic cover. The basement represents a fragment of late-Variscan lower crust, most likely derived from the European continental margin, which partially escaped the Alpine tectono-metamorphic event. The lower crustal rocks include a High Grade Mafic Complex and a Granitoid Complex of Early Permian age [1, 2, 3]. The High Grade Mafic complex, in particular, consists of a layered gabbroic sequence that contains lenses of felsic granulites and displays a pervasive recrystallisation under granulite facies conditions (P = 0.7-1.0 GPa, T = 800-900°C: [3, 4]). The base of the mafic sequence is associated with up to 50 m thick mantle slices.

The mantle slices consist of foliated spinel-bearing lherzolites (clinopyroxene = 10-15 vol.%) including cm-thick pyroxenite layers that are elongated concordantly with the foliation of host rocks. The peridotites show a subvertical mylonitic to ultramylonitic foliation roughly concordant with that of the nearby metagabbroic rocks [4]. The mylonite microstructure in the peridotite is characterised by aligned porphyroclasts of pyroxene (and rare spinel) in a very fine-grained polyphase matrix composed of olivine (Fo_{88-89}) + pyroxenes + spinel (Cr# =0.12) occurring as mm-size bands, lenses and porphyroclast tails. Orthopyroxene porphyroclasts are stretched along the mylonitic foliation with high aspect ratio. Both pyroxenes commonly show evidence for intracrystalline deformation. Relics of an older low-strain spinel tectonite predating the mylonite deformation are locally preserved as large exsolved orthopyroxene porphyroclasts mantled by neoblastic clinopyroxene + orthopyroxene + spinel (Cr# = 0.11).

The composition of clinopyroxene (Al_2O_3 = 4.5-6.1 wt.%, Na_2O = 0.6-1.1 wt.%) and spinel porphyroclasts (Cr# = 10-14) shows a fertile geochemical signature. The pyroxenites are orthopyroxene-poor spinel websterites with disseminated kaersutite and accessory Fe-Ni sulphides. These rocks have fine-grained granoblastic texture and include elongated porphyroclasts of Al-Ti-rich clinopyroxene (Al_2O_3 = 6.5-7.3 wt.%, TiO_2 = 1.1-1.8 wt.%) and Cr-poor spinel (Cr# $\leq$ 7). There is no significant decrease from equilibration temperatures of the porphyroclastic (850-940°C) to the neoblastic tectonite assemblage (830-900°C) of the peridotites. However, a former high-T stage in the spinel stability field (T = 1000-1100°C) is recorded by the orthopyroxene porphyroclasts of the peridotites, in agreement with the occurrence of mutual pyroxene exsolution lamellae and tiny Cr-spinel exsolutions in both pyroxenes. Temperature estimates for the spinel-facies mylonite recrystallization in both peridotites and pyroxenites (820-870°C) are similar to those reported for the granulite-facies recrystallization of associated lower crustal rocks.

As a whole, the new data on the Santa Lucia mantle rocks document similarities to the fossil mantle-lower crust association of Malenco (Central-Eastern Alps, *e.g.* [5]) that was exhumed during the Mesozoic rifting of the Western Ligurian Tethys.

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HETEROGENEOUS MELTING AND REFERTILIZATION OF A MANTLE PARCEL IN A COLD SPOT: ANDREW BAIN FRACTURE ZONE (SWIR)

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The Andrew Bain Fracture Zone (ABFZ) represents one of the largest transform faults in the ridge system. The ABFZ is located on the South West Indian Ridge and, together with Du Toit FZ, Prince Edward FZ and Marion FZ, it constitutes part of the plate margin between Africa and Antarctica. It reaches 750 km in length and it is characterized by a lens-shape structure. In this area, the lithosphere is thick and constituted mainly by ultramafic rocks and the system is characterized by a negative thermal anomaly.

During the Italian-Russian expedition S23-AB06, the seafloor in the Southern Ridge Transform Intersection (RTI) has been sampled and in the major part of the dredging sites only ultramafic material has been recovered. The sampled peridotites show hybrid textures. Based on the impregnating paragenesis it is possible to distinguish three different groups : a) deep spinel-field impregnation assemblages (sp + cpx ± opx ± ol); b) plagioclase-field equilibrated patches and mineral trails (pl + cpx ± ol) marked by both crystallization of newly formed plagioclase-field equilibrated trails and formation of plagioclase coronas around pristine spinel; c) late gabbroic pockets and veins, variably enriched in clinopyroxene.

Major and trace element composition have been carried out by EMPA and LA-ICP-MS analysis. Concerning the major element analysis, Group 2 and Group 1 pyroxenes and spinels follow a main melting trend accompanied by a progressive re-equilibration to plagioclase facies at all scales. Thin section-scale variability matches inter-site compositional variability, while Group 3 peridotites appear to have been re-equilibrated with liquids crystallizing gabbroic (cpx-pl) pockets. Progressive re-equilibration to lower P/T conditions can be accounted for by the presence of percolating melts and solid diffusion.

Major and trace element systematic shows that percolating melts are generated over a wide pressure range starting in the garnet stability field. They also show that some melts are possibly generated by incompatible element enriched lithologies. However there is no link between melt composition and mineral percolating assemblage. Therefore source heterogeneities are not smoothed out during melting in a cold melting region because of differential trapping of melts partially aggregated or derived by variably enriched heterogeneities.

THE FREETOWN LAYERED COMPLEX (SIERRA LEONE): MINERAL TRACE ELEMENT EVIDENCE FOR MULTIPLE MAGMA INJECTIONS

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The Freetown layered complex (FLC) is a tholeiitic mafic intrusion in Sierra Leone, west Africa dated at 193 Ma (Rb-Sr isochron age; [1]). It may have been intruded as part of the Central Atlantic magmatic province, (CAMP) during the break-up of Pangea. The preserved rocks of the FLC outcrop over a distance of 64 × 15 km and a thickness of about 7 km and are mostly gabbroic. Variable relative proportions of the main minerals (olivine, orthopyroxene, clinopyroxene, and plagioclase) suggest that the FLC can be divided into four zones (z-1, z-2, z-3, z-4) characterized by topographic expression and repetition of rock types [2], which vary from olivine- to plagioclase-rich. Major and trace element whole-rock concentrations have been measured by X-ray fluorescence, mineral compositions have been analysed by mean of electron microprobe on 12 selected samples, and trace element contents in plagioclases and pyroxenes have been determined using LA-ICP-MS microprobe on four samples, one for each zone. Whole-rock compositions show a large compositional scatter (*e.g.*, MgO 3-25 wt.%, SiO_2 40-51 wt.%) which is probably due to mineral accumulation effects. Minor and trace element contents and ratios for whole-rocks suggest that z-1 rocks are generally the most enriched ones in incompatible elements (*e.g.* in TiO_2, Nb/Y), whereas zone 4 is the most depleted one.

Mineral major element compositions are quite homogeneous in general for all analyzed FLC minerals. The crystals are poorly zoned in terms of major elements. An contents in plagioclases range from 55 to 65, while Fo contents of the olivines range from 58 to 71. Pyroxenes show frequently exolution lamellae (cpx in opx and *vice-versa*), and yield relatively high Mg# (70-85 in cpx, 62-73 in opx). Pyroxene compositions have been used to calculate crystallization pressures of 4-6 kbar [3] and temperatures ranges from 850 to 1000°C [4]. Oxides (magnetite and ilmenite) yield low temperatures of 350-600°C, suggesting a Fe-Ti subsolidus re-equilibration, and fO_2 (*ca*. QFM buffer).

Globally, trace element compositions of plagioclases and pyroxenes are relatively variable, compared to quite homogeneous major elements. Clinopyroxenes are moderately depleted in LREE *vs*. HREE, which results in LREE-enriched equilibrium magmas. The z-1 clinopyroxenes (and orthopyroxenes) yield substantially higher incompatible element contents (*e.g.*, REE and, notably, Th and U) compared to z-2, z-3 and z-4 crystals. Z-1 clinopyroxenes seem to be also slightly enriched in incompatible elements (*e.g.*, LREE) compared to plagioclase crystals from the same rock sample, *i.e.*, these clinopyroxenes probably crystallized from a more enriched magma. Further systematic differences for the clinopyroxenes among the four zones concerns (i) the Nb and Ta contents, lowest in z-1 and z-3 and close to 1 × C1 in z-2 and z-4, therefore resulting in negative Nb-Ta anomalies for the calculated equilibrium magma of z-1 and z-3, but not for z-2 and z-4; (ii) the Ti of the clinopyroxenes shows a negative anomaly compared to HREE for z-1 and z-3, but not for z-2 and z-4. In the associated orthopyroxene, the Ti content varies consistently. Globally, these data suggest that the FLC crystallized from distinct magma batches (more enriched for z-1 and z-3, more depleted for z-2 and z-4), possibly reflecting the involvement of distinct amounts of crustal contributions and of a heterogeneous mantle source. This will be further explored through isotopic analyses of the FLC rocks.

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WEBSTERITE AND CLINOPYROXENITE XENOLITHS FROM MIDDLE ATLAS (MOROCCO): A PRELIMINARY STUDY

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The presence of Cenozoic (35 to 0.5 Ma) alkaline volcanics, widespread in the Middle Atlas (Morocco), together with low seismic velocities suggest the existence of a thermally anomalous mantle contributing to uplift in the region. Near Azrou the late Pliocene to Quaternary volcanism formed a volcanic group (about 120 km long) of more than 100 monogenic edifices oriented N170° and brought to the surface abundant mantle xenoliths. Whereas harzburgites and lherzolites have been widely investigated [1], pyroxenite sampling is still scarce and a detailed study lacking [2]. We report here preliminary results on websterite and clinopyroxenite samples collected from two different maars deposits occurring between Bou Ibalrhatene and Boutagarouine. Pyroxenite samples from the two maars are clinopyroxenites and websterites. They are characterized by porphyroclastic texture, with wide neoblastic crystallization of clinopyroxene and orthopyroxene. Clinopyroxene porphyroclasts show orthopyroxene and garnet exsolutions, whereas orthopyroxene porphyroclasts are deformed. Moreover, the samples are characterized by extended garnet kelyphitisation around spinel grains. One olivine clinopyroxenite sample does not contain garnet and is characterized by porphyroclastic textures with neoblastic crystallization of olivine, clinopyroxene and orthopyroxene. In particular, the porphyroclasts of clinopyroxene show spinel exsolutions. At Boutagarouine maar, one olivine-bearing clinopyroxenite is characterized by porphyroblastic texture, in which clinopyroxene shows embayded boundary against neoblastic clinopyroxene. Both porphyroblasts and neoblasts show spongy outer rims. Geothermobarometry estimates based on major element chemistry suggest that websterite and clinopyroxenite samples formed in mantle domain, at pressures of 1.2-1.9 GPa, in accordance with P conditions calculated by Raffone and co-workers [1] and France [2]. Petrographic features of pyroxenites from the Bou Ibarhatene maar and their mineral chemistry data suggest progressive lithosphere cooling. Garnet exsolutions are rare in porphyroclastics clinopyroxene; they have been described by Kornprobst [3] in pyroxenites from Beni Bouchera massif (Morocco) and have been interpreted as the result of destabilization of Tschermack molecules in pyroxenes structures (mainly clinopyroxenes) after T drop. Accordingly, destabilized Al-rich clinopyroxenes produced Al-poor clinopyroxenes and garnet. T decrease was then followed by P decrease, as shown by garnet destabilizations and spinel formations, and further T decrease, as documented by garnet kelyphitisation around spinel grains that marks the changeover from Seiland subfacies conditions to Ariegite subfacies conditions [3]. Clinopyroxenites and websterites most probably formed in the mantle domains (P between 1 and 2 GPa) during collisional or post-collisional magmatism that followed Panafrican orogenic events. In contrast, pyroxenites with neoblastic textures may record the alkaline melt percolation that during Cenozoic times partially overprinted the thermally re-equilibrated lithospheric domains. This hypothesis will be discussed based on the trace elements signatures of selected pyroxenes and garnet crystals determined by LAM. The presence of widely distributed pyroxenites in old lithospheric mantle sectors is important because it imparts peculiar physical and chemical characteristics to these domains, which are thus refertilised and may become through time possible zones for enhanced magmatic activity.

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SiO_2-RICH VEINS IN THE TALLANTE MANTLE XENOLITHS (SE SPAIN): INFERENCES ON THEIR ORIGIN AND GEODYNAMIC SIGNIFICANCE

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Gabbronoritic - dioritic veins and opx-enriched harzburgites with high amounts of LILE and volatile elements are rarely documented in peridotites from mantle wedge environments, and are considered the product of SiO_2-rich melt/fluid agents of slab origin percolating and interacting with the overlying mantle [1, 2, 3, 4]. Mantle xenoliths from Cabezo Tallante (SE Spain), an eroded cinder cone of Pliocene age (2.93-2.29 Ma [5]), constitute one of these unique geologic occurrences. These xenoliths pertain to a complex geodynamic setting, the Alboran Region, featured by Neogene extension and opening of the Alboran Sea, concomitant to progressive westward retreating and roll-back of a subducting slab. In response to such geodynamic evolution, this region has been affected by widespread magmatic activity involving tholeiitic to calc-alkaline magmas followed by Late Neogene alkaline basalts (*e.g.* the Cabezo Tallante). Recent work [6] have documented that the Tallante xenoliths exceptionally record a multi-stage history of melt-rock interaction and melt intrusion tracking an extension-related 30 km uplift, consistent with the observed transition from subduction-related to alkaline magmatism. Textural relationships observed in xenoliths indicate that tholeiitic melt percolation at spinel- and plag-facies mantle depths was followed by the intrusion of opx-rich veins, in turn followed by the intrusion of alkaline amphibole pyroxenites; this constrains the gabbronoritic veining at 0.7-1 GPa. In this paper, we present the results of ongoing microstructural and geochemical studies on the opx-rich veins, aimed to define their origin and discuss the significance of this magmatic event in the context of the geodynamic evolution of the Alboran Region. Different types of opx-bearing veins, likely reflecting multiple melt inputs, have been observed in the xenoliths: i) coarse opx-rich veins, mostly consisting of large (mm-sized) orthopyroxene grains showing clear replacive contacts against mantle olivine; similar texture is also observed in some opx-enriched harzburgite xenoliths, ii) thin fine-grained cross-cutting gabbronoritic veins, constituted by opx, plagioclase and subordinate cpx, showing a fine-grained opx reaction rim against the host peridotite. Remarkably, plag and opx in these latter veins host Cl-apatite micro-crystals. Minerals in the veins are all significantly and selectively enriched in Th, U, LREE (apatite up to 30000-80000 × PM). These features indicate that parental melts to the gabbronoritic veins were Si-saturated, enriched in LILE and volatile (Cl) components and depleted in Nb, Ta, consistent with subduction-related melts reflecting either a continental crust or terrigenous sediment source. *In situ* U-Pb dating on zircons in the veins [7] have yielded 2.2-4.4 Ma ages, thus indicating a close temporal relation of this magmatic event with the Late Miocene slab detachment and the host alkaline Tallante volcanism. According to recent models [5], we propose that Neogene lithosphere extension led to uplift and migration of lithospheric mantle sectors (as the mantle presently sampled at Tallante) from an inner part of the mantle wedge towards a position above a slab edge or slab detachment zone. This allowed upwelling of hot asthenosphere which generated the alkaline magmatism, and possibly induced melting of the subducting slab [8], that originated the observed SiO_2-rich melts.

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ORIGIN OF OLIVINE-RICH TROCTOLITES FROM LIGURIAN OPHIOLITES (ITALY): IMPLICATIONS FOR OCEANIC CRUSTAL ACCRETION

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The Internal Ligurian ophiolites from Northern Apennine represent lithosphere fragments of an intra-oceanic domain of the Middle-Upper Jurassic Ligurian-Piedmontese basin. The gabbroic plutons from Internal Ligurian ophiolites include up to 80 m thick bodies made up of olivine-rich troctolite [1, 2]. The olivine-rich troctolites consist mainly of olivine (Fo = 87-88 mol.%), minor anhedral plagioclase and accessory amounts of spinel and poikilitic clinopyroxene. The olivine-rich troctolites locally include: (i) spinel-bearing dunitic clots, (ii) plagioclase-clinopyroxene veins showing diffuse margins against host rocks, (iii) spinel-plagioclase layers. In addition, one of the studied olivine-rich troctolite bodies contains a lens displaying a "harrisitic" pegmatoid texture, in which coarse-grained dendritic olivine is intergrown with plagioclase and clinopyroxene. The rounded to embayed morphology of olivine and spinel from the olivine-rich troctolites, together with the anomalously high Mg# (88-90) and Cr (2400-3000 ppm) values of associated clinopyroxene, indicate that these rocks formed by reaction between an olivine-spinel matrix and an infiltrating melt. This interpretation is substantiated by the occurrence of spinel-bearing dunitic clots and plagioclase-clinopyroxene veins, which are interpreted as relics of pre-existing olivine-spinel matrix and crystallization products of infiltrating melts, respectively. A similar hypothesis was recently proposed for the origin of olivine-rich troctolites from Atlantis Massif (Mid Atlantic Ridge, 30°N) [3, 4]. The incompatible element signature of clinopyroxene from olivine-rich troctolites of Internal Ligurian ophiolites shows that the infiltrating melts were similar to MORB. The amount of melt added to the olivine-spinel matrix to produce the olivine-rich troctolites is estimated to be of ~ 25%. Spinel from the olivine-rich troctolites, dunitic clots and spinel-plagioclase layers contain inclusions of Ti-pargasite/kaersutite, phlogopite/aspidolite, orthopyroxene and, locally, of ilmenite and loveringite. The origin of the inclusion-bearing spinels is attributed to crystallization of hybrid melts derived from interaction of evolved melts rich in incompatible melts with injections of primitive melts. We propose that the evolved melts formed in mantle dunitic conduits, near the base of the conductive boundary layer. In this context, an olivine-spinel matrix of replacive origin was impregnated by MORB-type melts saturated in plagioclase + clinopyroxene, thus giving rise to olivine-rich troctolites bodies. These bodies were subsequently dissected by multiple gabbroic sill intrusions, which gave rise to the gabbroic plutons. The harrisite-textured lenses presumably formed by crystallization of undercooled hybrid melts, produced by interaction of MORB-type melt injections with residual melts formed by precipitation of the spinel-plagioclase layers.

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A 2 KM THICK LAYERED GABBRO SECTION FROM ALPINE JURASSIC OPHIOLITE (PINETO MASSIF, NORTHERN CORSICA)

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The Pineto Massif from Northern Corsica consists of a layered gabbroic section locally intruded by basalt dykes with N-MORB geochemical signature [1, 2]. The gabbroic section is covered by a thin sedimentary cover made of Middle-Upper Jurassic radiolarian cherts and Createaceous Palombini shales [3]. In addition, a basalt flow layer (a few metres thick) with N-MORB geochemical signature is locally present at the contact between the gabbros and overlying sedimentary cover. The reduced thickness of the Jurassic volcano-sedimentary cover was attributed to a paleo-morphological high in the Ligurian-Piedmontese basin [3]. New field and petrographic investigations allowed us to reconstruct the original pseudo-stratigraphy of the Pineto gabbroic section, which may be subdivided into two distinct units. The Lower unit consists mainly of troctolites and minor olivine-gabbros displaying a well developed modal and/or grain size layering, as for instance shown by frequent pegmatoid lenses or by levels of foliated troctolites. The Upper unit is mostly made up of coarse-grained clinopyroxene-rich gabbros, which display a weak modal and/or grain size layering, which is mainly revealed by pegmatoid and microgabbro lenses. In addition, these clinopyroxene-rich gabbros are locally intruded by Fe-Ti-oxide gabbro bodies showing diffuse contacts with host rocks. In the Upper unit, we also found troctolite and olivine-rich troctolite bodies (up to a few tens of metres in thickness) interlayered with the clinopyroxene-rich gabbros. Modal/grain size layering in the gabbroic rocks from Upper and Lower units is concordant and roughly parallel to the stratification of the sedimentary cover. We have thus evaluated the thickness of the exposed gabbroic section, which reaches about 2000 m. Furthermore, the Pineto gabbroic section contains a few mantle peridotite bodies (up to about 100 m in thickness) that are mainly located near the transition between the Lower and Upper units. These mantle peridotites display a spinel-facies foliation which forms a high angle with respect to the layering of host gabbros and are locally crosscut by gabbroic dykes. Our preliminary data suggest that the Pineto gabbroic section formed by a process of sills accretion, as recently indicated for the building of the gabbroic plutons exposed along (ultra-)slow spreading ridges [4].

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INTERPLAY BETWEEN TECTONIC AND MAGMATIC EVENTS DURING EXHUMATION OF A GABBRO-PERIDOTITE SECTION TO THE SEAFLOOR (INTERNAL LIGURIAN OPHIOLITES)

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The Scogna-Rocchetta Vara ophiolite (Internal Ligurian units, Northern Apennine) is attributed to an intra-oceanic domain of the Jurassic Ligurian-Piedmontese basin and is characterised by the lack of the basalt flow layer, similar to many magma-poor segments from (ultra-)slow spreading ridges [3]. The mantle sequence of the Scogna-Rocchetta Vara ophiolite consists mostly of spinel facies lherzolites with tectonitic to mylonitic fabric. The chemical compositions of porphyroclastic clinopyroxene from these lherzolites document a depleted geochemical signature, similar to what found by [1, 2] for another mantle sequence of Internal Ligurian ophiolites. The lherzolites locally include thin pyroxenite layers, which are boudinaged and elongated concordantly with respect to the foliation of host rocks. The origin of the pyroxenites is attributed to infiltration of MORB-type melts under spinel facies conditions. In addition, the lherzolites contain a high modal proportion of plagioclase, which commonly forms micro-veins that are oriented nearly parallel to the spinel facies foliation of host rocks. These veinlets show that the decompression of the mantle sequence to plagioclase facies conditions was associated with melt impregnation by silica-oversatured melts. The lherzolite structures are locally replaced by dunite bodies, which include spinel trails that are oriented nearly concordant with the contact with host lherzolites and their foliation. These dunites are interpreted to derive from pyroxene reactive dissolution by silica-undersaturated melts. The mantle ultramafics are crosscut by two generations of gabbroic bodies, which both retain a MORB-type geochemical signature. The first is represented by olivine-rich gabbroic dykes that are nearly parallel to the mantle structures and display diffuse contacts with host peridotites. These dykes are post-dated by sills made up of clinopyroxene-rich gabbro, which show sharp planar boundaries and crosscut at a high angle the foliation of host peridotites. The formation of the gabbroic sills is most likely associated with the building of a huge gabbroic pluton (up to 400 m thick) that intrudes the mantle sequence. The gabbroic pluton consists mainly of clinopyroxene-rich gabbros and minor olivine-gabbros to troctolites. Gabbros to troctolites are locally characterised by a weak modal and/or grain size layering, which is nearly parallel to the orientation of the gabbroic sills. The gabbroic pluton contains up to 80 m thick bodies made up of olivine-rich troctolites and up to 50 m thick mantle lenses. The structural and compositional features of these mantle lenses reveal the same origin and exhumation-related history of the mantle sequence enclosing the gabbroic pluton. In particular, the structures of the mantle lenses and the mantle sequence are geometrically concordant. The clinopyroxene-rich gabbros from the gabbroic pluton are in places characterised by a ductile shear foliation that forms a low angle with respect to the igneous layering. The ductile deformation evolution comprises early re-crystallisation of clinopyroxene and plagioclase (± Ti-pargasite) at T ~ 850°C, followed by an amphibolite facies event associated with development of hornblende and plagioclase at T ~ 700°C. The gabbroic pluton is finally crosscut by basalt dykes with chilled margins, which form a high angle with respect to the igneous fabric of host gabbros. The basalt dyking represents the last event of injection of MORB-type melts that occurred during exhumation of studied section to the seafloor.

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MINERALS FROM EMILIAN OPHIOLITES

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Ophiolites of the Northern Apennine [1] differ from Western Alps ones because of the lack of eclogite- and blueschist-facies orogenic metamorphism. However, they display a low-grade oceanic metamorphism and syn-orogenic deformation caused by north-eastwards thrusting onto the Adriatic continental margin. Emilian ophiolites belong to the Esternal Liguride domains and represent an ocean-continent transition zone. However, they accommodate some volcanic-associated massive sulfides (VMS), so we can emphasize two main mineralogical associations, the VMS one and the low-grade oceanic metamorphism one.

VMS deposits are stratiform ores in seafloor breccia (Corchia, PR), stockwork veins in serpentinites (Ferriere, Vigonzano and Groppallo, PC) or in basalts (Boccassuolo and Montecreto, MO) [2]. Sulfides occur also as stratiform ore in massive serpentine in Corchia (PR), whereas in Bisano (BO) sulfides occur in basalts. These sulfide deposits in Emilian ophiolites are characterized by the typical hydrothermal assemblage pyrite-chalcopyrite-sphalerite, often accompanied by pyrrhotite, galena, magnetite. There are numerous other accessory ore minerals like gold, silver, linneite, acanthite, freibergite, uraninite, hydroromarchite, siegenite, molybdenite, smithsonite (Corchia, PR), millerite, hematite, marcasite, chromite (Vigonzano and Ferriere, PC), rutile, ilmenite and limonite (Boccassuolo and Montecreto, MO). The major gangue minerals are quartz, chlorite and Ca- and Fe-carbonates, with accessory epidote, titanite, apatite and zircon. Superficial alterations of the sulfides, like hydratation or oxydation reactions, produce new minerals, especially carbonates and sulfates, like aurichalcite, azurite, hydrozincite, malachite and serpierite (Boccassuolo), or brochantite, chrysocolla, delafossite, ferricopiapite, halotrichite, hydrohonessite, langite, mooihoekite, posnjakite, romerite, szomolnokite (Corchia).

In Emilian ophiolites primary assemblage is replaced by a greenschist- to prehnite-pumpellyite- facies metamorphic one related to oceanic hydrothermal alteration. The main effects of this alteration are silica liberation and calcium mobilization. In ophiolitic basalts and gabbros plagioclase is altered into albite + prehnite ± epidote ± pumpellyite association, clinopyroxene is partially replaced by chlorite + amphibole (actinolite) and Fe-Ti oxide phases are frequently converted into titanite. Many hydrothermal veins are hosted in basalts and gabbros, and here several minerals occur in euhedral or subhedral crystals: datolite, calcite, prehnite and minor natrolite, analcime, barite, hematite, magnetite, andradite and laumontite. Emilian serpentinites are mainly fertile spinel lherzolites containing sometimes pyroxenite layers; the most important phases are lizardite, chrysotile, magnetite, Cr-spinel and chlorite. Several thin hydrothermal veins are hosted in these rocks, with aragonite, calcite, titanite and some Mg-rich phases like artinite (Val Taro, PR), hydromagnesite and pyroaurite (S. Agostino, PC). Some rodingite dikes intrude serpentinitic bodies (Groppo Gorro, PR, Serra del Zanchetto, BO), with their characteristic mineralogical assemblage: prehnite, grossular, diopside and sometimes vesuvianite. Hydrothermally altered rocks, always in small blocks of few cubic meters, have a lot of fractures filled with quartz and carbonates. In several cases, in these fractures are present crystals of anatase, brookite, millerite, vaesite, jamborite, reevesite.

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ZrO_2-$ZrTi_2O_6$ SOLID SOLUTIONS IN GARNET PERIDOTITE FROM MONTE DURIA (CENTRAL ALPS): PETROLOGICAL AND GEOCHEMICAL IMPLICATIONS

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Garnet lherzolites have been found in the upper part of the Adula-Cima Lunga unit, which represents the uppermost nappe of the lower Penninic system of the Central Alps. They were reported at three localities: 1) Monte Duria, 2) Alpe Arami, and 3) Cima di Gagnone [1].

At Monte Duria (Como, Italy), garnet lherzolites occur in > 20 ultramafic bodies, which form 10-100 m boudins within migmatitic gneisses. Garnet (grt) is porphyroblastic occurring in a porphyroclastic matrix composed of olivine (ol), orthopyroxene (opx), clinopyroxene (cpx) and amphibole (amph). Grt is prograde and developed after an amph + spl stage. The metamorphic peak has been estimated at 3 GPa and 830°C by [1]. Isothermal decompression down to 0.7 GPa, 720°C led to development of spl + cpx + opx + amph assemblages [2]. Zircons from spl-bearing assemblages yielded SHRIMP ages of 33-34 Ma [2], confirming that these mantle-wedge peridotites equilibrated during the Alpine orogeny.

We recently collected several samples of garnet peridotite and garnet clinopyroxenite from Monte Duria, and the host gneiss. Rocks are first investigated by backscattered-electron microscopy followed by electron-microprobe analysis.

Ultramafic rocks are embedded in migmatitic sillimanite+biotite metapelites. The more preserved rock samples contain garnet (X_{Mg} = 0.16) with inclusions of staurolite (X_{Mg} = 17), quartz, white mica (X_{Mg} = 0.48; Si = 3.11 apfu), and kyanite.

Garnet clinopyroxenite is composed of garnet (Py_{52}; Cr_2O_3 up to 0.10 wt.%) and clinopyroxene ($Jd_{0.5}$). Clinopyroxene is often replaced by amphibole (edenite). Accessory phases are: rutile, ilmenite, and unzoned zircon (up to 100 μm).

Garnet peridotite is composed of olivine (X_{Mg} = 0.88), orthopyroxene (X_{Mg} = 0.88), clinopyroxene ($Jd_{0.5}$) and garnet (Py_{68}; Cr_2O_3 up to 1.45 wt.%). Common accessory phases are ilmenite, rutile and sulphides. Cr-rich spinel (up to Cr/(Al+Cr) = 0.55) is sometimes included in garnet. Kelyphitic symplectites surround garnet as a result of the reaction ol + grt = opx + cpx + spl or ol + grt + H_2O = opx + amph + spl. These reactions produced double coronas, one composed of opx (former ol) and one composed of cpx/amph + opx+ spl (former grt).

In one kelyphite, we observe the uncommon occurrence of ZrO_2 (baddeleyite) and $ZrTi_2O_6$ (srilankite). This is the first report of baddeleyite in peridotite and the second of srilankite in ultramafics [3]. The tiny crystals (~ 1 μm) are invariably located in the opx corona after ol. The cpx + opx + spl corona (after grt) contains, instead, zircon. Zirconium oxides should have formed during decompression through a reaction of the type $Mg_2SiO_4 + ZrSiO_4 = MgSiO_3 + ZrO_2$, already predicted by [4] but never reported in natural rocks. ZrO_2 and $ZrTi_2O_6$ display a low amount of solid solution. According to [5], these compositions are consistent with T well below 1200°C, above which $ZrTi_2O_6$ becomes disordered $(Zr,Ti)_2O_4$ with Zr/(Zr+Ti) ~ 0.5 and ZrO_2 becomes Ti rich (Zr/(Zr+Ti) = 0.8 at 1200°C, 2 GPa). Thermodynamic modeling of the proposed reaction will be performed in order to check its consistency with published P-T estimates. We believe that these Zr-bearing phases could provide information about petrogenetic conditions of the peridotite from Duria. In addition, they will constrain Zr mobility in mantle wedge and zircon stability in mantle rocks.

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GEOCHEMISTRY OF GARNETS AND CLINOPYROXENES IN MICROXENOLITHS FROM THE ZAGADOCHNAYA KIMBERLITE (YAKUTIA, RUSSIA)

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The major and trace element composition of garnets and clinopyroxenes in microxenoliths from the Zagadochnaya kimberlite (Yakutia, Russia) has been investigated by EMPA and LA-ICP-MS analysis. The microxenoliths consist of coarse garnet xenocrysts, which sometimes contain or are intergrown with mm-sized, primary grains of clinopyroxene and of a completely serpentinized mineral (olivine or orthopyroxene?). The garnets show broadly lherzolitic to megacryst-like major element compositions, with Cr_2O_3 1.3-8.6 wt.%, CaO 4.2-7.4 wt.%, and Mg# 79-82. On the basis of petrographic and geochemical features, the garnets can be subdivided into three main groups.

Group A garnets are unzoned and are associated with coarse, sub-round chromian diopsides. They have moderate Cr_2O_3 contents (1.3-5.2 wt.%) and are characterized by progressively increasing CI-normalized REE from La to Lu, with HREE close to 10 × CI. In primitive-mantle-normalized multielement diagrams, they show strong negative Sr anomalies, no Zr-Hf anomaly, and small negative Ti anomalies. The associated diopsides are moderately LREE-enriched, with La_N/Sm_N ratios between 0.9 and 4.2, and exhibit an intermediate character between groups IIa and IIb studied by [1], which were interpreted as fragments of variably metasomatized lherzolites. This group broadly resembles garnets and clinopyroxenes from high-temperature lherzolites and megacrysts from the nearby Udachnaya kimberlite [2], suggesting derivation from strongly metasomatized peridotites or, possibly, magmatic segregates (*cf.* Type II garnets of [3]). Group B garnets are variably enriched in Cr_2O_3 (5.4-8.6 wt.%) and are distinguished from group A by a less LREE-depleted composition and nearly flat normalized pattern from Sm to Lu. Grain to grain REE variations are larger than in Group A (HREE *ca.* 1 to 10 × CI). The most REE-rich samples show similarities with garnets from some high-temperature lherzolites from Udachnaya [4] and other kimberlites (cf. some cores of Type Ia garnets of [3]). Group C garnets are Cr_2O_3-rich (7.3-8.4 wt.%) and are characterized by strongly sinusoidal REE patterns with Yb_N between 0.5 and 3.0. These compositions are typical for cratonic garnet lherzolites produced by refertilization of strongly refractory peridotites.

Some garnets in groups B and C show areas rich in secondary chromian diopside + chromian spinel ± phlogopite ± amphibole inclusions. The distribution of the inclusions suggests formation by reaction with an infiltrating melt. These garnets show pronounced patchy zoning, with development of (Ca, Cr)-poor domains in the inclusion-rich areas. In these (Ca, Cr)-poor domains, the REE tend to show convex-upward patterns with a maximum at Eu and a negative slope for the HREE, associated with strong negative Sr, Hf and Ti anomalies. The secondary diopsides are enriched in Cr and Na (up to 13 mol.% of kosmochlor component), which are negatively correlated with Mg#, and show strongly LREE-enriched (La_N ~100), convex-upward patterns. Their compositions essentially correspond to those of group IIIa diopsides of [1], thus supporting the interpretation of these clinopyroxenes as products of second-stage melt infiltration on metasomatized garnet lherzolites.

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SESSION 1.4

Magmatism and Geodynamics (session in memory of Fabrizio Innocenti)

Convenors:

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E. Rampone (*Univ. of Genova*)

MAGMATIC CONSTRAINTS TO THE GEODYNAMIC EVOLUTION OF THE EASTERN MEDITERRANEAN – IN HONOUR OF FABRIZIO INNOCENTI

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From his first time working in the Eastern Mediterranean (1969, Western Anatolia and Lesvos island) to his last field trip in the Volos-Evia area (June 2007) Fabrizio Innocenti has always been thinking that this region was one of the best natural laboratory to study the relationships between plate dynamics and magmatic activity, especially concerning the recycling of subducted materials and the subduction-related extension. He was attracted, since his very last days, from the unique variety of volcanic products erupted in a limited space-time interval, and he stimulated many researchers to build a multidisciplinary team to describe the evolution of magmatic activity and the relationships between magmatism and geodynamics.

The main questions triggering his interests for this region were: "why in this subduction zone the magmatism is far more complex than in other bigger and older subduction zones?" and "why this northeastward-directed subduction zone has a backarc and does not fit the rule of subduction asymmetries according to their polarity?".

These topics were faced in the last ten years and were recently reviewed [1]. Here, Magmatism in the eastern Mediterranean region (FYROM, Greece, South Bulgaria as well as Thrace, Western and Central Anatolia of Turkey) was subdivided in 18 magmatic provinces, ranging in age from Eocene to present: most of the products exhibit a calc-alkaline (*sensu lato*) geochemical affinity and the typical characters of rocks sourced in a subduction-modified mantle wedge. In addition, asthenosphere-sourced alkali basalts are found, with ages variable from Upper Miocene to Pleistocene. Some systematic differences in trace elements ratios as well as Sr and Nd isotopes are found among subduction-related products erupted north and south of the Pelagonian-Actic-Cycladic-Menderes massif pointing out that a lithospheric mantle wedge occurs northward and a depleted asthenospheric mantle wedge southward [2]. The evolution of subduction related products from calc-alkaline to shoshonitic to ultra-K is matched by progressive lowering of δ^{11}B and δ^{7}Li down to extreme light B and Li isotope signatures: this was interpreted as due to the occurrence of a thin, non-convecting mantle wedge.

The magmatologic constraints were merged with new geodetic computations, geophysical and geo-structural data in order to build a new geodynamic model explaining the evolution of the region, and its backarc extension [3]. The Aegean is an atypical backarc, where extension is not linked to progressive slab roll-back and steepening, but to the differential advancement of the upper lithosphere over a heterogeneous lower African plate: The Greek microplate overrides the Ionian oceanic segment of the African plate faster than the Anatolian microplate over the thicker Levantine more continental segment. The subducted slab has a very low angle and, in an "absolute" reference frame, is not sinking into the mantle, but it is rather moving out, triggering a suction flow from the underlying asthenosphere and the lower part of the upper mantle.

The geodynamic model developed for the Aegean area may have important implications for two more general topics: the fate of the subducted slabs along east- and northeast-directed subduction systems, the recycling of crustal material into the mantle, and the mechanisms of growth of the continental lithosphere.

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PERIDOTITE XENOLITHS FROM ETHIOPIA: INFERENCES ON MANTLE PROCESSES FROM PLUME TO RIFT SETTINGS

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A comprehensive petrological study has been carried out on Ethiopian mantle xenoliths entrained in Neogene-Quaternary alkaline lavas both overlying the Continental Flood Basalt area (Dedessa River - Wollega Region, Injibara - Gojam Region) and from southern Main Ethiopian Rift (MER - Mega, Sidamo Region) in order to investigate the mantle evolution from plume to rift settings.

Mantle xenoliths from the plateau area (Injibara, Dedessa River) range in composition from spinel lherzolite to harzburgite and olivine websterite, showing P-T equilibration conditions in the range of 1-2 GPa/950-1050°C. These xenoliths show flat chondrite-normalized bulk-rock REE patterns, with only few LREE-enriched samples (La_N/Yb_N up to 5). Clinopyroxene (cpx) REE patterns are generally flat or LREE depleted (La_N/Yb_N down to 0.6). Sr-Nd isotopes on separated cpx mainly show compositions ($^{87}Sr/^{86}Sr < 0.7030$; $^{143}Nd/^{144}Nd > 0.5132$) approaching the Depleted Mantle end-member, or displaced ($^{87}Sr/^{86}Sr$ 0.7033-0.7034; $^{143}Nd/^{144}Nd$ 0.5129-0.5128) toward the Enriched Mantle components which also characterize the Ethiopian Oligocene plateau basalts. These characteristics indicate that most xenoliths reflect complex asthenosphere/lithosphere interactions due to plume-related refertilization processes, whose agents may be envisaged as mafic subalkaline melts that infiltrated and reacted with the pristine parageneses ultimately leading to the formation of olivine-websterite domains.

On the other hand, mantle xenoliths from southern MER (Mega) consist of spinel lherzolite to harzburgites showing various degrees of deformation and recrystallization coupled with an extremely wide incompatible element distribution. Bulk rock Rare Earth Element (REE) patterns show generally flat HREE ranging from 0.1 × chondrite (ch) in harzburgites up to 2 × ch in fertile lherzolites, and are variably enriched in LREE, with La_N/Yb_N up to 41.5. The constituent clinopyroxenes have flat HREE distribution and La_N/Yb_N between 0.1 and 55, in general agreement with the respective bulk rock chemistry. Sr-Nd-Pb on separeted clinopyroxenes are $^{87}Sr/^{86}Sr$ 0.70220-0.70310, $^{143}Nd/^{144}Nd$ 0.51301-0.51379, $^{206}Pb/^{204}Pb$ 18.38-19.34 for lherzolites, and $^{87}Sr/^{86}Sr$ 0.70268-0.70326, $^{143}Nd/^{144}Nd$ 0.51275-0.51305, $^{206}Pb/^{204}Pb$ 18.46-18.52 for harzburgites, thus ranging in composition between the DM and HIMU mantle end-members. These data suggest variably carbonated alkali-silicate melt(s) as the main metasomatic agent(s) of southern MER xenoliths in agreement with what observed in other mantle xenolith occurrences set along the Red Sea and Gulf of Aden rifted continental margins which radiate from the Afar triple point.

The decidedly different types of metasomatic agents recorded in Ethiopian mantle xenoliths, from the CFB area to the Rift system, clearly reflect distinct tectonomagmatic settings, *i.e.* the plume-related Oligocene subalkaline magmatism and the Neogene rift-related alkaline volcanism.

FELSIC VEINS IN PERIDOTITE XENOLITHS FROM TALLANTE (BETIC CORDILLERA, SPAIN)

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Mantle xenoliths from Tallante (Betic Cordillera, Spain) include samples recording a peculiar style of metasomatism that induces orthopyroxene (opx), plagioclase (pl), phlogopite (ph) and amphibole (amph) crystallisation, forming mantle domains characterized by “hydrous” opx-rich peridotites, locally crosscut by felsic veinlets containing pl and opx + quartz + ph + amph, *i.e.* ph/amph-bearing anorthosites, diorites and gabbronorites [1, 2, 3]. This indicates that the causative agents were hydrous silica-oversaturated melts rich in alkalis, plausibly related to the recycle - *via* subduction - of crust components within the mantle.

To find new evidences we sampled and carefully sliced *ca.* 250 xenoliths finding 9 samples with clear evidences of felsic (gabbroic) veins/lenses cross-cutting the peridotite matrix. These are extremely variable in size, from millimetric up to centimetric. In general, we observed that thinner lenses (possibly representing apophyses of bigger veins) tend to have more complex mineral parageneses, also including traces apatite, zircon, Ti (Nb) oxide (rutile), and crystals mainly made by thorium + cerium, lanthanum, phosphorous (huttonite/monazite mineral groups).

Sr-Nd analyses have been carried out at the IGG-CNR of Pisa on a) plagioclase carefully separated from distinct felsic veins, and b) cpx separated from the surrounding peridotite matrix. The data reveal that centimetric veins are characterized by extremely high Sr isotopic composition (^{87}Sr/^{86}Sr up to 0.71266) and low Nd isotopic composition (^{143}Nd/^{144}Nd down to 0.51211) recording remarkable isotopic difference with the surrounding peridotite country rock. This isotopic fingerprint indicates the involvement of “continental” crust (sediments?) within the subducted lithologies. Millimeter veinlets tend to re- equilibrate with the surrounding peridotite matrix showing Sr-Nd isotopic values within the range of unveined (anhydrous) peridotite xenoliths from Tallante.

In situ U-Pb datings have been performed at the IGG-CNR of Pavia on zircons from two different samples by laser-ablation microprobe (GeoLas200Q-Microlas) coupled to a magnetic sector HR-ICPMS (Element from ThermoFinnigan), suggesting that the age of the veining event ranges between 4.4 and 2.2 Ma, thus implying a clear relation with the Tertiary subduction process that ultimately lead to the formation of the Betic Cordillera.

In this framework, we propose relationships between these exotic mantle lithologies and the Cenozoic subduction related magmas (including lamproites; [4]) that are widespread in the region.

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PYROXENITES IN THE WESTERN EXTERNAL LIGURIDE OPHIOLITIC PERIDOTITE MASSIFS (N. APENNINES, ITALY): ORIGIN AND IMPLICATIONS ON MANTLE HETEROGENEITY

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Pyroxenites are largely considered a minor, but ubiquitous, mantle component capable to explain a large part of the compositional variability observed in oceanic basalts [1, 2, 3]. Layers, irregular bodies and dykes of pyroxenites are commonly documented in the subcontinental lithospheric mantle [1], and rarely found in abyssal peridotites [*e.g.* 4]. They have been related to crystal accumulation of mantle-derived magmas, melt-peridotite interaction and recycling of ancient oceanic crust [5]. Pyroxenites are diffuse in the ophiolitic mantle peridotites from the Alpine-Apennine system. Here we report preliminary results of field, microstructural and bulk-mineral chemistry investigations on pyroxenites from the western peridotite massifs of the External Liguride ophiolitic Units (Northern Apennines, Italy). The aim is two-fold: i) to widen knowledge on the origin of pyroxenites in MORB-type settings and discuss the effects of small-scale chemical heterogeneities in the mantle, ii) to provide insights on the oldest and deepest magmatic stages recorded in the Northern Apennine ophiolitic peridotites. Pyroxenites mostly occur as cm-thick bands (up to 12 cm) parallel to the tectonite mantle foliation, and range from spinel-bearing websterites to clinopyroxenites. They show mineralogical zoning and, frequently, opx-rich rims towards the wall-rock peridotites. Both pyroxenites and hosting peridotites are partially re-equilibrated at plagioclase-facies conditions. One sample consists of a thicker clinopyroxenite lens, and it shows the occurrence of Al-rich spinel + clinopyroxene clusters. Rare clinopyroxenites also occur as later dm-thick dykes crosscutting the peridotite foliation. In representative outcrops, pyroxenite, wall-rock and host peridotite from single dm-scale profiles were also sampled. Pyroxenite whole-rock and mineral compositions are extremely heterogeneous. Major element bulk abundances almost cover the whole compositional range of worldwide lithospheric pyroxenites (Mg# = 74-88, Al_2O_3 = 10-17 wt.%, CaO = 7-20 wt.%). On the basis of bulk and mineral REE concentrations four major groups of pyroxenites have been identified. *Group A* shows cpx with LREE-depleted and M-H-REE variably enriched spectra coupled to high Sc, V contents (Sm_N/Yb_N = 0.23-0.29); *Group B* has cpx and bulk with homogeneous, slightly LREE depleted spectra (cpx: Sm_N/Yb_N = 0.58-0.86); *Group C* shows slight LREE enrichment (cpx: Sm_N/Yb_N = 0.9-1.4); *Group D*, the clinopyroxenite dyke, has cpx and bulk with convex REE patterns and absent Ti, Zr, Hf anomalies. The chemistry of most pyroxenites seems to reflect high-pressure magma segregation of tholeiitic melts dominated by clinopyroxene crystallization and, for some of them (Group A), by variable amount of garnet. On the other hand, the later pyroxenite dyke exhibits an alkaline affinity. Bulk and mineral chemical profiles indicate that cm-scale element diffusion from pyroxenite to wall-rock and host peridotite occurred, presumably during emplacement or subsequent incipient melting of pyroxenites. Sr, Nd, Hf isotopic investigations on pyroxenites and peridotites, actually in progress, will contribute to define the age and origin of different pyroxenites, and the role of peridotite-pyroxenite interaction in generating small-scale isotopic mantle heterogeneities.

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GEOCHEMISTRY OF CAMP DYKES AND SILLS FROM EASTERN NORTH AMERICA

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Numerous dykes and a few sills outcrop in the south-eastern U.S.A., between the Piedmont area of the Appalachians and the Atlantic coast, from Georgia to Virginia. Aeromagnetic data allowed the recognition of three different dyke swarms on the basis of their directions: NW, NE and N-S trending dykes [1] the latter being the youngest, according to intersection relationships. $^{40}Ar/^{39}Ar$ ages (*ca.* 199-197 Ma; *e.g.* [2]) proved these dykes to belong to the Central Atlantic Magmatic province (CAMP; [3]). Here we present geochemical data for 77 newly sampled dykes and sills intruded either in the Paleo-Proterozoic crystalline basement or in the Triassic sedimentary basins of the Newark supergroup.

The studied rocks show ophitic, intergranular or porphyiritic textures; some are olivine- and orthopyroxene-bearing, whereas others show a more evolved character, with well developed pigeonite crystals and graphic quartz and feldspar intergrowths. Major element analyses indicate a large compositional spectrum (SiO_2 46-54 wt.%, MgO 5-13 wt.%) for these rocks that classify as basalts and basaltic andesites. These large variations are partly due to mineral accumulation and to different degrees of differentiation, but do not highlight systematic differences linked to the trend of the dykes, nor to their geographic position.

Preliminary isotopic analyses are presently limited to $^{87}Sr/^{86}Sr$ and will be completed with $^{143}Nd/^{144}Nd$ and Pb isotopic ratios. $^{87}Sr/^{86}Sr_i$ (back-corrected to 200 Ma) for 24 samples (0.70395-0.70812) are in good agreement with the previously published $^{87}Sr/^{86}Sr$ data (0.7044-0.7072) [4]. The large variations of $^{87}Sr/^{86}Sr_i$ do not show clear correlations with major and available trace element data and are in general lower than those of the CAMP lava flows from the Newark basins ($^{87}Sr/^{86}Sr_i$ *ca.* 0.705-0.707) suggesting either a strongly heterogeneous mantle-source composition or variable degrees of crustal contamination.

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MAGMA EMPLACEMENT IN A TRANSFER ZONE: THE MIOCENE MAFIC ORANO DYKE SWARM OF ELBA ISLAND, TUSCANY

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Dykes represent the common pathways of magmas ascending through the crust and offer the potential to reconstruct stress fields at the time of their intrusion because they directly record the strain associated with emplacement. However, the reconstruction of the paleostress can be biased by other factors, such as the magma driving pressure as well as structure of the crust and its rheological heterogeneities. In this respect, the study of dyke swarms emplaced in a granitic host can mitigate this overall complexity affecting paleostress reconstruction. Indeed, because of the high degree of mechanical isotropy of the granitic host, these dykes have the potential to provide more straightforward information about the stress field active during dyke emplacement than do dykes in layered sedimentary or metamorphic host rocks.

The Late Miocene Monte Capanne pluton of Elba Island (Tuscany, Italy) is crosscut by the late- to post-plutonic mafic Orano dyke swarm [1], which provides information on the activity within a regional transfer zone and its relationships with the Miocene-Quaternary magmatism throughout the northern Tyrrhenian region.

The magmatic activity in the western part of Elba Island, which lasted approximately 1.5 Ma during the late Miocene, built an intrusive complex of nested Christmas-tree laccoliths, a 10 km-diameter pluton (Monte Capanne) and, finally, the steeply dipping Orano dyke swarm. This igneous activity occurred in an extensional regime at a magmatic centre in the wake of the eastward-migrating compression of the Apennine front. The Orano dyke swarm consists of hybridized mantle-derived magmas, constituting about 200 dykes totalling a length of approximately 90 km. These dykes intruded the north-western part of the pluton and its contact aureole, as well as several kilometres of sedimentary rock above. Dyke emplacement occurred near the end of pluton crystallization, above a source region marked by a positive magnetic anomaly located in the north-western part of the pluton. Dyke orientations are dominated by a major system trending N78E, and a minor system of dykes with N38W and N22E trends.

The emplacement patterns of the Orano dykes preserve the strain that resulted in exploitation of Riedel fractures in a NE-SW dextral shear zone; local internal zones of sinistral shear account for one set of the minor system [1]. This shearing occurred between offset segments of the Elba Ridge in the Western Elba transfer zone, where strain concentrated magma flow to build the western Elba magmatic complex. This zone developed as a result of differential extension rates during the formation of the north-trending Neogene-Quaternary sedimentary basins. Such basins are connected regionally by NE-trending lineaments, along which all the magmatic centres in the northern Tyrrhenian-Tuscan area are distributed. The magmatic activity developed as a wave moving northeastward across the region, suggesting that magmatism was focused by transfer zone development, as back-arc extension migrated in that direction and reactivated older faults.

Magmatic activity at most of the Tuscan igneous centres was short-lived, occurring with the emplacement of either a single magmatic mass or a few intrusive units in a short time span. In contrast, formation of the western Elba magmatic complex [1] and the Larderello-Travale buried intrusions [2], were long-lived events (1.5 to 2.5 Ma). The fact that these two igneous centres lie on the "Western Elba-Piombino-Faenza" transversal line suggests that it represents the most significant alignment of transfer zones in the northern Tyrrhenian-Apennine system.

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THE MAGMATIC FEEDING SYSTEM OF THE CAMPI FLEGREI CALDERA: ARCHITECTURE AND TEMPORAL EVOLUTION

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Sr, Nd, Pb and B isotopic data are combined with composition of the Campi Flegrei erupted magmas, and structural setting and dynamics of the resurgent caldera to develop a model on both structure and evolution of its magmatic feeding system.

Campi Flegrei parental magmas (K basalts) are generated in a subduction modified mantle and rise up to the middle crust, where they form a deep reservoir (top at 8 km of depth), and evolve to shoshonite through combined crustal contamination and fractional crystallization processes.

Time variation of the isotopic compositions suggests that both the mantle source magma supply and the role of crustal contamination have been either decreasing or increasing over the past 60 ka. The shoshonitic magmas either rise to the surface along regional faults, or evolve by fractional crystallization to trachyte. The differentiated magmas accumulate in the upper portion of the deep reservoir and migrate to shallow depth, where they differentiate and mix before eruptions. These processes occurred at different scale through time, *i.e.* before the Campanian Ignimbrite (39.28 ka) and the Neapolitan Yellow Tuff (14.9 ka) eruptions, when large amounts of trachytic magmas were stored in crustal reservoirs and, in the last 15 ka, when shoshonitic-trachytic magmas, representing at least 2 isotopically distinct magmatic components, entering the Campi Flegrei caldera magmatic system have rose to shallow depth, differentiated and mixed with magma residual of the earlier voluminous NYT, caldera forming eruption.

All these processes were responsible for the temporal evolution and spatial configuration of the Campi Flegrei magmatic structure. The inferred present structure of the feeding system is characterised by a deep reservoir, whose top is at about 8 km depth, that hosts shoshonitic-trachytic magmas. Remnants of the NYT magma reside at shallow depth in different sectors of the crust underlying CFc, and were sometimes intercepted by volatile-rich magmas of deep provenance, during the three epochs of CFc volcanic activity.

THE CENOZOIC BASALTS FROM CENTRAL-SOUTHERN PATAGONIA (44-52° S): GEOCHEMICAL DATA AND GEODYNAMIC INTERPRETATIONS

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Cenozoic volcanic rocks are exposed over a significant fraction of the extra-Andean Patagonia, forming extensive lava plateaus, hundreds of monogenetic scoria cones and other volcanic and subvolcanic structures. These rocks were erupted in a continental back-arc setting, along the eastern side of the Andean Cordillera and at variable distance from it. The igneous products, occurring in the central-southern sector of the extra-Andean Patagonia (44-52° S), are dominantly mafic with minor slightly evolved compositions and rare highly differentiated products. Mafic lavas range from strongly silica undersaturated basanites to oversaturated basaltic andesites, and most of them have a typical within-plate geochemical signature. However, a number of lavas, generally erupted in the western-central sectors of Patagonia, closer to the Cordillera, are characterized by different distributions of the incompatible elements with high LILE/HFSE and LREE/HFSE ratios. Modelling of REE distribution and major-element composition of the most primitive lavas suggests a low degree of melting of a deep (> 70 km) garnet-bearing source for the alkaline magmas, and a higher degree of melting of the same source, or an even higher degree of melting of an enriched source, for the subalkaline magmas. The available Sr-Nd-Pb isotope compositions suggest a major rough geographic variation: the southernmost lavas have lower $^{87}Sr/^{86}Sr$ and higher $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ ratios with respect to those erupted to the north. The geochemical variations of the central-southern Patagonia lavas are discussed in terms of different geochemical components: depleted and enriched sub-slab asthenosphere, enriched continental lithospheric mantle, continental crust and subducted materials. The geodynamic significance of this magmatism, which is neither correlated to a marked lithospheric extension (*e.g.* rift), nor to hot-spot activity, is interpreted in the frame of its space-time evolution, and in the wider frame of the Cenozoic history of the Pacific margin of southern South America. The opening of slab windows, associated to the collision between oceanic spreading ridges and the Chile Trench, is the preferred geodynamic interpretation of the southern Patagonia magmatism. However, the occurrence of many volcanic formations whose age and location are not entirely compatible to slab window models, suggests that other geodynamic processes inducing mantle melting could have been active during Cenozoic in the extra Andean Patagonia.

PETROLOGICAL FEATURES OF MANTLE XENOLITHS FROM SOUTH AUCKLAND VOLCANIC PROVINCES, NORTH ISLAND, NEW ZEALAND

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Two suites of mantle xenoliths have been collected from basaltic outcrops of Ngatutura and Alexandra Volcanic Fields. These alkaline volcanics are situated in the western part of the North Island (New Zealand) and belong to the South Auckland Volcanic Province. They are situated in an intraplate tectonic setting behind the currently active Taupo Volcanic Zone, and 300 km above the subducting slab. The lavas have restricted compositions, ranging from hawaiites to nepheline hawaiites, and are characterized by enriched LIL, LRE, and HFS elements.

The majority of Ngatutura samples are equigranular and protogranular dunites, with two porphyroclastic harzburgites. One websterites and one wehrlite show cumulitic features. In dunites olivine (ol) can be found as medium grained (average 2.5 mm) crystals; kink-banding is visible in some cases. Orthopyroxene (opx), where present, is smaller (up to 1 mm) and interstitial. Spinel (sp) is very small, black, euhedral and often enclosed within olivine. Dunite NG6 is crosscut by a network of veins where secondary opx are found. Ol in harzburgites is smaller than opx (< 1 mm), sometimes kinked; opx is found as large porphyroclasts (up to 4 mm) with exsolution lamellae. In the websterite and wehrlite ol is small and rounded, while opx is constituted by large crystals (up to 1.5 mm), often with exsolution lamellae. In the wehrlite clinopyroxene (cpx) forms big crystals (up to 2 mm) with spongy surface.

The majority of Alexandra samples is constituted by protogranular and porphyroclastic lherzolites. Three cumulitic clinopyroxenites have been also collected. Ol, in lherzolites and harzburgites, present a medium grain size (up to 9 mm), with the characteristic kink-banding. Opx can be found as medium-coarse grained (up to 5.5 mm in porphyroclastic samples), with exsolution lamellae. Cpx is small (up to 1.5 mm), and appears with spongy textures. Sp can be found both as primary, bigger crystals (sometimes with reaction rims) or as secondary idiomorphic and smaller crystals. In the dunitic sample ol is medium grained (up to 2 mm) and characterized by kink-banding, while cpx is smaller (up to 1 mm) and interstitial. Sp can be found as small, secondary and idiomorphic, crystals. In clinopyroxenites ol is characterized by medium grain (up to 2 mm) kink-banded crystals. Cpx is big (up to 3.5 mm), with exsolution lamellae. In one clinopyroxenite amphibole can also be found, characterized by a medium grain (up to 2 mm), with a few crystals presenting reaction products.

Two kinds of reaction textures are found. In the first a previous phase (not recognizable) is completely recrystallized into a mingling of small secondary iso-oriented minerals dispersed into an altered glassy matrix. The second involves mainly opx, which is partially destabilized and forms thick, interconnected areas made up of secondary phases and glass. Metasomatic reactions occur in both mantle and cumulitic lithotypes, where opx with exsolution lamellae can be present. This fact indicates recent infiltration of metasomatizing agents, even after crystallization processes occurred.

The host basalts do not present geochemical evidence for any influence of the subducted slab, even though they overlie the subduction zone. This implies that the extent of subduction-related contamination in the mantle wedge is not pervasive. This contamination maybe testified by the presence in some xenoliths of small veins filled with secondary opx. “Deep mantle plume” responsible for the alkalic magmatism are excluded, because it seems unlikely that such a plume could have occurred at a deeper level and penetrate the slab without some evidence, thus limiting the origin of these plumes to a depth < than 300 km.

MAGMATIC STRUCTURE IN THE PENINSULA PLUTON (SOUTH AFRICA): MULTI-BATCH ASSEMBLY CAUSING LATE STAGE MECHANICAL INSTABILITIES

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The understanding of the mechanisms and timing of formation of magmatic structures is crucial for our interpretation of magma chamber construction, evolution and dynamics.

The S-type granodioritic to monzogranitic Peninsula Pluton (South Africa) hosts a large variety of mafic and felsic magmatic enclaves with contrasting textures and compositions (*e.g.* $SiO_2 \approx 65\text{-}80$ wt.%, initial $^{87}Sr/^{86}Sr \approx 0.700\text{-}0.715$) and is characterized by mechanical concentrations of K-feldspar megacrysts, cordierite and biotite generating a complex array of magmatic structures that may be interpreted to include tubes, pipes, troughs, diapirs and plumes. In addition, a spectacular well-developed magmatic layering is preserved in one specific locality, with layered elements in other areas interpreted to represent similar features disrupted and disaggregated by magma flow. This layering shows extreme enrichment of the dense mafic minerals at the base of layers, with a rapid decrease in the proportion of these minerals upwards, so that the upper half of 10 to 30 cm thick layers is leucocratic and enriched in plagioclase, K-feldspar and quartz.

Field, textural and geochemical data suggest that the magmatic structures form by flow of crystal-bearing magmas through crystal-rich magma mushes assembled from older magma batches that had achieved crystal fractions that allowed the material to act as a solid, whilst maintaining sufficient melt that “hard” intrusional contacts are not preserved. Moreover, evidences of segregation of interstitial melt from accumulated crystal aggregates are common. The released felsic liquids form leucocratic veins, pipe-like structures and irregular intrusion locally disrupting earlier cumulate structures.

These structures, formed in an existing magma chamber, involve crystals with different magma histories and ages, generating great local compositional and textural diversity. The genesis of these magmatic structures is due to mechanical instabilities in a crystal-rich magma chamber triggered by successive emplacement of pulses of new magma derived from the melting of a metasedimentary, compositionally zoned, source.

TUFFACEOUS DEPOSITS IN THE SEDIMENTARY COVER OF THE STRONA-CENERI ZONE AND IN THE VILLAFORTUNA-TRECATE OIL SYSTEM: PETROLOGICAL, GEOCHEMICAL AND GEOCHRONOLOGICAL CHARACTERIZATION

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In the western sector of the Southern Alps, tuffaceous levels are occasionally found in Triassic sedimentary sequences and the age of the related magmatism is still matter of debate. The few available geochronological data on these tuffites (M. San Giorgio area, Lugano, CH) yield Triassic ages (245±1 Ma; U-Pb zircon [1]), which are slightly older than the stratigraphic position. The precise definition of the tuffite age is, however, important for the Triassic evolution of the western Alps. In particular, if the magmatism is synchronous with their stratigraphic position, tuffites might be linked to the Triassic magmatism documented by the Finero area (NE Ivrea-Verbano Zone [2]). However, it cannot be presently excluded that they are the product of erosion and re-deposition of the Permian acid volcanics located at the base of the Mesozoic sedimentary cover [3].

In this work, we have considered the tuffaceous deposits occurring within a late Anisian-Ladinian succession in the Mesozoic sedimentary cover of the Strona-Ceneri Zone in the Borgosesia area [3, 4] and the tuffites at the same stratigraphic position found in some wells of the Villafortuna-Trecate oil system field (western Po Plain, Piedmont region, NW Italy) [5]. These tuffaceous deposits are constituted by a variable mixture of magmatic and sedimentary components. Available chemical data on the magmatic component suggests a calc-alkaline affinity.

Zircons have been separated with conventional methods from four samples, mounted in epoxy resin and characterised under cathodoluminescence (CL). Based on colour, morphology and internal structure, zircons have been divided in two populations. One group is constituted by light-pink coloured zircons with prismatic habits and tight oscillatory zoning suggesting growth under magmatic conditions. Zircons from the second group are colourless, rounded in shape and with only relics of magmatic zoning. They most likely suffered metamorphic recrystallization.

Ongoing ELA-ICP-MS characterizations of both trace elements composition and U-Pb age of these zircons is expected to provide valuable constraints on the geodynamic evolution of the Southern Alps Domain in Permo-Triassic times.

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A JOURNEY INTO THE HAWAIIAN PLUME: TOP TO BOTTOM AND BACK

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The geochemistry of oceanic hotspot volcanism has been studied extensively in many locations, but especially so in Hawaii. These investigations are directed primarily at three questions: (1) Is hotspot magmatism caused by the upwelling of a deep mantle plume? (2) What is the ultimate origin of the chemical and isotopic heterogeneities found in the magmas? (3) What do these heterogeneities tell us about the internal structure of a mantle plume?

The first of these questions cannot really be answered by geochemistry, in spite of numerous attempts to do so. The tools used in mantle geochemistry, *i.e.* trace elements and their isotopes, are passive tracers that require an a priori model of the physical mantle structure and dynamics. In particular, evidence from $^3He/^4He$ ratios neither proves nor disproves the existence of mantle plumes. However, recent seismological evidence has lent strong support to the plume model for some hotspots. Moreover, the very long-lived nature ($\geq$ 80 Ma) and the age progression of the Hawaiian hotspot, which originally led to the plume model [1], have been amply confirmed. I will therefore use the plume model for the interpretation of geochemical data.

The second question, the ultimate origin of Hawaiian source rocks, is a more appropriate subject for geochemistry. Recycling of ancient, subducted crust and lithosphere originally proposed on the basis of trace elements and radiogenic isotopes, has been confirmed by recent work on melt inclusions in olivine phenocrysts, as well as the composition of olivines (Ni, Mn, Ca). Trace element patterns of melt inclusions show characteristic “fingerprints” which can be traced directly to an originally gabbroic source rock [2]. Anomalously high Ni and low Mn abundances of Hawaiian olivine phenocrysts, are also consistent with source rocks consisting partly of eclogite/pyroxenite, rather than pure peridotite [3].

The third question, the internal structure of the plume, also requires a physical model of the plume as framework for interpreting geochemical data [4, 5]. In our model, a plume rising from the lower boundary of the mantle (the subduction “graveyard”) will preserve, but vertically stretch, the chemical and isotopic heterogeneities accumulated in that source region. Although we cannot address the short-term fluctuation of magma chemistry seen in Hawaiian volcanoes, because we lack detailed knowledge of the magma extraction processes, our dynamic model explains the systematic compositional differences between the two parallel chains of Hawaiian volcanoes. They reflect large-scale heterogeneities near the core-mantle boundary, which are drawn into, laterally compressed and preserved in the conduit, and ultimately sampled by the volcanoes. This model also explains the systematic similarities and differences, occurring on a 10^5 yr time scale, found in the progression of volcanism seen on Mauna Kea and Kilauea volcanoes. These represent medium scale (tens of kilometers), highly stretched “filaments” of diverse but distinct source rocks, which must have lengths of at least 600 km in the plume conduit. Thus, extreme vertical stretching of heterogeneities, rather than concentric zoning, dominates the internal composition of the Hawaiian plume.

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OLIVINE NEPHELINITE, PYROXENE NEPHELINITE, PERIDOTITE XENOLITHS AND CARBONATITE (ANTI-ATLAS, MOROCCO): RELATION AND ORIGIN

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The volcanism of the district of Foum El Kouss (Anti-Atlas, Morocco) belongs to the alkali province of Jbel Saghro. The K-Ar isotopic ages range from 4.8 to 2.9 Ma. Pyroxene-rich nephelinite, is more recent (2.9 Ma) [1, 2], bearing carbonatitic xenoliths, peridotite xenoliths affected by a fluid carbonatitic metasomatism, green pyroxenes rich in CO_2 fluid inclusions with reverse zonation and a strong enrichment in rare earth elements and incompatible elements. The mineralogical and geochemical characteristics of the pyroxene-rich nephelinites may be explained by incorporation of carbonatitic segregates. During a Plio-Quaternary volcanic event, carbonatitic enclaves were taken off and mixed, after their partial fusion, with the liquid anatectic products. The restite of this fusion is documented by the presence of reaction rim around the small carbonatitic enclaves. The assimilation of these enclaves is probably pyroxene nephelinites-generated.

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CRETACEOUS AMPHIBOLE-RICH INTRUSIVES WITH HIGH-Mg ANDESITE AFFINITY FROM JAPAN: A PETROLOGICAL AND GEOCHRONOLOGICAL STUDY

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High-Mg andesites (HMA) are a group of arc products, usually rich in amphibole, whose origin is still debated. High-Mg diorites (HMD) are intrusive counterparts of HMA and are locally found in exhumed arc sections. In places, HMD are closely associated with ultramafic amphibole-rich rocks and may provide further constrains on the role of amphibole in the origin of HMA and in the petrogenesis of arc related-magmas.

Small bodies of Cretaceous amph-rich mafic and ultramafic intrusives with similar petrographic features and HMA affinity (*e.g.* [1]) are exhumed together with granitoid rocks along the Japan arc. These rocks, originated during the Cretaceous subduction of the Pacific plate under Asia, give the opportunity to investigate modifications in the composition of melts with HMA affinity as a function of the along-margin position and time.

Mafic and ultramafic intrusives were sampled in different localities of the Honshu (NE Japan arc) and Kyushu Island (SW Japan arc). *In situ* U-Pb zircon geochronology by laser ablation ICPMS was carried out to constrain the time relationships among the different intrusive bodies. U-Pb concordia ages show that the HMD were mostly emplaced from *ca.* 100 Ma up to 118 Ma. In only one case (Honshu Island) U-Pb concordia ages as young as 70 Ma were obtained.

High modal proportions of amphibole (40-60 vol.%) with pargasite cores (Mg# = 0.66-0.77) characterize all studied samples. In ultramafic rocks (Ol-hornblendites and Cpx-hornblendites), pargasitic amphibole is poikilitic on sub-rounded clinopyroxene (Mg# up to 88) and olivine (Fo_{61-78}). In mafic rocks (amph-gabbros and amph-diorites), large amphibole grains are dispersed in a fine-grained matrix defining a porphyritic texture. The matrix consists mainly of Mg-hornblende, plagioclase and clinopyroxene. The cores of pargasitic amphibole from mafic rocks have clinopyroxene inclusions with Mg# up to 88, similar to what found in ultramafic rocks.

Independently from the age and the location, the occurrence of clinopyroxenes and olivine in textural and chemical disequilibrium with the host pargasitic amphibole is common feature of the HMD and associated ultramafic amph-rich rocks. Clinopyroxene and olivine are interpreted as relics of ultramafic cumulates assimilated at mid/low crustal levels by the hydrous magma. Results of this work suggest that the involvement (through assimilation) of a deep-crust ultramafic component may be a common process in the petrogenesis of melts with HMA affinity.

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BASIC MAGMATISM IN THE TRIASSIC SEQUENCES FROM THE ALPUJARRIDE COMPLEX (BETIC CORDILLERA, SPAIN) AND THE LUNGRO-VERBICARO UNIT (SOUTHERN APENNINES, ITALY)

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This research project is focused on the study of the basic magmatism in the Triassic metacarbonate and metapelitic rocks belonging to the Alpujàrride Complex (Betic Cordillera, SE Spain) and Lungro-Verbicaro Unit (Southern Apennines, Italy). These domains were involved in the geodynamic processes active in the Mediterranean region from the Mesozoic onwards and, in particular, in the opening of the Jurassic Tethys. In literature, both the HP/LT Alpujàrride Complex and the San Donato Unit are interpreted as passive margin successions deposited during the Triassic rifting, pointing to a stratigraphic correlation for that regarding the paleogeographic context. The aim of this study is to characterize the source, the petrogenetic process and to determine the age of the basic magmatism affecting the Betic and the Triassic successions, in order to test this hypothesis.

Triassic magmatic rocks in the Mediterranean area are distributed along the orogenic Apennines-Alpine-Dinaric-Hellenic-Rif-Betic belts. In the Northern Calabria basic rocks are represented by pillow-lavas and dykes cutting through Triassic and Jurassic formations [1]. In the Betic Cordillera gabbros intrude sedimentary successions until Middle Trias ([2], and references therein).

Preliminary petrographic analysis on samples from both the studied areas allow to recognize three main lithotypes: i) metagabbros showing ophitic to subophitic texture, with a mineral assemblage made of Pl + Cpx + Amph + Ep-Chl + Qz + Mg; ii) fine grained metabasites whose original magmatic texture is completely reworked by metamorphic recrystallization, the mineral assemblage is made of Na-amph + Stp + Chl + Pmp + Cal + Mg; iii) gabbros with ophitic structure with mineral assemblage made of Pl + Cpx + Na-Cl-amph + Act + Ep + Bt + K-mica + Chl + Mg.

Bulk rock compositions obtained by XRF indicate the presence of two suites: 1) the samples from Northern Calabria and four from the Betic Cordillera show an alkaline to alkaline-transitional character and have a relatively low Y/Nb *vs.* Zr/Nb ratio; For these samples, according to the La/10-Y/15-Nb/8 diagram, a continental to intracontinental rift context is supposed; 2) most of the samples from the Alpujarride complex show a linear fractionation trend in the Ti/V diagram, according to the La/10-Y/15-Nb/8 diagram they plot in the basalt calc-alkaline fields.

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SiO_2-, Al_2O_3-RICH METASOMATIZING AGENT IN THE LITHOSPHERIC MANTLE OF ESTANCIA SOL DE MAYO, SOUTHERN PATAGONIA

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Xenoliths from Estancia Sol de Mayo entrained in alkali basalts are protogranular spinel-bearing harzburgites and dunites, with two lherzolites and one wehrlite. They do not present any metasomatic features such as glassy veins or pyrometamorphic textures. Olivine is the most abundant and largest mineral (0.5-0.6 mm in size) often with kink-banding. Orthopyroxene is present as both protogranular crystal (opx1), with size comparable to olivine, and smaller crystals arranged in vein (opx2). Clinopyroxene has variable dimension but it is always rather small. Two texturally different clinopyroxenes, one protogranular (cpx1) and another that grows around the spinel (cpx2) are recognized. Finally, the spinel has the smallest dimension, is always black and anhedral.

In the Al_2O_3 *vs.* Mg# diagram clinopyroxenes define two trends: a depletion trend from high-Al and Fe to low-Al and Fe and another toward high Al_2O_3 values at almost constant and high Mg#. All cpx2 belong to this latter trend, together with some cpx1. These latter however, at comparable Mg# ((Mg/Mg+Fe)·100 mol.%) and within the same sample, appear depleted in Al_2O_3.

Analogously opx1 show a depletion trend from high Al_2O_3 and low Mg# (3.32 wt.% and 84.70 respectively) to low Al_2O_3 content (1.39 wt.%) at high Mg# (91.51) and an Al_2O_3-enriched trend (2.62-2.97 wt.%) at constant and high Mg# (90.79-92.76). Small opx crystals (opx2) arranged in veins also belong to this latter trend.

Two well-defined trends are also shown by spinel compositions. Isolated spinels plot along the mantle array with Mg# and Cr# ((Cr/Cr+Al)·100 mol.%) varying between 53.14-58.83 and 57.88-60.60 respectively, whereas spinels surrounded by cpx are characterized by MgO and Al_2O_3 enrichments (Mg#, 67.02-71.57; Cr#, 36.36-40.47) well outside the mantle array.

In chondrite-normalized incompatible trace elements diagrams, cpx1 and cpx2 show similar patterns, with the former having more enriched REE patterns. They are both characterized by Th positive anomaly, a slightly negative anomaly in Sr and prominent negative anomalies in Nb, Zr and Ti.

Opx1 present negative anomalies in Sr, Zr and Ti and positive anomaly in Th. A remarkable positive Zr anomaly, together with La and Ce enrichment is typical of opx2.

These textural and geochemical features indicate that 1) opx2 was added to the system after the harzburgites was formed, and 2) cpx growing around spinel is not an isochemical process, due to a simple deformation and recrystallization event, but, at least Al_2O_3 and TiO_2, should have been added to the system.

The parallel Al enrichment in opx, cpx and sp point toward a common process for the formation of secondary opx and cpx, probably related to the infiltration of a SiO_2-, Al_2O_3- and TiO_2-rich metasomatizing agent affecting an already moderately to strongly depleted peridotite.

THE UNUSUAL PICRITE BASALT/RHYOLITE ASSOCIATION AS AN INDICATOR OF RIFTING PROCESSES IN A PLUME AREA: THE CASE OF NORTHERN ETHIOPIAN PLATEAU

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The Oligocene Continental Flood Basalts (CFB) of the Northern Ethiopia and the conjugate Yemen province testifies a huge volcanic event related to the "Afar plume" occurred at *ca.* 30 Ma (in 1 Ma or less; [3]) prior to the continental rifting stage. The zonal arrangement of CFB lavas with low-Ti tholeiites (LT) in the west, high-Ti tholeiites (HT1) to the east and very high-Ti transitional basalts and picrites (HT2, TiO_2 4-6 wt.%) closer to the Afar triple junction has been considered a record of magmas generated from the flanks to the centre of a plume head, currently corresponding to the Afar hotspot [2].

In the central-eastern part of the plateau (Lalibela area), neighbouring the Afar escarpment, abundant rhyolites characterize the upper part of the volcanic sequence and have been interpreted as the differentiated products of CFB magmas [1].

The unusual association of picrite and rhyolite magmas erupted in an elongated area, parallel to the Afar escarpment, appears to be related to peculiar tectonomagmatic events developed in the apical zone of a stretched lithosphere impinged by a mantle plume.

As previously suggested, the HT basaltic and picritic magmas could have been generated in the innermost part (core) of the plume head from the hottest, deepest and most metasomatised mantle domains, enriched by "plume components" [2]. The late stages of these magmatic events were accompanied by the onset of continental rifting, with faulting and block tilting, leading to favourable conditions for magma differentiation in shallow (crustal) chambers located N-S along the future Afar Escarpment. Quantitative petrological modelling shows that efficient fractional crystallization processes of HT transitional basaltic/picritic magmas could result in highly differentiated peralkaline rhyolitic products, generally localized at the top (lower density) of the magma reservoirs.

From these latter, abundant rhyolitic magma were erupted (sometimes alternating to HT basalts and picrites) during the paroxystic extensional phases which ultimately led to continental break-up and the formation of the Red Sea-Gulf of Aden-East African rift system centred in the Afar "triple junction".

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INSIGHTS INTO THE EVOLUTION OF THE EAST AFRICAN LITHOSPHERE: HAFNIUM ISOTOPE COMPOSITIONS OF CLINOPYROXENE FROM MEGA PERIDOTITE XENOLITHS (ETHIOPIA)

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Mantle xenoliths from the Sidamo region, in the southern tip of the Main Ethiopian Rift, have been extensively studied [1, 2, 3, 4, 5] and have provided many insights into the chemical and thermal history of this active rift region. In this study, we focus on a collection of spinel-peridotite xenoliths from Mega previously characterized in terms of major and trace elements in both bulk rocks and constituent minerals and Sr-Nd isotopic compositions of separated clinopyroxene (cpx) [5]. The new Hf isotopic analyses carried out on mantle cpx by multi-collector inductively-coupled plasma mass spectrometry show extremely heterogeneous ^{176}Hf/^{177}Hf varying from slightly sub-chondritic (0.282737) to extremely radiogenic compositions (0.313198 in sample MA35, a cpx-poor lithology). ^{176}Hf/^{177}Hf correlates positively with Lu/Hf, providing an apparent time-integrated ingrowth of 1.96 Ga across the suite, close to the CHUR model age of the most radiogenic sample (1.99 Ga). Interestingly, ^{176}Hf/^{177}Hf also correlates with the modal abundance of cpx, with the more enriched Hf isotopic compositions (corresponding to the lower Lu/Hf ratios) recorded in the most refractory harzburgites. These observations, taken together, indicate that melt extraction alone cannot explain the process that led to these signatures. We therefore propose a multi-step model that includes metasomatism, which affected preferentially the more refractory olivine-rich (more permeable) mantle domains. The anomalously radiogenic Hf isotopic composition of MA35 (and also MA19, another cpx-poor peridotite) is particularly visible when expressed with the $\Delta\varepsilon_{Hf}$ parameter, which is a measure of the displacement of the Hf isotopic signature from the mantle array as defined by oceanic basalts ($\Delta\varepsilon_{Hf} = \varepsilon_{Hf} - 1.36\cdot\varepsilon_{Nd}+3$, after [6], revised from [7]). Extremely radiogenic ε_{Hf} (up to +1076 in sample MA35) accompanied by relatively normal mantle-like Nd isotopic compositions, are reflected by positive $\Delta\varepsilon_{Hf}$ of over +1000, clearly indicating the decoupling of the Lu-Hf and Sm-Nd isotopic systems. One explanation for these observations may be found in a two-step process of (1) ancient melt extraction in the presence of residual garnet, which fractionated Lu from Hf [7, 8], followed by (2) subsequent ascent of this mantle domain to depths shallower than the spinel-garnet transition [9, 10]. A second explanation, provided by [11], is that diffusional loss of Nd is faster than Hf at mantle temperatures, leading to the development of what appears to be anomalously high ε_{Hf} for a given ε_{Nd} value.

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TRIASSIC GRANITOIDS IN THE SERBO-MACEDONIAN MASSIF (GREECE) AND THEIR GEODYNAMIC SIGNIFICANCE

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Arnea and Kerkini complexes are the largest granitic bodies in the Vertiskos Unit (Serbo-Macedonian Massif, Greece). They were studied using new and literature U-Pb geochronological zircon data as well as new whole rock geochemical data, aiming at investigating the origin and evolution of the two complexes as well as providing constraints on their geodynamic environment [1].

Arnea complex shows an age span of 230-265 Ma with two pulses of magma intrusion at 253 Ma and 240 Ma, whereas Kerkini has an age of 247 Ma. Arnea and Kerkini complexes are two-mica syenogranite and alkali-feldspar granites containing quartz, K-feldspar, plagioclase, and biotite, and allanite, titanite, zircon, and fluorite as typical main and accessory minerals, respectively. They are variably peraluminous with ASI values of 0.96-1.34. Both complexes evolved mainly by Fractional Crystallization, separating assemblages consisting of feldspars, biotite, allanite and zircon. Parental magmas are crustal melts derived by partial melting of TTG sources.

Our new U-Pb geochronological data, obtained on zircon oscillatory rims and having an excellent concordance, indicate that the obtained ages can be considered as the crystallization ages, at the boundary between Permian and Triassic. All the rocks belonging to the magmatism intruding the Vertiskos Unit show variable behaviour using all the main parameters able to discriminate A-type granite igneous suites are used. Some parameters indicate a clear A-type affinity for both the complexes, but conversely other parameters indicate a clear differentiated I-type affinity. In addition, all the rocks plot in the A2 subtype, indicating that the magmatism is connected with a post-collisional rather than an intra-plate rifting environment.

Time distribution and geochemical and petrological features of the plutonic rocks intruding the Vertiskos Unit furnished some fundamental constraints on the geodynamic evolution of the region. We suggest that, at the boundary between Permian and Triassic, the area was in an incipient rift environment, and as such oceanization had not still occurred and continental crust accreted during previous continental collision is present at the rift floor. Such a crust could melt partially to produce batches of magma similar to the studied magmatism. A submarine rhyolitic magmatism of similar age and geochemistry to the granitoid magmatism exists [2], outcropping on the floor of the epicontinental sea, indicating that melts, produced by partial melting of the crust, either remained at depth, generating the granitic complexes, or extruded as rhyolitic lavas. Magmatism intruding the Vertiskos Unit emplaced, hence, in the post-orogenic environment that follows the subduction of Gondwana under Eurasia, at the beginning of the rifting leading to the opening of the Vardar-Meliata Ocean.

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DELAYED MAGMATISM ON "PASSIVE" MARGINS

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Passive continental margins created during the oceanization rift-drift transition stage are commonly regarded as volcanic or non-volcanic according to the amount of igneous products emplaced during the break-up stage. In this respect, the Atlantic Ocean is acknowledged as bounded by Paleocene volcanic margins in the north, and Jurassic-Cretaceous non-volcanic margins in the central part. Here, however, both western and eastern conjugated rifted margins are the site of small-volume magmatism much younger than the rift-drift stage.

A prime example of this type of magmatism is found in Senegal, whose continental margin developed in Middle-Late Jurassic and is affected by Oligocene to Quaternary alkaline magmatism. The igneous products are scattered over the Cap-Vert peninsula as lava flows and shallow level intrusions. Additional saucer-shaped sills have been detected offshore from Senegal on the basis of integrated seismic, magnetic and gravimetric surveys. The occurrence of hydrothermal vents and forced folds related to sill intrusion allows dating of the igneous event to the Miocene. The age of magmatism displays a minimum delay of 130 Ma with respect to rifting, with consequent decoupling of any cause-effect link between rifting and magmatism.

Additional examples of similar delayed alkaline magmatism come from other Atlantic margins such as Newfoundland-Grand Banks and its conjugate Iberian margin along the Tore-Madeira Rise. Southwards, cases of delayed magmatism are also found in the Canary Islands and along the Cameroon line as well as its conjugate counterpart offshore northeastern Brazil.

In the Senegal margin, onshore structural data, offshore seismic sections, and gravimetrically-magnetically defined shapes and arrays of offshore sills all indicate that magma emplacement followed the geometric impact of Atlantic oceanic fracture zones into the transitional-continental crust. Therefore, we propose that the engine for the generation of alkaline magmas on passive margins tens of Ma after the rift-drift transition is linked to the reactivation of oceanic fracture zones.

This mechanism is currently at work in the Antarctic rift. Here, the main rifting episode is of Late Cretaceous age, while alkaline magmatism is active since the Middle Eocene, some 50 Ma later. The igneous activity shows a tight genetic-geometric-geochronological link with the activity of a dextral strike-slip fault system affecting the continental crust and in turn linked to the Southern Ocean fracture zone system.

The reported examples call for the inclusion in the inventory of passive margin types of a "new" type of margin: besides volcanic and non-volcanic margins, "delayed-volcanic" passive margin with alkaline magmatism should be accounted for.

MESOZOIC ALKALINE MAGMATISM IN CENTRAL SICILY (SOUTHERN ITALY): NEW PETROLOGICAL DATA ON THE MOUNT ALTESINA SILL

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Stratigraphic and petrographic studies carried out in the last decades ([1, 2] and references therein) have highlighted the occurrence, in western-central Sicily, of a multi-stage Mesozoic magmatic activity. In this area, three are the main magmatic phases recognized during the entire Mesozoic time: 1) late Triassic, 2) middle Jurassic, 3) late Cretaceous.

Early Triassic to early Jurassic magmatic rocks were produced within a tensive tectonic regime linked to the first opening stages of the ocean realms in the Central Mediterranea area [1, 3, 4].

Igneous products mainly consist of submarine lava-flows and less numerous subvolcanic bodies (dykes, sills and laccoliths).

Triassic volcanic and sub-volcanic rocks have been found exclusively enclosed in the sedimentary sequences of the Mufara Formation [1]. In this work, we report petrographic, geochemical and thermobarometric data for a body cropping out on the southern slope of Mount Altesina (central Sicily). It consists of a sill, ranging in thickness from 15 to 2 m, intruded between a pelagic sequence of cherty siltites attributed to the Ladinic Lercara Formation and black shales and micritic limestones belonging to the Mufara Formation, dated at the early Carnian.

Sampled rocks show prominent spilitic transformation. They are fine to medium grained, holocrystalline with an ophitic texture, where laths of plagioclase, albitic in composition, are embedded in zoned, intensively fractured but unaltered Ti-augite crystals. Olivine is absent, as well as its alteration products. Small amount of biotite, partially replaced by chlorite, ilmenite and apatite complete the paragenesis. Secondary products are represented by chlorite, calcite, epidote and some spectacular radial prehnite crystals filling the fractures.

Thermobarometric estimates on clinopyroxene, made using the thermobarometer of Putirka [5], provide a crystallization temperature of about 1160°C and pressure of 7 kbar. This data is also confirmed by MELTS calculations [6].

Geochemical features indicate an alkali basaltic composition and a within plate affinity. Trace and REE elements concentrations produce patterns characterized by strong enrichments in LILE, HFSE and LREE and strikingly similar to those of P-MORB produced in continental rifting settings.

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FROM DEEP EARTH TO VOLCANOES –
CLUES FROM SOUTH AMERICAN PACIFIC MARGIN

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A volcano-seismic correlation was for a long time suspected to occur for the Pacific margin events of South America. During his trip on the Beagle, Charles Darwin [1] wrote about the eruptions associated to the Conception earthquake of 1835. Casertano's survey [2] following the 1960 great Chilean earthquake found some unclear evidence of a link between eruptions and the seismic event. Scalera [3] using the data available in 2006 in the Smithsonian Institution Catalogue of volcanic eruptions revealed grounded evidence that South-American Wadati-Benioff zone earthquakes with magnitude greater than 8.4 are associated to an enhanced rate of volcanic eruptions, but still it was impossible to determine the causal chain between the two phenomena. An average return period of about 45 years was deducible from the data for the time window 1800-2010. After 2006, the Smithsonian Institution effort to improve our knowledge of this region has greatly increased the completeness of the catalogue adding the new eruptions for the 2000-2010 interval, but also adding a 60% of new entries in the list of the Andean volcanoes. The occurrence of the Chilean Maule earthquake of 27th February, 2010 (M = 8.8) – occurred at five decades from the 1960 one – has been the occasion to rework all the data in searching for additional clues able to indicate a preferred causal direction eruptions-earthquakes or earthquakes-eruptions or from a third more general cause (*e.g.* a mantle movements) to both eruptions and earthquakes.

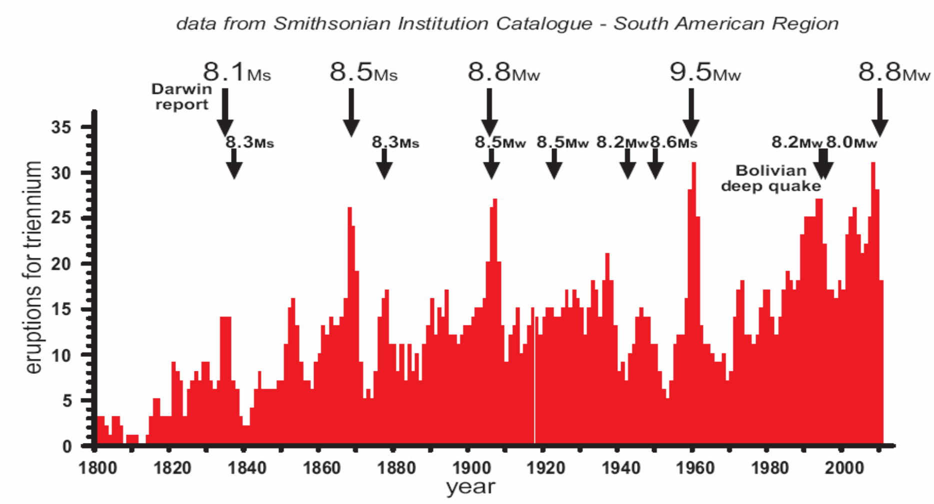

Fig. 1. Rate of eruptions for triennium on the entire Andean Pacific margin. Sharp maxima of the eruptions rate are revealed when great earthquakes occur (large black arrows). Their average return time is about 45 years.

Passing from the oldest (1868) coincidence event to the 2010 one, it is clear the trend – as soon as the data have become more precisely located on the time axis – toward an enhanced rate of eruptions that precedes the main seismic event. Between the second half of '800 and the first decades of '900, both some incompleteness of the data and peculiar limitations in collecting the evidence of occurred eruptions can hide this precursory occurrence of eruptions in the occasion of the 1868 and 1906 seismic events.

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THE Th/La AND Sm/La CONUNDRUM OF THE TETHYAN REALM LAMPROITES

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The Oligocene-Pleistocene Tethyan Realm Lamproites (TRL), from Mediterranean to Himalayas, have a clear orogenic signature and represent one of the most exotic and rare ultrapotassic mantle-derived magmas. They are invariably associated with calc-alkaline and shoshonitic rocks. Their average depleted mantle model age (τ_{DM} = 1.6±0.3 Ga, 1σ) is rather uniform all along the Tethyan realm orogenic belts, indicating a common crustal component responsible for re-fertilisation of the depleted mantle source. The TRL share the major element and mineralogical characteristics of the lamproite clan rocks; they clearly define, however, a distinct sub-group on the basis of a number of key trace element ratios (*e.g.* Rb/Sr, Ba/Rb, Th/La, Sm/La) and radiogenic isotopes (Sr, Nd, Pb). The most striking characteristic is the positive correlation between Th/La (up to > 1.5) and Sm/La (up to > 0.3), which is at odd with mantle sources metasomatised by slab-derived components as observed in volcanic arc magmas. The geochemical conundrum of the TRL is thus related to the requirement of a mantle source consisting of K-bearing crust-like domains and barren peridotite, although, modern arc volcanic magmas and experimental petrology studies provide compelling evidence that the crustal signature cannot be formed during normal sediment melting in the subduction factory.

We propose a multi-stage process for the formation of the TRL mantle source, which has to be found in the tectonic mélange domains (*i.e.* chaotic mixture of barren peridotite, basalt, and sediment) accreted to the Eurasia plate during one of the collisional events of the northward drifting continental slivers from Gondwana. During accretion, the mélange domains experienced high P and low T metamorphism with widespread development of lawsonite and zoisite/epidote veins, minerals that have the appropriate Th/La and Sm/La required by the TRL. Successively, the continuous H_2O supply from the subducting Neotethys and Alpine Tethys oceanic plates promoted melting of the low-solidus fractions of these mélange domains with the formation of metasomatic agents with low (normal sediment) and high (lawsonite and zoisite/epidote veins) Th/La and Sm/La. The Tertiary orogenic belt collapse eventually triggered the onset of low-degree melting of these heavily metasomatised peridotite domains which produced lamproitic magmas with a unique geochemical signature.

The Pb isotope composition of the TRL, requiring a history of high time-integrated κ ($^{232}Th/^{238}U$) and low time-integrated μ ($^{238}U/^{204}Pb$), is consistent with the U/Th/Pb characteristics of lawsonite and zoisite/epidote minerals, and places constraints on the timing of accretion of these tectonic mélange domains to the Eurasia plate at nominal ages of some 700-300 Ma. The proposed model adds new insight into the origin of the mantle source of orogenic lamproites, and questions a previous model relating the formation of the mantle source of the Western Mediterranean lamproites entirely to the Alpine SE-verging subduction of the European plate.

THE BORON TRANSFER FROM THE SLAB TO THE MANTLE WEDGE: A COMBINED STUDY IN SOUTH SANDWICH ISLAND ARC AND SOUTHERN VOLCANIC ZONE IN THE CHILE ANDES

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Volcanic arc lavas define generally coherent intra-arc correlation between B-enrichment and isotopic composition that provide unique insights into material recycling processes at convergent margin. The fact that B-enrichment is decoupled from fluid immobile elements but parallels that of fluid-mobile elements implies dominant transfer of boron into arc magma sources *via* aqueous fluids. The South Sandwich Island (SSI) arc and the South Volcanic Zone (SVZ) in the Chile Andes are ideal systems to investigate the boron transfer from the slab to the mantle source. Unusually heavy δ^{11}B values (+12 to +18‰) have been measured in the South Sandwich volcanic arc that is characterized by a simple tectonic setting: it is far from any continental crust, there is no collisions with seamount chain or with oceanic plateaux and ridges, no intra-arc rifting and moreover there is no complex mixture of pelagic and volcanogenic sediments on the downgoing plate. Forearc peridotites have high δ^{11}B (+9.0 and +10.2‰) and B-enrichment. South Sandwich trench sediments (ODP 701) display a wide range of δ^{11}B (+5 to -13‰) with negative values most common. These data suggest that the unusually high δ^{11}B values of South Sandwich arc-magmas are not simply inherent to subducting slab material. Rather this signature is attributed to mantle wedge modification by fluids derived from previously altered forearc materials that were recycled by subduction erosion. This multi-stage process can produce the extremely ^{11}B-enriched fluids required to develop the arc magma sources.

In contrast, the Andean Southern Volcanic Zone (SVZ) is affected by interaction between the active Chile Ridge spreading centre and the trench. This complex geodynamic setting is characterized by diverse magmatism and association of typical calc-alkaline rocks with monogenetic volcanic centres comprising basalts of OIB affinity. δ^{11}B values of CA rocks show a wide range between +5.5 and -7‰, with the volcanites from northern segment characterized by the higher B enrichment and δ^{11}B with respect to lavas from the southern segment. Moreover, the calc-alkaline rocks of SVZ show clear decreasing of δ^{11}B coupled with increasing Th/Ta (Ba/Nb) ratios, from north to south. Thus, the positive B isotope and high B/Nb in the CA lavas from the northern sector suggests a prevailing importance of fluid originated from the altered portion of the slab, whereas the negative δ^{11}B and high Th/Ta in lavas from the southern sector suggests the involvement of subducted sediments.

The OIB-like basalts have δ^{11}B between -1.2 and -5.2‰ and low B/Nb, suggesting that their sources have not been significantly modified by subduction. Thus, the alkali basalts are probably souced in a lithospheric mantle and the measured δ^{11}B may represent the local lithospheric mantle values. Alkalic basalts with intraplate signature from behind the Andean arc in Patagonia are characterized by low δ^{11}B (-4.5 to -6.6‰) and low B/Nb, reflecting the local asthenospheric mantle values.

SESSION 1.5

“Subduction factory”: magmatic and metamorphic processes

Convenors:

D. Castelli (*Univ. of Torino*)
P. Comodi (*Univ. of Perugia*)
M. Scambelluri (*Univ. of Genova*)

EXPERIMENTS ON METAPELITIC AND METAGREYWACKE COMPOSITIONS TO DETERMINE THERMODYNAMIC CONTROLS FOR THE TRANSITION FROM GARNET-BIOTITE TO GARNET-TALC

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The thermodynamic controls which govern the transition from garnet-biotite to garnet-talc assemblages during the metamorphism of mica-dominated sediments are not yet well understood. Investigations on synthetic compositions in the model system CaO-K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O are carried out in a piston cylinder apparatus at pressures and temperatures from 2 to 3 GPa and to 600-700°C. Experiments are buffered with graphite, and are generally run under fluid saturated conditions.

The experiments are run using bulk compositions representative of both metapelites (NM and H) and metagreywackes (NP and L). Variations in the bulk compositions studied were chosen to bracket the almandine-chlorite tie line in the Al_2O_3-Annite-Phlogopite plane and the annite-aluminosilciate and annite-almendine tie lines in the Al_2O_3-K_2O-(Mg,Fe)O plane (Fig. 1). Two bulk compositions, one metapelite, and one metagreywacke, are run at each experimental temperature and pressure to provide greater control of the compositional effects on the reactions. The preliminary results of this study (Fig. 2) are presented.

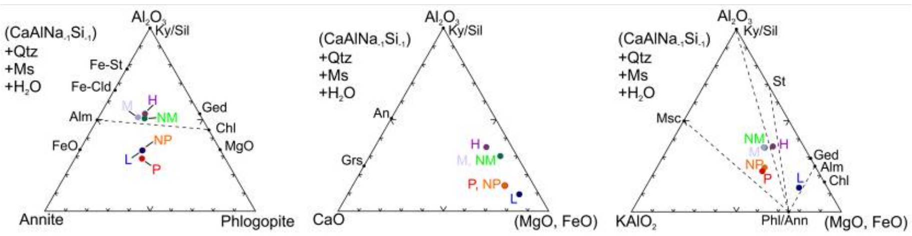

Fig. 1. (left) Projection from Ms, Qtz, H_2O and exchange vector $CaAlNa_{-1}Si_{-1}$ in the Al_2O_3-Annite-Phlohopite plane (note that H and NM plot above the almandine-chlorite join, L and NP below). (centre) Projection from Ms, Qtz, H_2O and exchange vector $CaAlNa_{-1}Si_{-1}$ in the Al_2O_3-CaO-(Mg,Fe)O plane. (right) Projection from Ms, Qtz, H_2O and exchange vector $CaAlNa_{-1}Si_{-1}$ in the Al_2O_3-K_2O-(Mg,Fe)O plane; H and L plot on the right-hand side of the join connecting Ky/Sil to Phl/Ann (*i.e.* lower $KAlO_2$ than NM and NP).

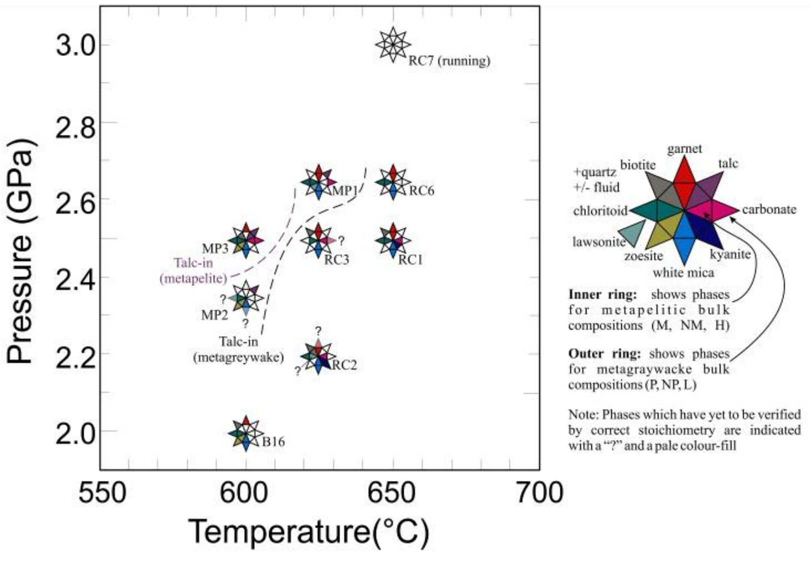

Fig. 2. Mineral phases present in each experimental run.

SLAB-DERIVED MELT METASOMATISM AT CERRO DEL FRAILE (PATAGONIA)

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Slab-melts percolating the mantle wedge induce various kinds of reactions in the peridotite, and, depending on melt/rock ratio, they can cause cryptic and/or modal enrichments. A peculiar feature of this metasomatismo is the production of orthopyroxene, both as crystals formed at the expense of olivine and as fibrous aggregates in the peridotitic matrix, and as veins [1].

Ultramafic xenoliths found in Quaternary volcanics at Cerro del Fraile, Patagonia (only 150 km from the trench) represent fragments of the mantle wedge above the subducting Antarctic plate. Samples are protogranular lherzolites, with minor harzburgites, dunites and plagioclase-bearing orthopyroxenites and websterites. Two composite samples are dunites cut by orthopyroxenite or clinopyroxenite veins.

Primary cpx of peridotites (cpx1) and of the clinopyroxenite vein have Mg# ranging from 88.5 to 93.5 with very low TiO_2 contents, whereas cpx in orthopyroxenites have lower Mg# and higher Al_2O_3 and TiO_2 contents. Mg#, Al_2O_3 and Na_2O of peridotitic opx range from 87.9 to 91.4, 1.33 to 4.20 wt.% and 0.02 to 0.17 wt.%, respectively. Opx in orthopyroxenites and websterites are characterized by lower and more variable Mg# (71.9-86.9), higher Al_2O_3 (2.98-5.35 wt.%) but similar Na_2O values with respect to those in peridotites.

Based on trace element contents cpx1 can be divided into two groups. Group1 has convex downward pattern from Gd to Lu, and variable enrichments from Eu to La: $(La/Yb)_N$, 0.05-4.04. It has positive Sr anomaly, variable Th and U contents and a positive Zr-Hf anomaly. Group2 has lower HREE content with respect to Group1 at comparable LREE, leading to higher $(La/Yb)_N$ (1.83-14.23). It has the highest Th and U contents, the widest Zr-Hf positive anomalies and a huge Ti through. Cpx of clinopyroxenite vein have a flat REE pattern [$(La/Yb)_N$, 1.24-1.74] with a marked positive Sr spike. Opx in peridotites are of two types, sometimes even in the same sample: the first, more abundant, is characterised by fractionated HREE, a negative Sr anomaly and low LREE [$(La/Yb)_N$, 0.01-0.70]. The second type has identical HREE values but it is variably enriched in LREE [$(La/Yb)_N$, 1.18-2.81]. Opx of orthopyroxenites and websterites are different, with flat REE pattern at about 1 × Ch, and Sr and Ti contents higher than opx in peridotites.

Opx and cpx composition in peridotite xenoliths is consistent with interaction and hybridization with a Si-Al-rich melt, deriving from the partial melting of the subducting Antarctic plate. Modellization of melting of a phengite-bearing eclogite gave trace element patterns with positive Zr-Hf anomalies; this melt hybridized with peridotites, caused LREE-enrichments in both pyroxenes and the onset of positive Zr-Hf anomalies in cpx1. Calculated melts in equilibrium with cpx of all lithologies closely resemble the composition of adakitic magmas erupted in the AVZ.

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A POSSIBLE COMMON GENESIS FOR WHITESCHISTS AND OTHER CONTINENTAL Mg-Al-RICH ROCKS IN THE ALPS?

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A number of studies in the Alps have been devoted to whiteschists [1, 2] and other Mg-Al-rich and Fe^{2+}-Ca-alkalies-poor schists (*e.g.* leucophyllites) [3, 4], which peak conditions range from P ~ 1.0 GPa and T ~ 500°C [5] to P ~ 4.5 GPa and T ~ 750°C [2]. Firstly considered as formed by isochemical metamorphism of a sedimentary protolith, these rocks are now interpreted as originated by metasomatism of orthogneisses, thought both the timing of metasomatism and origin of metasomatic fluids are still a matter of debate. The common occurrence of these metasomatic rocks testifies the widespread presence of local processes of Mg-metasomatism in the Alpine collisional orogen.

A review of published data on whiteschists and other continental Mg-Al-rich rocks derived from post-Variscan granitoids from the main tectonic Units of the Alps is proposed to test the hypothesis of a common genesis for the Mg-Al-rich rocks of the Alps and to improve the understanding of the Mg-metasomatism. Because previous works show different scientific approaches and analytical methods, the data are not homogeneous for all the localities. However, some common features have been recognized in both whiteschists and other Mg-Al-rich rocks: 1) they occur along shear zones within the metagranitoids; 2) they display a simple $MgO-Al_2O_3-SiO_2-H_2O\pm K_2O$-silicate mineralogy; 3) based on major and trace element compositions, they can be grouped in four homogeneous classes, representative of a progressively increasing metasomatism.

A recent petrological, geochemical and fluid inclusion study [2] indicates that the ultrahigh-pressure, pyrope-bearing whiteschists from the Brossasco-Isasca Unit of the Southern Dora-Maira Massif (Western Alps) derived from brine infiltrated along shear zones during prograde, high-pressure Alpine metamorphism (P = 1.7-2.1 GPa; T = 560-590°C). Geochemical features (enrichment in Mg and depletion in Na, K, Ca and LILE – *i.e.* Cs, Pb, Rb, Sr, Ba – with respect to the metagranite) and fluid inclusion data (prograde $NaCl-MgCl_2$-rich brine) are compatible with the influx of external fluids originated from antigorite breakdown in subducting oceanic serpentinites.

Overall, the data collected on whiteschists and other Mg-Al-rich rocks seem to point to a genesis similar to that invoked for the Dora-Maira pyrope-bearing whiteschists, though further multidisciplinary studies should be performed to confirm this hypothesis.

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POLYPHASE INCLUSIONS IN GARNET PYROXENITES FROM SULU (CHINA) AS CARRIERS OF SEAWATER AT ULTRAHIGH PRESSURE

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Unravelling processes of fluid-mediated element exchange between slab lithologies and the mantle wedge is of primary importance in understanding element mobility in subduction zones. Several studies have addressed element transfer related to fluid release during prograde metamorphism in subduction zones [1, 2, 3, 4]. Nevertheless, detailed studies documenting interactions between felsic, mafic and ultramafic rocks at ultrahigh-pressure (UHP) are still scarce [5]. For this reason, UHP metasomatised rocks represent ideal materials to study the element exchange at pressures corresponding to sub-arc depths in subduction zones.

We present preliminary results of Ca-rich garnet-clinopyroxenites from Suolushu, occurring as layers in a large serpentinite body at Hujialin, Rizhao County, in the Sulu UHP metamorphic terrane (eastern China). Both clinopyroxenites and hosting serpentinites are intercalated with coesite-eclogites and hosted by coesite-bearing gneiss. Similar garnet-clinpyroxene layers from Hujialin have been studied by [6] and interpreted as cumulates crystallised from a hydrous, subduction related magma at ~ 1 GPa and 1000°C. They were subjected to minor Ca enrichment coeval with serpentinisation of the host ultramafic rocks and then subducted at UHP (4.8±0.6 GPa and 750±50°C). Ca-rich garnet-clinopyroxenites are composed of centimeter-sized garnet porphyroblasts in a matrix of fine-grained green diopside, opaque minerals associated with green spinel, and garnet. Garnet porphyroblasts include rounded clinopyroxene, opaque minerals, and/or spinel grains. Aggregates of magnetite and spinel are abundant in some samples. Peak porphyroblastic garnets preserve primary polyphase inclusions in their cores, consisting of amphibole(s), chlorite, pyroxene, micas and spinel. We studied these inclusions with the Transmission Electron Microscope at the University of Milano. They show an inner part formed by amphibole and clinopyroxene surrounded by Al rich Mg-silicates. Amphibole and pyroxene grow coherently by sharing the [001] direction, the one parallel to the tetrahedral chains. At the grain boundary between amphiboles and pyroxene, or amphiboles and Al rich Mg silicates, smaller amphibole grains extremely enriched in both Cl (up to 8 at.%) and Sr (up to 1.5 at.%) occasionally occur. Such Cl-amphiboles grow coherently with the neighbouring amphibole. The Al rich Mg-silicate phases show electron diffraction patterns with several streaking, indicating possible polytypic disorder. They exhibit periodicities of 14.1 Å, characteristic of chlorite. These phases form a rim between the inclusion precipitates and the hosting garnet, whereas a direct contact between garnet and amphibole or pyroxene has never been observed.

Serpentinites act as carriers of oceanic Cl, B, Sr, Rb, Cs, and alkalis which are recycled into variably saline fluids within the stability field of antigorite serpentine [7]. Polyphase inclusions studied in Hujalin clinopyroxenites likely derive from the interaction with the hosting serpentinites at HP-UHP and could represent a snapshot of such fluid-mediated element recycling occurring in the slab at sub-arc depths.

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SLAB-TO-MANTLE "OXIDATION" TRANSFER: INSIGHTS FROM DIAMOND-BEARING MAJORITIC GARNETS (WESTERN NORWAY)

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The majoritic garnet-bearing websterites from Bardane (Western Gneiss Region, Norway) are unique examples of metasomatised mantle wedge that interacted with C-saturated COH subduction fluid phases at 200 km depth. These peridotites represent slices of former Archean transition zone mantle that upwelled, melted and accreted to a thick cratonic lithosphere, where it cooled until the Middle Proterozoic (stages M1-M2). During the subsequent Caledonian to Scandian subduction cycle (stage M3) these depleted mantle rocks were dragged into deep portions of the supra-subduction mantle wedge, where the infiltration of crustal fluids initiated diamond and majoritic garnet crystallisation [1, 2]. The infiltration of subduction fluids in these rocks at increasing depth promoted crystallisation of microdiamonds in polyphase, fluid-related, inclusions and of majoritic garnet in veins. We studied the peak (stage M3) mineral assemblage garnet + orthopyroxene + olivine ± clinopyroxene ± phlogopite, where garnet turns to majoritic with pressure increase from 3 to 6.5 GPa and 800-1000°C temperature. Majoritic garnet contains polyphase inclusions with daughter Cr-spinel + phlogopite/K-amphibole + dolomite/magnesite + graphite/diamond. They witness COH-fluid/mineral interaction closely related to the oxidation state of the rock and responsible for diamond formation. We determined the fO_2 in the M3 assemblage starting from Fe^{3+} analyses in majoritic garnet which results progressively enriched in $Fe^{3+}/\Sigma Fe$ up to 0.15. The fO_2 values obtained for the Bardane mantle wedge garnet peridotites are up to -2 log units lower than the fayalite-quartz-magnetite (FMQ) buffer along a trend from arc lavas (FMQ+1.5 - FMQ+3) [3, 4] to mantle wedge garnet peridotites equilibrated at 4-5 GPa (FMQ - FMQ+2) [5]. Such a trend record the same systematic ΔFMQ decrease with depth as subcratonic xenoliths from South Africa [6], but shifted towards higher fugacities.

The determination of oxygen fugacity of the hydrate-carbonate-bearing M3 mineral association enabled to estimate the speciation of slab-derived metasomatic COH fluids responsible for polyphase inclusions precipitation. Such fluids are H_2O-CO_2 mixtures, whereby the H_2O/CO_2 ratio increases with increasing pressure. The peculiar composition of majorite-hosted diamond-bearing polyphase inclusions from Bardane and the speciation of its COH component point to an "oxidised" silicate-rich aqueous fluid contaminant from the subducted slab to the mantle wedge which could be regarded as carrier of dissolved oxidised components from the subducted slab to the mantle wedge [7, 5]. Such a mechanism opens new possibilities to unravel the redox processes occurring in arc mantle sources and their role in precipitating diamond.

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EQUATION OF STATE OF Fe^{3+}-BEARING PHASE-X

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Phase X is a synthetic phase with general formula $A_{2-x}M_2Si_2O_7H_x$ where A = K, Na, Ca, □, and M = Mg, Fe, Al, Cr^{3+} (with H_2O contents from 1.8 to 4.2 wt.%) [1]. Experimental petrology showed that it coexists with a typical mantle assemblage (olivine/wadsleyite, clinopyroxene and garnet) in a pressure range of 14-20 GPa and temperature up to 1600°C. Besides, phase X represents a potential host for incompatible and large elements (Na, K, Rb, Cs, Ba) in metasomatized upper mantle and transition zone. In subduction slabs settings, it was found from the breakdown of phlogopite and K-rich amphibole [2], thus it might be one of the possible candidates for carrying water and K deep into the Earth's mantle.

The structure of phase X, space group $P6_3cm$, consists of di-octahedral sheets of MO_6 octahedron stacked along the *c* axis and linked together by Si_2O_7 group, which form pillars between the layer where A atoms are contained. Two different OH environments were found by Raman spectroscopy.

The HP behaviour of hydrous and anhydrous end-members $K_2Mg_2Si_2O_7$ was studied by synchrotron X-ray diffraction and IR spectroscopy [3]. Only limited variation on the EoS of the two compositions was found with a $K_0 \sim 74$ GPa for both, and the structures remain stable up to 30 GPa. The hydrous sample showed a softening and broadening of the OH stretching modes by increasing pressure up to 20 GPa when they become very weak. However, density functional based computations [4] showed bulk moduli about twice than that measured by Liu *et al.* [3] for the Na ($K_0 = 128$ GPa, $K' = 4.0$) and K ($K_0 = 132$ GPa, $K' = 4.4$) anhydrous end-members. So up to now the baric behaviour of phase X it not well constrained. To better define the EoS of phase X, and how the $Fe^{3+} \rightarrow Mg$ substitution may influence the elastic constants, we investigate the sample studied by Bindi *et al.* [5] with chemical composition $(K_{1.307}Na_{0.015})(Mg_{1.504}Fe^{3+}_{0.373}Al_{0.053}Ti^{4+}_{0.004})Si_2O_7H_{0.36}$, [space group $P6_3cm$, lattice constants $a = 5.005(1)$ Å, $c = 13.148(2)$ Å; $V = 285.23(9)$ Å^3]. The sample was synthesized with the high-pressure toroidal "anvil-with-hole" apparatus at 7 GPa and 1650°C in the model peridotite system with 70 wt.% of chemical K_2CO_3. Peridotite was prepared from a mixture of stoichiometric gels (60 wt.% olivine, 16 wt.% orthopyroxene, 12 wt.% clinopyroxene, and 12 wt.% garnet), and had the composition of garnet lherzolite (wt.%) similar to pyrolite. HP single-crystal X-ray diffraction data from in house apparatus (Perugia University) and synchrotron source (ID-27 beamline ESRF, Grenoble) were collected by using diamond anvil cell loaded with different pressure media (methanol-ethanol-water mixture, neon) and pressure calibrant (ruby, quartz, Sm^{2+}:BaFCl).

Preliminary compressibility data at low pressure (< 5 GPa) give a bulk modulus $K_0 = 135(10)$ GPa with *K'* fixed to 4, more similar to the calculated than measured values for the potassium end-member. Details on the compressibility pattern and the stability over a large pressure range will be presented.

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HIGH-Mg ANDESITE PETROGENESIS BY AMPHIBOLE CRYSTALLIZATION AND ULTRAMAFIC CRUST ASSIMILATION

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High-Mg andesites (HMA) are a group of subduction related magmas of great importance for the Earth's evolution because they share striking similarities with the composition of the continental crust. These melts may have contributed in the Archean to its formation [1]. The origin of HMA is debated and although they are commonly considered as primary mantle melts [1, 2, 3, 4], a not primary origin has been recently proposed [5].

Mafic and ultramafic intrusives with HMA affinity are occasionally found in collisional settings. These amphibole-rich rocks preserve chemical and textural heterogeneities that are important records of the petrogenetic processes occurring in the deep portions of the arc crust. New insights into the origin of HMA are inferred from the Tertiary amphibole-rich ultramafic intrusives of the southern Adamello batholith (Central Alps). These rocks consist mostly of amphibole grains with brown cores (Ti-pargasite) that progressively grade through brownish green (Mg-hornblende) and light green (edenite) rims. Brown amphibole has inclusions of olivine (Fo = 85-87 mol.%) and clinopyroxene (± spinel) with irregular boundaries indicating disequilibrium with host amphibole.

Amphibole shows a marked chemical zoning. From the core to the rim of the crystal, a significant enrichment in LREE, Th, U coupled with a decrease in Ti and HREE is observed. According to the current knowledge of amphibole/liquid partition coefficients, a fractional crystallization process driven by amphibole may explain most of the observed elemental variations. However, the increase from core to rim of highly compatible elements in amphibole such as MgO, Co, Zn and Ni argues against a closed system fractional crystallization. The assimilation/resorption of olivine is considered the most efficient mechanism to supply or buffer MgO and Ni in the evolving system during amphibole crystallization. In addition, we found cm-scale clusters made up of olivine (Fo up to 85 mol.%), minor clinopyroxene and accessory spinel. These clusters are interpreted to represent fragments of older ultramafic intrusives dismembered by the injection of the amphibole-forming magma. Assimilation of older intrusives is confirmed by *in situ* U-Pb zircon geochronology that reveals the presence of slightly older inherited cores.

The process of amphibole crystallization and concomitant assimilation of ultramafic crust revealed by the southern Adamello ultramafic intrusives may have implications in the genesis of evolved melts with relatively high MgO contents as the HMA.

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BORON AND STRONTIUM ISOTOPE SYSTEMATICS IN DEEPLY SUBDUCTED ALPINE-SERPENTINITES: EVIDENCE OF HIGH-^{11}B FLUID FLOW

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B is an important tracer of slab-derived components in arc magmas. It is uptaken in the oceanic crust during alteration by seawater that drives to a general enrichment in B and ^{11}B prior to subduction. However, the δ^{11}B of arc lavas does not simply reflect the values measured in the slab materials prior subduction. Boron isotopic studies of accretionary prisms, fore-arc mantle and residual slab materials indicate substantial B loss from the slab and B isotope fractionation during subduction-zone dehydration. Since ^{11}B preferentially partitions in fluids, the δ^{11}B in the residual slab is expected to decrease as subduction proceeds. Deeply subducted, mafic eclogites display negative δ^{11}B signatures due to loss of ^{11}B by the altered mafic oceanic crust before it reaches sub-arc depths: this reservoir cannot release ^{11}B-enriched fluids. This is at odds with the well-documented high δ^{11}B signature of arc magmas, and several models have tried to explain this discrepancy. However, very few studies are addressed to the geochemical behaviour of boron isotope in high (HP) to ultrahigh pressure (UHP) serpentinites that experienced pressure-temperature conditions similar to those occurring in modern subduction zones. We present δ^{11}B and ^{87}Sr/^{86}Sr ratios on the Erro-Tobbio peridotite (Ligurian Alps) a slice of serpentinized mantle involved in subduction and high-pressure recrystallisation during the Alpine orogeny. The analyzed sample set includes serpentinized peridotite samples recrystallized at increasing P-T conditions: from relatively low P-T (chrysotile and lizardite are the dominant serpentine minerals) to eclogite facies conditions (antigorite + olivine + Ti clinohumite form the stable paragenesis). During subduction, ductile deformation under HP conditions was focused in serpentinite mylonite shear zones (high-strain domains) surrounding volumes of HP serpentinized peridotite unaffected by plastic deformation (low-strain domains). The latter diffusely preserve serpentinized mantle peridotites with low P-T overprint retaining the original mantle textures and assemblages. In general, the δ^{11}B in these rocks is heavy, with the majority of samples exceeding δ^{11}B of 16‰ and reaching extreme values of +24‰. The ^{87}Sr/^{86}Sr ratios range between 0.7044 and 0.7065, significantly lower than the values of serpentinites formed during interaction with seawater-dominated fluids and close to the seawater ^{87}Sr/^{86}Sr.

In more detail, the low P-T serpentinized peridotites are characterized by the wider range of δ^{11}B variability (+3.8 to +24‰). The low-strain HP peridotites show a comparably wide range in δ^{11}B (+6.8 to +20‰). More homogeneous and generally higher δ^{11}B were measured in HP mylonitic serpentinites (δ^{11}B between +16.7 and +24‰): these rocks also display the highest Sr and, to a lesser extent, B contents. The heavy δ^{11}B and the relatively low ^{87}Sr/^{86}Sr ratios of HP rocks are not consistent an overprint of a former oceanic mantle by seawater-derived fluids and with the progressive dehydration of this type of serpentinized mantle rocks. Rather, our isotopic data suggest that the source of the serpentinizing fluids was a subducting slab and imply a supra-subduction environment for serpentinization of the Erro-Tobbio mantle rocks. Whatever the case, here we demonstrate that serpentinites are the best candidates to provide high δ^{11}B fluids to the sub-arc mantle: they represent the missing link to solve the geochemical dilemma on the B slab reservoirs for arc magmas.

CARBONATES, HYDRATES AND MELTS IN FLUID-SATURATED PERIDOTITE AT HIGH P-T CONDITIONS

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The mass transfer from the subducting lithosphere to the overlying mantle wedge is mediated by complex solutions deriving from dehydration and decarbonation processes. High-pressure relations among fluids/melts, carbonates, hydrous silicates, graphite/diamond and nominally volatile-free phases in COH-bearing ultramafic systems are substantially unexplored in the subsolidus and in the near-solidus, with the exception of a couple of pioneer works [1, 2, 3].

We experimentally investigated the system KNCFMAS + COH at P = 1.8-3.2 GPa, T = 900-1080°C, fO_2 = NNO, under fluid + graphite saturated conditions. The bulk composition is that of a spinel lherzolite, 30% olivine + 5% phlogopite [4], thus representing a metasomatised mantle-wedge peridotite. Seeded gels were loaded in a piston-cylinder using double capsule technique. GCOH fluids have been generated by addition of 10 wt.% oxalic acid dihydrate and pure graphite. Following thermodynamic modeling (Perplex package), we expect in our experiments binary H_2O-CO_2 fluids characterized by intermediate XCO_2 and $X(O)$.

The stable carbonates are dolomite at low-P (1.8 GPa at 900°C), magnesite at high-P conditions (2.6 GPa at 900°C). We observe in between a region where both magnesite and dolomite are stable. In this region, an increase in T up to 1060°C at 2.6 GPa induces the melting of the system, without entirely consuming the carbonates. Carbonate-out occurs at lower-P conditions, in the subsolidus region. We observe a carbonate-free assemblage at 1.8 GPa at 1050°C up to the solidus, encountered at 1075°C. Amphibole stability field extends up to 3 GPa at 900°C and it is delimited by the solidus. By increasing P, mass-balance calculations suggest that amphibole breakdown reaction produces clinopyroxene, while magnesite develops at the expenses of olivine reacting with COH fluid, which increases its XH_2O.

The near-solidus melts above 2.3 GPa display quench-related textures, showing dendritic intergrowth of nearly stoichiometric dolomite and a K-silicate close to phlogopite. The analysis of this magnesiocarbonatitic melt has been performed at the electron microprobe. The silicate phase is the sink of Si, K, Al, Fe and Na. The melt composition is comparable with published data concerning peridotite + COH and peridotite + CO_2 systems. We provide also direct microprobe analyses of carbon in the melt, while H_2O is estimated by total subtraction. The H_2O content of ~ 25 wt.% is consistent with water-solubility data in carbonatites reported by [5]. Melting takes place at the expenses of clinopyroxene and amphibole which represent the source of Ca in the magnesiocarbonatitic melt, while dolomite is not consumed, suggesting that CO_2 in the melt derives from the fluid. The residual water should dissolve into the melt up to water-saturated conditions, which are unknown at present in this P-T range.

The near solidus melt at low pressure is silicatic and potassic. At 1.8 GPa, 1075°C melt pools, coexisting with augitic clinopyroxene + olivine + garnet, are characterized by SiO_2 ~ 57 wt.% and K_2O up to 12 wt.%, being trachyandesitic (shoshonitic) in composition. Similar melts have been produced by [6] in CO_2-free, water-saturated K-bearing peridotite at similar P-T conditions (1 GPa, 1050°C).

The presented experimental data constrain the mineral assemblages expected at different P-T conditions in metasomatised mantle-wedge peridotites. Furthermore, they allow speculating about the genesis of carbonatites and potassic magmas in the upper mantle.

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SESSION 1.6

Metamorphism and Magmatism in the crustal evolution

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NEW INSIGHTS FROM MEXICAN EARLY PALEOCENE GRANITOIDS (SW MEXICO): ADAKITE-LIKE SIGNATURE MOULDED IN A SHALLOW MAGMATIC CHAMBER

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The arc-related magmatism occurring along the western Mexican Pacific Coast is commonly linked to convergence of the Pacific oceanic plates (Farallon, Rivera and Cocos) and the North American continental margin. The Chacala and the El Salto plutons (Colima State), as well as the southestward Maruata magmatic body (Guerrero State) mainly intrude the Early Cretaceous volcano-sedimentary sequences of the Guerrero composite terrene [1].

These three plutons mainly consist of high- to medium-K calcalkaline granodiorites and granites, with minor diorites. SHRIMP U-Th-Pb analyses on Zrn provide coeval emplacement ages within errors: 63±1 (MSWD = 1) for Chacala, 63±2 (MSWD = 0.8) for El Salto and 62±2 Ma (MSWD = 0.7) for Maruata plutons. Diorites and granodiorites mainly consist of Pl, Qtz, Kfs, Mg-Hbl, Bt, ±Di, Zrn, Ap, Mag, ±Ttn, whereas in granities Cpx is absent, Am is subordinated to Bt, and Ttn increases in abundance as main accessory phase.

They present typical HSi adakite-like signature [2, 3] with SiO_2 = 57-70 wt.%, high Al_2O_3 (15-18 wt.%), Na_2O (4-6 wt.%), Ba (550-1000 ppm) and Sr (550-700 ppm) and low MgO (1-4 wt.%), Rb (15-60 ppm), Y (6-25 ppm) and Yb (0.5-2.2 ppm) values. Their isotopic composition recalls that of typical adakitic granitoids: $(^{87}Sr/^{86}Sr)_i$ = 0.7035-0.7037, $(^{143}Nd/^{144}Nd)_i$ = 0.51282-0.51290, $(\varepsilon Nd)_i$ = 5.3-6.7. They also show listric-shaped REE pattern with moderate to steep slope ($(La/Yb)_n$ = 6-21) and no Eu anomaly (Eu/Eu* = 0.7-1.01). LILE, HREE and Y decrease with silica increasing. Sr/Y (20-110) and La/Yb (8-30) ratios consistently increase with SiO_2, so that the studied samples evolve from "normal" calcalkaline into "adakitic" field.

Depletions in HREE and Y are usually interpreted to reflect the role of Grt as a residual phase during melting or a fractionating phase during differentiation.

As our data suggest that the Chacala, El Salto and Maruata magmas crystallized at low-P conditions, we show that their evolution from an "ordinary", moderate Sr/Y and La/Yb dioritic parental magma to more evolved "adakitic" granites can be ascribed to simple AFC processes. We suggest that a combination of modally abundant Hbl (3%) + Ttn (0.1%), 10% of crustal assimilant (Tizupan pluton) and high compatibilities of Y and HREE [4] are sufficient to deplete these elements in residual melts. Relatively high Sr and Ba contents instead suggest partial feldspar dissolution and a late release of these elements to the residual melt, in agreement with textural evidence for feldspar resorption. Thus, the adakitic Sr/Y and La/Yb values showed by our samples could be related to crustal assimilation + fractionation of Hbl and Ttn from a "normal" calcalkaline H_2O-rich [5] dioritic parental magma, from which Y and Yb are respectively depleted at roughly constant Sr and slightly decreasing La concentrations, in absence of significant Pl fractionation.

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VOLCANIC COMPLEX FROM THE VALGANNA AREA (VA, N-ITALY): NEW PRELIMINARY FIELD, PETROGRAPHIC AND GEOCHEMICAL DATA

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In the Southern Alps, during the Permian, post-Variscan extension is commonly associated with widespread plutonic and volcanic activities [1, 2].

We present preliminary field, petrographic and geochemical data of the area comprised between Lugano and Maggiore lakes (Valganna area), where an almost tectonically undisturbed sequence of Permian [1, 3] volcanic to subvolcanic (Valganna granophyre) rocks occur. From new detailed field and petrographic relationships we have subdivided this volcanic complex in 3 sequences [3]. From the bottom to the top: A) the basal extrusive sequence (1800-2000 m in thickness) starts with rhyolite lava flows, tuffs and ignimbritic units directly deposited on a non-conformity surface over the Scisti dei Laghi basement [4]. A few metres-thick of pebble conglomerate are locally preserved between basement and volcanic rocks; B) dacitic lava flows, tuffs and rhyolitic ignimbritic deposits postdate the basal acidic sequence and are in turn covered by C) late andesitic to dacitic lava flows followed by rhyolitic tuffs levels, minor rhyolite flows and a final ignimbrite. The boundaries among volcanic sequences, as defined by flow indicators, dip towards S-SE with dip angles of 30-45°. Due to the thick forest cover and paucity of outcrops, the geometrical relationships are often unclear even if the subvolcanic Valganna granophyre was suggested to postdate the volcanic sequence [3].

Generally, all samples from these three sequences show high-K calcalkaline affinity with similar PM- and REE-normalized patterns, which are characterized by LILE and LREE enrichment relative to HFSE and HREE, respectively. As the andesitic to dacitic extrusive products show very similar geochemical behaviour, the most outstanding differences are among the acidic volcanic products. The latest acidic products mainly differ in: 1) higher K_2O content, which increases with silica increasing; 2) higher Rb and Y and lower Na_2O, MgO, CaO, TiO_2, Sr and Zr contents; 3) more pronounced negative Ba, Nb, Sr, P, Zr and Ti and positive Th, K, Pb spikes in PM- normalized spiderdiagram; 4) higher HREE, but similar LREE, contents that lead to a flatter REE pattern characterized by a more pronounced Eu anomaly.

Petrographic and geochemical data reveal a magma evolution within each sequence through fractional crystallization rather than partial melting or simple mixing. The enrichments in LILE and LREE observed from the basal to the late sequences could be instead related either to different abundance of involved crustal component or even to different crustal sources in magma genesis. Moreover, the transition from high-K calcalkaline (basal and second sequences) to transitional affinity with Y+Nb enrichments (late sequence) can suggest for their magma a transtensive emplacement setting probably driven by Permian strike-slip faults, as already reported for the Collio and Orobic basins [2, 5]. In progress geochronological dating of the key-units will allow to make regional scale correlations with volcanic rocks of similar age and evolution [1, 2, 6].

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CALCULATIONS OF WALLROCK MELTING DEGREE IN AFC PROCESSES

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Analytical solutions are found of differential equations which describe isotopic and trace element concentration changes in magmatic liquids which evolve by assimilation-fractional crystallization (AFC) where the assimilated material changes its composition as the instantaneous melt in fractional melting model of Shaw [1]. These differential equations are obtained by relating melting model [1] to DePaolo's AFC model [2] through a relationship between instantaneous wallrock melting degree and residual liquid fraction in the assimilating magma.

The chemical and isotopic evolution of a magmatic liquid by AFC as the concentration in the assimilated changes according to fractional melting model [1] was modelled by [3, 4], who calculated the effect of the behaviour of the element in melting on concentration and isotopic paths. However, these authors did not solve any differential equation, giving only numerical results.

The analytical solutions are easy to use and versatile. They are obtained by integrating with DePaolo's parameter r (the ratio between assimilation and crystallization rates) as a constant, and describe very well the concentration and the isotopic changes in a large range of residual liquid fraction. In any case, an exact solution exists and is given, which is analytical-numerical, as it involves a hypergeometric ${}_2F_1$ function.

These calculations are important as they can aid in ascertaining if an isotopic and concentration data set can be interpreted in terms of a certain AFC process or not. In interpreting a data set in terms of an AFC process, we assume starting from a parental liquid characterized by certain chemical and isotopic compositions which crystallizes and assimilates melt produced by melting of a wallrock characterized by certain chemical and isotopic compositions. Moreover, we also assume a value for ratio r, and, in the model which is proposed here, an other parameter must be assumed to trace the evolution path, which is the ratio μ between the mass of the liquid when assimilation begins and the mass of the wallrock which is involved in the melting process.

Parameters r and μ calculate the melting degree of the wallrock at any step, and the melting degree cannot exceed 1. Moreover, for the AFC process to be a single one – *i.e.* for the concentration and isotopic data-set can be interpreted as the result of the evolution of a single mass of magma – values of μ must fall in a reasonably narrow range.

As an example of application, we consider Sr isotopic and concentration data of the mafic to intermediate volcanic rocks from the Long Valley caldera and Devil's Postpile National Monument, Eastern California (data from [5] and [6]), which were interpreted by [4] as the result of a single AFC process.

Assuming the same concentration and isotopic parameters used by [4] for the initial uncontaminated liquid and the wallrock, and the same values for Sr distribution coefficients in crystallization and melting, both the analytical solutions show, however, that for any r value too much different values of ratio μ, which differ by a factor of two, should be input into the equations to generate paths which describe the data point distribution. We thus infer that this rock distribution cannot be actually interpreted as derived by AFC starting from a single mass of liquid in the terms proposed by [4].

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ROCKS EVOLVING THROUGH MAGMATIC, HYDROTHERMAL AND PYROMETAMORPHIC PROCESSES IN THE SHALLOW SYSTEM OF PERSISTENTLY ACTIVE BASALTIC VOLCANOES: EVIDENCE FROM THE STROMBOLI EJECTA (ITALY)

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Magmatism, hydrothermalism and contact metamorphism usually describe different geological processes occurring in distinct environmental conditions. This can be not true when we are going to deal with the shallow part of a persistently active basaltic volcano, where the magma feeder dykes are coupled with an active acid-sulphate hydrothermal system. In this case, magmatic, hydrothermal and high-T, low-P contact metamorphism (*i.e.* pyrometamorphism) processes coexist, generating rocks with hybrid modal mineralogy and microstructures [1].

Besides dolerite blocks from the shallow magmatic system [2], the youngest paroxysmal eruptions of Stromboli allowed us to collect a large quantity of ballistic ejecta coming from the summit crater area and consisting of: (i) fresh, crystal rich scoriae and lava fragments (shoshonitic basalts of the persistent Stromboli activity), (ii) weakly to strongly hydrothermally-altered extrusive blocks, (iii) sanidinite to buchite facies rocks, and (iv) samples with intermediate magmatic, hydrothermal and pyrometamorphic features (hereafter *recycled hybrid lithic tuffs*). According to microstructural features and grain size, we studied the above samples through a combination of analytical methods: polarizing microscope observations, whole rock major-trace elements chemistry, SEM and EMP analyses on thin sections. In addition, we performed, on the hydrothermally-altered samples, XRD analyses coupled with *p*H determination of the rock and ion chromatography of the soluble salts.

The study of the *recycled hybrid lithic tuffs* gave us a series of snapshots of the petrogenetic processes continuously occurring in the summit cones of Stromboli. We observed the leaching of the erupted extrusives due to percolation of the hydrothermal sulphur-rich acid fluids and the process of compaction of the erupted scoriae and ash induced by their high-T reheating in an oxidizing environment [3, 4]. This latter sub-solidus process is mostly emphasized by Fo_{96}-En_{98} symplectitic texture of pseudomorphs after olivines, associated with vermicular and lamellar Fe-oxides [5]. Nevertheless, the presence of reactions involving anhydrite and gehlenite, coupled with metastable osumilite and cordierite testify high-T, reduced conditions. Finally, the interaction of the high-T Stromboli basalts with peraluminous and/or Si-rich hydrothermally-altered rocks give rise to buchite/sanidinite facies, with a multitude of pyrometamorphic characteristics, concerning both mineralogy and microstructure [6, 7].

We are going to explain how hydrothermally-altered extrusives may transform to buchite/sanidinite and we are going to describe how in the summit crater area of persistently active basaltic volcanoes the variation of the redox conditions and the high-T temperature gradient can generate *recycled hybrid lithic tuffs* with a wide range of exotic rock-forming minerals and microstructures.

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INSIGHTS OF AN ALPINE SHEAR REACTIVATION IN THE CASTAGNA UNIT (SILA PICCOLA MASSIF, MIDDLE-NORTHERN CALABRIA)

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In the nappe-edifice of the northern Calabria-Peloritani Orogen (CPO), the Castagna Unit represents one of the continental crust-derived units of the Calabride Complex [2]. This latter has been interpreted as an entire Hercynian continental crust section [3, 4].

The Castagna Unit has been established by Dubois & Glangeaud [1] and it consists of medium-high grade metamorphic rocks (para- and orthogneiss, micaschist, marble and amphibolite gneiss) intruded by late-Hercynian granitoids. It occupies the intermediate position in the Calabride Complex, between the granulite facies rocks of the Polia-Copanello Unit at the top, and the low grade metamorphic rocks of the Bagni Unit at the base of the nappe-edifice.

This study is aimed to understand the role, the metamorphic conditions and possibly, the age of shear deformation event involving the Castagna Unit's rocks. In fact, its geological-metamorphic significance represents a subject of interest for the understanding of the tectonic evolution of the crystalline basement nappes of the northern CPO.

An integrated structural, petrographic and petrological study carried out on mylonitic rocks outcropping in the Sila Piccola Massif, mostly paragneiss and orthogneiss, allowed to delineate the tectono-metamorphic history for the Castagna Unit detecting two different deformational events developed under different P-T conditions and highlighting a retrograde overprint occurred during the shearing event.

Structural and microstructural investigations suggest that a former two-stages deformative event (D_1), developed in ductile conditions, it is responsible to the production of a penetrative and pervasive mylonitic planar fabric representing the field foliation, averagely striking E-W, as well as supported by a complete record of structural and microstructural features (a related and well developed stretching lineation, marked by elongate quartz and feldspar crystals alignment, an extensional crenulation cleavage and, several kinematic indicators) suggesting an extensional tectonic regime. Petrografic and petrological evidences enhance that during the first deformative event a metamorphic retrograde overprint from granulite to amphibolite and greenschist facies conditions occurred.

The second deformative event (D_2) developed in transitional to brittle conditions, affecting previously mylonitic foliation and generating asymmetric folding; along axial plane of the folds often thrusts planes developed. In the Sila Piccola area the kinematic of this second deformational event shows a sense of overthrust toward W-SW.

The field evidences of undeformed aplitic- pegmatitic dikes, probably linked to the Sila Batholith emplacement, crosscutting the mylonitic foliation could be an important time constraint on the age of the shearing event, enhancing the hypothesis of a late-Hercinian shear zone probably reactivated during the Alpine fold-thrust belt building.

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SOURCE CONTROLLED ^{87}Sr/^{86}Sr ISOTOPE VARIABILITY IN GRANITIC MAGMAS: THE INEVITABLE CONSEQUENCE OF DISEQUILIBRIUM PARTIAL MELTING OF THE PROTOLITH

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The broad Sr isotopic variability exhibited by granitoid rocks is commonly interpreted to reflect magma evolution through the mixing of magma batches from different sources. However, evidence from granites and migmatites indicates that melting and melt extraction from crustal sources occurs sufficiently rapidly that equilibration between liquid and residual phases is commonly not achieved. Additionally, evidence from un-melted high-grade metamorphic rocks indicates that major reactant minerals in the fluid-absent melting process, principally biotite and plagioclase, do not attain isotopic equilibrium during regional metamorphism. When these two circumstances occur in combination, the melt does not inherit it's radiogenic isotopic signature from the bulk source in a simple way and its isotopic composition is dependent on: i) the isotopic compositions of the reactant phases; ii) the stoichiometry of the melting reaction; and, iii) the extent of isotopic re-equilibration between melt and residuum prior to melt segregation. Consequently, a range of isotopically distinct melts can arise from progressive melting of a single compositionally heterogeneous source that is able to undergo melting *via* different reactions as temperature increases.

This study investigates the ^{87}Sr/^{86}Sr isotopic variability that would be expected to arise *via* fluid-absent partial melting of theoretical metagreywacke and metapelitic sources as a function of age and composition of the protolith. The model demonstrates that the Sr isotopic variability commonly observed within granitic suites, as well as the isotopic heterogeneity at the grain and sub-grain scale in a single magmatic body can be primary, reflecting differences in composition between magma batches produced from a single source.

GRAIN SIZE *VS.* Th-Pb AGES OF MONAZITE: EXAMPLES FROM HIGH-GRADE METAPELITIC GNEISS FROM THE ULTEN ZONE, EASTERN ALPS

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Monazite is a well suited mineral for dating amphibolite-facies and higher-grade metamorphic events of metapelites [1]. A single monazite grain can record multiple geologic events within single grains, and different generations of monazite can be crystallised in response to changes of the P-T conditions and fluids composition. In order to gain as much petrological information as possible, textural and chemical criteria are needed to distinguish early-stage monazite from peak and late-stage monazite. Generally, enclosed monazite is believed to yield older ages compared to the ages obtained from matrix monazite thanks to the armouring effect of host minerals. However, the assumption of a complete shielding by porphyroclasts/blasts is debated [2]. Another textural criterion that is usually neglected during the petrographic observation is monazite dimensions. Within the same textural site, monazite grain size may vary considerably, suggesting that different generations of monazite can coexist within the same textural site.

This hypothesis has been tested in a migmatitic garnet-kyanite paragneiss from the Variscan Ulten Zone, which contains monazite in different textural sites and with highly variable grain size, from $30\times20\ \mu m^2$ to $500\times250\ \mu m^2$. Monazite grains have been detected and microstructurally characterised at the SEM. Chemical analyses and X-ray elemental (Th, Ca, Y, La and Ce) mapping have been performed by electron microprobe. On selected monazite grains, *in situ* U-Th-Pb dating by LA-ICP-MS directly in thin section has also been carried out.

On the basis of textural position, monazite grains were grouped in: i) monazite grains within garnet and kyanite porphyroblasts (hereafter, included Mnz), and ii) monazite grains disseminated within the matrix (hereafter, matrix Mnz). Locally, microcracks intersect included Mnz creating a connection between the monazite grain and the matrix.

The $^{208}Pb/^{232}Th$ ages range nearly continuously between 365 and 306 Ma, defining three major clusters at *ca.* 350, 333, and 314 Ma. Monazite grains yielding Th-Pb ages in the range of *ca.* 350 Ma correspond to large matrix Mnz. These grains are characterised by single or multiple Th(+Ca)-rich internal domains surrounded by La+Ce-rich external domains, suggesting a pseudomorphic replacement of allanite during the prograde metamorphic history. The Th-Pb ages clustering at *ca.* 330 Ma have been obtained from smaller matrix Mnz, from overgrowths of the larger matrix Mnz and from included Mnz, or domains of it. These ages have been attributed to a second crystallisation/re-equilibration event which occurred during (near-)peak metamorphic conditions and anatexis (340-330 Ma; [3]). The minor *ca.* 314 Ma Th-Pb ages resulted from external domains of matrix Mnz and have been assigned to a retrograde metamorphic evolution.

Different monazite grains form a single thin section yield an age span of nearly 60 Ma, from prograde amphibolite-facies conditions through peak metamorphism to subsequent retrograde amphibolite-facies conditions. We noted that the textural site occupied by monazite does not completely deliver relative time information. The armouring effect may be absent where microcracks connect included Mnz and the matrix. Interestingly, coarser monazite retains older ages, regardless its textural site. The larger older grains can be seen as clasts formed during the prograde metamorphic history and survived the 340-330 Ma anatectic event.

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CRUSTAL- *VS.* MANTLE-DERIVED MAGMAS IN THE SAN VINCENZO RHYOLITES (TUSCAN MAGMATIC PROVINCE, ITALY) AS CONSTRAINED BY TEXTURE AND THERMOBAROMETRY

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This work focuses on the physical-chemical conditions of genesis and evolution of the San Vincenzo rhyolites, one of the most significant examples of mixing between anatectic and mantle-derived magmas [1, and reference therein]. Rhyolite lavas often show quenched andesite/latite enclaves with clinopyroxene and plagioclase phenocrysts and a large variety of petrographic domains (*e.g.* quartz syenite autholiths, sillimanite-cordierite-quartz-spinel-ilmenite xenoliths, clinopyroxene-rich cumulates), and restitic and melt inclusion-bearing magmatic phases (plagioclase, sanidine, quartz, biotite, cordierite). Melt inclusion-free, mafic phenocryts (amphibole, garnet, clino- and orthopyroxenes), often showing reaction/overgrowth rims of biotite, are relatively widespread. In particular, the evidence of amphibole nucleation, growth and quenching is found in mixed domains next to the basic enclaves, whereas clinopyroxene-rich cumulates show inclusion and interstitial amphiboles with homogeneous compositions.

Various thermobarometric methods [2, 3, 4] were applied to the EMP data from the different domains showing equilibrium textures and compositions. In addition, we calibrated new cordierite-saturation thermobarometric formulations for peraluminous H_2O-undersaturated melts. These latest formulations are particularly suitable for constraining the P-T conditions of San Vincenzo peraluminous melts (ASI 1.05-1.32, H_2O 0.2-3.5 wt.%) as only a few plagioclase inclusions are inferred to approach water-saturation (H_2O 3.8-4.1 wt.%). In contrast, single-crystal amphibole thermobarometry indicates higher H_2O contents (3.7-6.8 wt.%) and shows a continuous P-T crystallization pattern from 991°C and 1085 MPa (amphibole crystals from clinopyroxene-rich cumulates) to 869°C and 207 MPa (micro-phenocryst cores) crossing the MOHO [22-23 km, *ca.* 600 MPa, 5] at 900-950°C. These results are consistent with a population of plagioclase-melt inclusion pairs indicating temperatures of 885-950°C. Clinopyroxene-liquid thermobarometry constrains the crystallization of basic enclave phenocrysts to higher-T (1060-1120°C) and mantle depths (800-1250 MPa). Sanidine-melt, sanidine-plagioclase and most of the plagioclase-melt pairs indicate temperatures of 837-720°C, closely matching the entrapment conditions of H_2O-undersaturated melt inclusions of cordierite phenocrysts (790-850°C; 275-370 MPa). Temperatures of micro-quartz syenite autoliths (662-713°C) and those of "flame"-like restitic biotites (640-735°C) are similar. Finally, the application of THERMOCALC program (average P-T calculation mode) to a sillimanite-cordierite-quartz-spinel-ilmenite xenolith suggests equilibrium conditions of 700-750°C and 320-350 MPa.

This textural and thermobarometric picture is consistent with the formation and evolution of the anatectic magma of San Vincenzo by "gas sparging" (*i.e.* rising of temperature and melting via fluid percolation [6]), magma mixing, assimilation and fractional crystallization processes at upper-mantle/crustal depths.

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ZIRCON AND MONAZITE RECORD OF PROTRACTED MELTING IN COLLISIONAL SETTINGS: ALPS AND HIMALAYA

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Partial melting of the continental crust commonly occurs in orogenic settings at the root of mountain belts. The timing of melting has significant implications for the secular evolution of the planet in terms of modeling of orogenic processes, heat transfer and rheology of the crust. We present here a detailed geochronological study of melting in anatectic terranes in the Alps and the Himalayas that record different melting conditions. U-Pb ion microprobe dating of zircon and monazite was used to time the growth of accessory minerals during melting.

The migmatite of the Central Alps are a well-preserved example of low temperature (650-700°C), fluid-assisted melting at pressures around 0.8 GPa. The different generations of leucosome that can be observed in the field contain zircon and to some extent allanite with multiple growth zones even within the same sample (Fig. 1). Ti-in-zircon temperature, inclusions and trace element composition indicate zircon growth during repeated melting events between ~ 32 and 22 Ma. The melting and re-melting events were controlled by the local rock composition and the influx of external fluids. This period of protracted melting was followed by rapid cooling and exhumation to upper crustal levels.

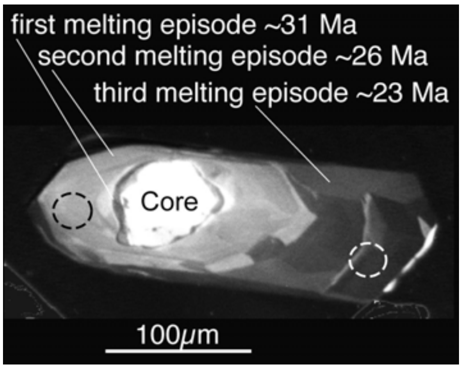

Fig. 1. Cathodoluminescence image of a zircon grain from an Alpine migmatite. The three distinct growth stages are record of episodic melting. Circles show the location of SHRIMP analyses.

The Sikkim sequence of the eastern Himalayas reached high-grade metamorphic conditions (800°C), thus entering the field of hydrate-breakdown melting. Similarly to the Alps, the Sikkim migmatites contain distinct generation of leucosomes. Zircon and monazite in the leucosomes and country rocks have multiple growth zones and ages ranging between ~ 16-32 Ma. In several cases, the accessory mineral growth can be related to melting.

The preservation of multiple growth stages in monazite and zircon, notwithstanding repeated melting, testifies to the physical robustness of these geochronometers. Despite the different metamorphic conditions, in either case melting was protracted over time, and allowed for the crystallization of accessory minerals, and likely of leucosomes, in episodic fashion. The timing of repeated accessory mineral crystallization was diachronous and not systematic within an area. Therefore, a high volume percent of leucosomes within migmatites might be misinterpreted as the result of a single, pervasive melting event. Instead the detailed chronology demonstrates that these rocks underwent several melting events, separated in time and likely preventing large melt volumes to accumulate. This has significant implications for tectonic models that predict fast exhumation driven by the buoyancy of large melt volumes.

FIELD, PETROGRAPHIC AND GEOCHEMICAL FEATURES OF LATE-HERCYNIAN GRANITOID BODIES FROM THE NORTH-EASTERN PELORITANI MOUNTAINS (SOUTHERN ITALY)

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Late Hercynian trondhjemites and granites from the area of Forte Cavalli in the north-eastern Peloritani Mountains were studied. Trondhjemites occur as bodies up to 300 m in thickness, as well as centimetric to metric dykes. They are typically heterogranular coarse- to very coarse-grained rocks mainly made up of large crystals of quartz and plagioclase up to 5 cm in length, with small to very small amounts of muscovite, biotite, K-feldspar and rare sillimanite. Many trondhjemite samples are affected by intense post-magmatic modification producing secondary plagioclase, muscovite, clinozoisite and chlorite. Granites crop out as bodies up to 100 m thick and as centimetric to metric dykes. They have an equigranular medium-coarse grained texture, are K-feldspar and biotite richer than trondhjemites and usually contain large amounts of muscovite as well as minor amounts of sillimanite. Intense post-magmatic modification occurs only locally. Studied rocks are weakly to strongly peraluminous and show random distribution on ASI *vs.* silica diagram, even if most trondhjemites fall into the I-type granite field and most granites into the S-type field. Granites have the same SiO_2 range of trondhjemites but are poorer in CaO, Na_2O and richer in K_2O. Trends observed in variation diagrams suggest the absence of genetic relationships between studied trondhjemites and granites. Multi-element diagrams for both rock types show general enrichment in LILE and LREE and depletion in HFSE, as typical for orogenic granites. All the granitoid rocks show a wide variability in REE contents, with LREE contents in the range of *ca.* 10-100 times chondrite. REE patterns are moderately fractionated, with Eu anomalies from negative to strongly positive for the trondhjemites and mostly weakly fractionated to flat, with a mildly negative to mildly positive Eu anomaly for the granites. In diagrams based on melting experiments of different crustal rocks [1] most granites compositions are similar to those of melts produced by dehydration melting of felsic metapelites. Most trondhjemites compositions show some similarities with those of melts produced by melting of greywackes and/or by reaction of the above rocks with basaltic melts at low pressure.

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PERMIAN EVOLUTION OF THE VALPELLINE SERIES (WESTERN ITALIAN ALPS): PRELIMINARY GEOCHRONOLOGICAL DATA

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We present preliminary geochronological data integrating tectonometamorphic studies in order to shed light on the evolution of Valpelline Series of the Dent Blanche nappe, belonging to the Austroalpine domain of the Western Italian Alps. The Valpelline Series is mainly composed of metapelites, mafic and carbonate rocks with a dominant metamorphic imprint under amphibolite to granulite facies conditions of pre-Alpine age. The Alpine imprint is localized along meter to hundreds of meters width high strain zones. The north-eastern part of the Valpelline valley is characterised by high-grade paragneisses with interlayered basic granulites, Grt-Cpx-bearing amphibolites, and Ol-bearing marbles belonging to the Valpelline Series. We focused on the tectonometamorphic evolution of metapelites outcropping in a small canyon, situated on the north side of the Valpelline Valley, between the villages of Valpelline and Oyace. The rock association consists of granulitic gneisses associated with boudins of Opx-bearing basic granulites, Ol-bearing marbles and meter-size lenses of Grt-bearing pegmatites. Seven evolutionary stages have been reconstructed by mesostructural and microstructural analysis: 5 are pre-Alpine and 2 Alpine. The first stage is associated with Opx-bearing basic granulites within migmatitic gneisses; stage 2 is defined by the migmatitic foliation S2. D3 mainly consists of the S3 foliation, in metapelites and metabasics under amphibolite facies conditions. D4 consists of isoclinal folds transposing S2 and S3 foliations (S4), associated with the intrusion (Mag4b) of Qtz-Fd-Grt-bearing pegmatites. Stage 5 is associated to the static growth of Chl, Ep and Wm. During stage 6 fractures, faults and cataclasites affect all lithotypes. An accurate study of thin sections and backscattered electron images revealed monazites suitable for microprobe analyses belonging to stage 2 and 3 of the structural evolution. Applying a rigorous analytical protocol we used a Jeol JXA-8200 electron microprobe to perform monazite analyses, Th, U, and Pb concentrations in monazite have been established and ages have been calculated using the calibration proposed by Montel *et al.* [1]. The pre-Alpine tectonometamorphic evolution shows an early stage under IP-HT granulite facies conditions, preserved in boudins of Opx-basic granulites, enclosed in stage 2 HP-HT migmatitic gneisses. The successive structural and metamorphic overprints (stages 3 and 4) occurred under IP-HT amphibolite to granulite facies conditions, closely related to the local production and intrusion of Grt-bearing melts. Stages 2-3 monazites shows ages between 260-220 Ma. This evolution is interpreted as the record of the Variscan collision, which followed Permian-Jurassic thinning (stages 2-3), associated with an astenosphere upwelling and high thermal regime causing high thermal metamorphism and partial melting processes. The formation of greenschist assemblages (stage 5) marks the end of thinning, which may be related to near-surface conditions or to the beginning of the Alpine evolution.

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SESSION 1.7

Crystal chemistry of minerals and petrogenetic implications

***Convenors*:**

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SINGLE CRYSTAL X-RAY DIFFRACTION STUDY OF EPSOMITE AT 298, 175 AND 102 K

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Epsomite, $MgSO_4·7H_2O$, is a widespread evaporite mineral on Earth, and on Mars too, as well as being a candidate rock-forming mineral inside the icy moons of the outer solar system [1]. Many spectroscopic, thermal and diffractometric studies have recently been undertaken to study the structural, thermodynamical and thermal stability of the salts of the $MgSO_4·nH_2O$ series, epsomite included, under different environmental conditions of relative humidity, pressure and temperatures.

In this work X-ray single crystal diffraction has been used to study the structure of epsomite at 298, 175 and 102 K, respectively, in order to 1) describe the structure of epsomite at low temperature, 2) systematically describe changes that occur in the epsomite structure at low temperature considering polyhedral geometries (bond distances, bond angles) and hydrogen bonds variations, 3) justify with structural evidences the observed changes that occur in this structure with changing temperatures. Single-crystal X-ray data collected on a Nonius Kappa CCD diffractometer (Mo*K*α radiation) were refined in the space group $P2_12_12_1$ using Shelx-97. (a = 11.8829(2), b = 11.9984(2), c = 6.86230(10) Å, V = 978.40(3) $Å^3$ at 298 K; a = 11.8796(2), b = 11.9571(3), c = 6.8203(10) Å, V = 968.79 $Å^3$ at 175 K; a = 11.8944(2), b = 11.9315(2), c = 6.80530(10) Å and V = 965.79(3) $Å^3$ at 102 K). Our results show that the hydrogen bonds in this structure get stronger or weaker depending on the necessity by the tetrahedral oxygen atoms to adjust their charge saturation. The polyhedrons, which behave as rigid bodies, tilt to compensate for these bond lengths adjustments. The non-bonded distances seem to be strongly influenced by these adjustments and their trends reflect the behaviour of unit cell parameters. The non bonded distances with a prevalent parallel component along the *b*- and *c*-axis decrease with decreasing temperature while the one parallel to the *a*-axis either increase or remain constant with decreasing temperature.

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DIFFERENT DEEP MAGMA DIFFERENTIATION PROCESSES IN THE BACK-ARC BASALTS FROM MARSILI VOLCANO (SOUTHERN TYRRHENIAN SEA): EVIDENCE FROM Sr AND Ba ZONING IN PLAGIOCLASE

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The Marsili seamount (Southern Tyrrhenian back-arc basin) erupted magmas ranging from dominant Island Arc Basalt (IAB)-type to younger, but sporadic, Ocean Island Basalt (OIB)-like. Geochemistry of plagioclase phenocrysts from MRS3 and D6 basaltic samples, representative of the IAB and OIB magmas, respectively, are used to obtain information on the processes occurring at the lower crust beneath the Marsili volcano.

Despite the analysed plagioclases show similar ranges in terms of the An composition (An_{69-88}) as well as of the major-element contents, the Sr and Ba data result different among the two basaltic samples, revealing a control from a crystallising assemblage richer in plagioclase for the IAB-type lava than for the OIB-like one. In detail, the occurrence of An-rich plagioclase (up to An_{88}) in the MRS3 IAB lava as well the absence of clinopyroxene among the first liquidus phases suggest that crystallization of the plagioclase phenocrysts occurred at conditions that unable the concurrent clinopyroxene fractionation (*i.e.*, pressure < 2.5 kbar; 1.5-3 wt.% of water content in the melt). Since the crust extends up to 8 km depth beneath Marsili volcano, this fractionation process likely occurred in the lower crust. A similar shallow depth of fractionation can be envisaged for the An-rich cores of the D6 OIB plagioclase phenocrysts also having the lowest Ba and Sr contents.

Nevertheless, during this early deep-seated stage of the D6 magma crystallization, some plagioclase crystals, or zones, record the presence of Sr-Ba enriched melts never observed in magmas erupted at Marsili volcano. This event, not recorded in all the D6 analysed plagioclase crystals, likely records the interaction of the D6 OIB magma body with wall rocks, where amphibole-rich bodies were present. Although amphibole has not been observed in the mineral assemblages of the Marsili lavas, small (millimetric) strongly resorbed crystals, having oxidated rims, have been recently recognized in two Marsili basaltic andesite samples recovered near to the site from which the D6 lava derives. This finding suggests that amphibole-bearing cumulates could be present at the crust level, beneath the Marsili volcano, probably related to the differentiation of hydrous Marsili basalts.

A P-MEMBER OF THE MIXITE GROUP FROM TUSCANY (ITALY): OCCURRENCE AND CRYSTAL STRUCTURE

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The mixite group is formed by hexagonal arsenates and phosphates, having general formula $M\mathrm{Cu}_6(X\mathrm{O}_4)_3(\mathrm{OH})_6\cdot3\mathrm{H}_2\mathrm{O}$. *M* site is occupied by REE^{3+}, Y^{3+}, Al^{3+}, Bi^{3+}, Ca^{2+}, or Pb^{2+}; *X* can be occupied by As or P. Up to now, only two phosphates have been described: petersite-(Y) and calciopetersite.

Petersite-(Y), ideally $\mathrm{YCu}_6(\mathrm{PO}_4)_3(\mathrm{OH})_6\cdot3\mathrm{H}_2\mathrm{O}$, was described by [1] and was found in very few localities around the world; calciopetersite [2], ideally $\mathrm{CaCu}_6[(\mathrm{PO}_4)_2(\mathrm{PO}_3\mathrm{OH})(\mathrm{OH})_6]\cdot3\mathrm{H}_2\mathrm{O}$, is rarer than the previous one and it was found only in three localities [3, 4]. Petersite-(Y) and calciopetersite are, respectively, the P-analogue of agardite-(Y) and zálesíite. Whereas the crystal structures of some arsenates of the mixite group were refined, the crystal structures of the P-dominant phases are still not determined.

A member of the mixite group was identified by XRPD in a sample from Fantoni quarry (Futa Pass, Florence, Tuscany). It occurs as very small blue-green hexagonal prismatic crystals, associated with a chrysocholla-like phase on altered chalcopyrite, in small veins embedded in ophiolitic rocks.

Preliminary EDS analyses showed the presence of Ca, Y, Cu, P, and Si as the only elements with $Z > 9$; in addition, small quantities of REE are probably present.

The P-member of the mixite group from Tuscany has cell parameters *a* 13.206(2), *c* 5.824(1) Å, space group $P6_3/m$. Owing to the very small crystal size (~ 80×5×5 $\mu\mathrm{m}^3$), intensity data were collected at the XRD1 beamline of the Elettra synchrotron facility (Basovizza, Trieste, Italy). The crystal structure was determined by direct methods and refined to R = 5.8% for all 253 reflections with $F_o > 4\sigma(F_o)$. As in the arsenates belonging to the mixite group, the crystal structure is formed by infinite chains of edge-sharing $\mathrm{Cu}^{[4+1]}\mathrm{O}_5$ pyramids, aligned parallel to [001] and linked to $M\mathrm{O}_9$ polyhedra by sharing edges. PO_4 tetrahedra complete the framework. In the minerals of the mixite group, tubular hexagonal channels host variable amounts of $\mathrm{H}_2\mathrm{O}$ molecules. In the studied sample, difference Fourier synthesis yielded a maximum at the origin, in the very centre of these channels. Coordination geometry and bond-valence balance from intraframework cation-oxygen bonding agreed with the presence of OH^- groups. Non framework $\mathrm{H}_2\mathrm{O}$ molecules have a zeolitic behaviour [4] and probably various degrees of hydration are possible. Refined occupancy of $\mathrm{H}_2\mathrm{O}$ molecule shows that the total amount, in the mixite group mineral from Tuscany, is very low. However, a direct determination of $\mathrm{H}_2\mathrm{O}$ will not be possible because of the small amount of available material.

This mineral is probably the product of leaching of chalcopyrite in an oxidizing and hydrous environment at a low temperature during weathering processes. The individual elements forming this phosphate were derived from chalcopyrite (Cu) and probably from “apatite” (Ca, P, Y, REE), identified as white prismatic crystals up to 5 mm in cumulitic levels of the ophiolitic rocks from the Fantoni quarry.

As an identification of individual members of the mixite group merely on the basis of XRPD and unit cell parameters is ambiguous, owing to the extensive substitutions at the *M* (and also *X*) sites, quantitative chemical analyses will be necessary for a correct determination of the mineral phase under study.

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CRYSTAL STRUCTURE REFINEMENT OF NATURAL BAGHDADITE FROM FUKA

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Baghdadite, $Ca_3Zr(Si_2O_7)O_2$, belongs to the cuspidine group, with general formula $M_4Si_2O_7X_2$; M denotes cations with variable charges and ionic radii, characterized by octahedral or roughly octahedral coordination and X is F^-, O^{2-}, or, according to literature, OH^-. The crystal structure of the phases of this group can be described with two "modules", namely "octahedral" walls and disilicate groups.

Baghdadite is a very rare mineral and it was found only in few localities world-wide. Baghdadite displays, together with burpalite, $Na_2CaZr(Si_2O_7)F_2$, a cell of type III according to [1]. The crystal structure of the synthetic counterpart of baghdadite was solved and refined by [2] using neutron powder diffraction data.

Grayish-white crystals of baghdadite from Fuka (Okayama Prefecture, Japan) were studied through single crystal techniques; the studied specimen is the same used by [3]. Its chemical composition is $(Ca_{3.03}Na_{0.02})(Zr_{0.83}Ti_{0.10}Mg_{0.01}Mn_{0.01})(Si_{2.04}Al_{0.02}Fe_{0.01})O_9$. Weissenberg photographs confirmed that space group and cell parameters are consistent with the structure type 6, as reported in [1].

Intensity data were collected with a Siemens P4 four-circle diffractometer, with graphite-monochromatized Mo$K\alpha$ radiation; the refinement of 25 reflections gave the cell parameters: a 10.432(3), b 10.163(2), c 7.356(2) Å, β 90.96(2)°. Crystal structure was determined by direct methods in the space group $P2_1/a$ to keep the same orientation of the other members of the cuspidine group. Crystal structure was refined to $R = 3.4\%$ for 1986 reflections with $F_o > 4\sigma(F_o)$.

As in the other phases of cuspidine group, tilleyite ribbons are condensed to build up a tessellation of four columns large polyhedral walls, developing along [001]. Each wall is connected by corner sharing to other four walls and to six disilicate groups, whereas each Si_2O_7 groups links three walls. In the polyhedral walls, the outer columns are made up of large polyhedra, Ca1 and Ca2, whereas the inner columns are formed by alternating Ca3 polyhedra and Zr octahedra. In agreement with [2], Zr octahedra are linked through edge-sharing. This violation of the fourth Pauling rule is required to satisfy the second Pauling rule, achieving a correct bond-valence balance.

Baghdadite is the only F-free mineral of the cuspidine group and was found in F-free mineral assemblages; the only exception is represented by the occurrence of baghdadite associated with cuspidine at Flekkeren [4]. This phase identification is based, however, on EPMA data only. It is worth noticing that two other distinct groups of minerals, the rosenbuschite-seidozerite-götzenite and the rinkite groups, display the same general formula of the cuspidine group, namely $M_4Si_2O_7X_2$, possibly pointing to a wrong identification of the Flekkeren mineral. In fact, crystal structure studies of cuspidines and experimental studies [5] show that OH^- can not be hosted in cuspidine derivative structures. Therefore, in F-free parageneses, X anion is represented by O^{2-}. The unusual edge-sharing between Zr octahedra is required to achieve the correct bond-valence balance (~ 2 *v.u.*) at the sites in which, in the other members of the cuspidine group, fluorine anion is hosted.

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CRYSTAL STRUCTURE OF HOLLANDITE FROM VAGLI (APUAN ALPS) AND POTENTIALLY NEW MINERAL SPECIES IN THE HOLLANDITE GROUP

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Small manganese ores have recently been investigated from the area of Vagli (Apuan Alps, Tuscany, Italy). They are embedded in metaradiolarites of the Diaspri formation, belonging to the metamorphic complex of Apuan Alps. Fieldwork allows the recognition of two different types of Mn ores: mm to dm thick syngenetic braunite layers and quartz-carbonate veins, cross-cutting both the country rocks and the braunite layers [1]. Hollandite crystals were identified in the latter kinds of occurrence. It forms prismatic crystals, up to 1.5 cm, striated along [010], associated with braunite, hematite, piemontite, and, rarely, scheelite, rutile, and titanite [2].

Preliminary chemical EDS analyses points to the crystal chemical formula $(Ba_{1.01}Sr_{0.13}K_{0.04})_{\Sigma=1.18}(Mn^{4+}_{5.68}Mn^{3+}_{1.24}Fe^{3+}_{0.95}Al_{0.12})_{\Sigma=7.99}O_{16}$. Iron was considered as Fe^{3+}, because of the oxidated nature of the paragenesis. The high Fe^{3+} content and the good quality of hollandite crystals from Vagli suggested the possibility of a new structural study. Oscillation photographs showed, in addition to the strong reflections of the 2.9 Å periodicity, also weak but sharp reflections, doubling the *b* parameter. This doubling was already observed also in the Fe-rich hollandite from Kajlidongri (India) [3]. Intensity data were collected with a Siemens P4 four-circle diffractometer, with graphite-monochromatized Mo*K*α radiation; the refinement of 32 reflections gave the cell parameters: *a* 9.938(4), *b* 5.828(2), *c* 10.152(4) Å, β 90.71(3)°, space group *P*2/*n*. Crystal structure was determined by direct methods and the refinement converged to $R = 5.01\%$ for 1641 unique reflections with $F_o > 4\sigma(F_o)$.

The crystal structure of hollandite from Vagli is characterized, as all the other members of the cryptomelane group, by octahedral arranged in edge-sharing columns, which in turn link together, again by edge-sharing, forming walls, two octahedra wide. Cross-linking of these walls by corner-sharing gives rise to a square 2×2 tunnel structure. Ba cations are located inside the tunnels. The doubling of the *b* periodicity is apparently related to an ordered distribution of two Ba sites inside these tunnels, at a distance of ~ 2.9 Å each other. This distance is shorter than the minimum Ba-Ba distance acceptable from the standpoint of electrostatic repulsion; therefore, partial occupancy at these sites is required. Ba1 and Ba2 have a refined occupancy of $Ba_{0.79}$ and $Ba_{0.24}$ respectively. Therefore, when Ba1 is occupied, Ba2 is empty (~ 80%), whereas when Ba1 is empty, Ba2 is occupied (~ 20%). It is possible that the order is one-dimensional, with different sequences in adjacent tunnels in the **a**,**c** plane.

As stated above, hollandite from Vagli has a high Fe content. The charge balance accompanying the introduction of mono- and divalent cations in the tunnels is achieved through the substitution of the tetravalent octahedrally-coordinated cation by a lower-valence one. Therefore, the nomenclature of these minerals needs to reflect the dominant occupancy at the tunnel sites and the dominant charge-compensating cation in the octahedrally coordinated sites. As already noted [4], whereas in the titanate subgroup the nomenclature of the different phases is based both on the tunnel cation and the dominant-compensating cation, in the manganate subgroup this rule is not followed. Therefore, hollandite is given the simplified chemical formula $Ba(Mn^{4+},Mn^{3+})_8O_{16}$ throughout, although the accurate scrutiny of chemical analyses reported in literature, as well as our preliminary EPMA data, point to the existence of hollandites with other dominant-compensating cations, *e.g.* Fe^{3+} (a potentially new mineral species). Hence we plan to propose to the IMA-CNMNC a reappraisal of the members of this group of tunnel oxides.

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CYMRITE AND BENSTONITE FROM THE MONTE ARSICCIO MINE (APUAN ALPS, TUSCANY, ITALY): FIRST ITALIAN OCCURRENCE

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The Monte Arsiccio mine is located in the easternmost portion of the Sant'Anna tectonic window (Apuan Alps). Other important ore bodies are hosted in this area: in fact, in addition to the Monte Arsiccio baryte-pyrite-iron oxides mine, other interesting ores are the Pollone baryte-pyrite-(Pb,Ag) deposit and the Cu-(Au) vein system from Buca dell'Angina mine.

At Monte Arsiccio, the main ore body is an almost conformable lens characterized by distinct zoning with pyrite + baryte at the bottom, and iron oxides (magnetite, hematite) + baryte at the top, with various accessory sulfides and sulfosalts [1]. The ore is embedded in a metavolcanic-metasedimentary sequence (Scisti di Fornovolasco Fm.) or at the contact between this formation and lenses of dolomitic marbles of uncertain stratigraphic settings.

The systematic study of the mineralogy from the Monte Arsiccio mine allowed the identification of two rare barium minerals, cymrite, $BaAl_2Si_2O_8{\cdot}nH_2O$ ($0 < n < 1$) and benstonite, $Ba_6Ca_6Mg[CO_3]_{13}$.

Cymrite was found as euhedral to subhedral crystals, up to 1 mm, in pyrite layers, in association with benstonite; the latter was observed in small white cleavable masses. Cymrite occurs also in thin baryte-dolomite veins embedded in dolomitic marbles and, rarely, in small vugs, as colourless and tabular crystals. Arsenopyrite, baryte, Fe-bearing dolomite, fluorapatite, Ba-rich K-feldspar ("hyalophane"), pyrite, quartz, and sphalerite are associated with cymrite and benstonite. The crystals of cymrite often show some inclusions, represented by baryte (in some cases Sr-rich), benstonite, and an undetermined Pb-Ag-Sb sulfosalt.

Cymrite and benstonite were identified by XRPD collected with a 114.6 mm Gandolfi camera and Ni-filtered Cu$K\alpha$ radiation.

The strongest observed lines of cymrite were at 3.943, 2.949, and 2.660 Å. Taking into account the cell parameters of cymrite suggested by [2], the refinement of 19 reflections gave the values a 5.333(2), b 36.58(1), c 7.669(5) Å, β 89.8(1)°. Normalized EDS chemical analyses gave (wt.%) SiO_2 32.11, Al_2O_3 26.99, BaO 40.48, K_2O 0.42; assuming the presence of H_2O, the chemical formula can be written as $(Ba_{0.99}K_{0.03})_{\Sigma=1.02}Al_{1.99}Si_{2.01}O_8{\cdot}nH_2O$. The occurrence of Ba-silicates in the baryte-pyrite-Fe oxides from Apuan Alps has been known since the identification of Ba-rich K-feldspar ("hyalophane") from Pollone mine [3] and Monte Arsiccio mine [4]. The chemical composition of "hyalophane" from Monte Arsiccio can be expressed as $Or_{65}Cn_{35}$.

Benstonite has cell parameters, refined on the basis of 21 reflections, a 18.31(2), c 8.647(3) Å; the strongest observed lines of benstonite were at 3.912, 3.086, and 2.532 Å. Normalized EDS chemical analyses gave (wt.%) BaO 65.92, CaO 25.25, MgO 3.04, SrO 5.79.

The presence of benstonite and cymrite in the baryte-pyrite-iron oxides ores from Apuan Alps is the first Italian occurrence of these two rare barium minerals.

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NEW DATA ON NATURAL QUASICRYSTALS REVEAL NEW CLUES FOR THEIR ORIGIN

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Throughout the history of geology spanning more than two millennia [*e.g.*, 1], all reported minerals with translational order have been crystals (or incommensurate crystals), with rotational symmetries restricted to a finite set of possibilities, as first established mathematically in the 19th Century [2]. Until twenty-five years ago, this seemed to be the only logical possibility since no other kind of translational order was known. However, twenty-five years ago, the concept of solids with quasiperiodic translational order, quasicrystals, was introduced whose structure is characterized by rotational symmetries forbidden to crystals, including five-fold symmetry in the plane and icosahedral symmetry in three dimensions [3]. At the same time, the first examples of quasicrystals began to be found in the laboratory [4]. By now, well over one hundred quasicrystalline materials have been synthesized, typically by mixing precise ratios of selected elemental components in the liquid and quenching under controlled conditions ranging from rapid to moderately slow [5]. For the last twenty-five years, though, an open question has been whether Nature has beaten us to the punch: Were quasicrystals formed through natural geologic processes long before they were discovered in the laboratory?

The answer to this question has been recently given by Bindi *et al.* [6]. These authors reported overwhelmingly strong evidence for the existence of the quasicrystal phase in a rock; however, a deeply puzzling aspect was the presence of metallic aluminum, which requires a highly reducing environment. The fact that the aluminum occurs in intermetallic compounds with copper and iron decreases the oxygen fugacity requirements. Nevertheless, the authors have had to give serious consideration to whether the sample could be slag or the result of some anthropogenic process. There is significant new evidence (and data) against this possibility that will be presented during the talk, including: the remote region where the sample was found being very far from any industries; the presence of forsterite and diopside in direct contact with metal alloys; the absence of glass or bubbles; unusual zoning of phosphorus and chromium in forsterite; new SIMS data on diopside in direct contact with quasicrystal grains; new nanoSIMS data on the phases belonging to the external material; oxygen isotopes on silicates and oxides of the external material; concentration of nickel in the forsterite but not in the metal alloys; absence of myrmekitic or skeletal texture; and new TEM studies revealing nanograins of stishovite in contact with quasicrystal. Each of these features is individually inconsistent with anthropogenic origin for different reasons; collectively, they make a compelling case that the rock was formed by some natural process.

The current evidence does not point strongly to any single formation mechanism. The key challenge is to explain the combination of (i) nearly pure forsterite and diopside; (ii) highly reduced metallic aluminum; and (iii) stishovite. At present, the three features appear to be most consistent with formation process in a high pressure environment, as might occur in a meteoritic impact or in the deep mantle or perhaps in a subduction zone combined with rapid tectonic uplift.

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PRELIMINARY STUDY OF OPHIOLITE AND ASBESTOS MINERALS IN THE GIMIGLIANO-MOUNT REVENTINO UNIT (CALABRIA, SOUTH ITALY)

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A preliminary study to investigate on the presence and nature of asbestos mineral is carrying out on 40 natural rock samples (areal distribution greater than 1 sample/km^2) collected in the metaophiolite sequences belonging to the Gimigliano-Mount Reventino Unit. A careful examination shows that the large opholitic lens is quite irregular and has a complicated internal structure [1]. The Unit consists of serpentinites, metabasalts, metagabbros/metadolerites with a sedimentary cover made up of marble alternating with calcschists and quartzites [2, 3]. Ophicalcites are found in close association with serpentinites and show brecciated fabrics.

Some of these lithologies, quarried for using as building and ornamental stones [4], could contain tremolite/actinolite asbestos and/or chrysotile. Owing to possible health problems due to asbestos fibre dispersion, these types of quarries are regulated by the Italian law (DM 14/06/1996) which demands the asbestos presence identification. So far no detailed observations on serpentine and amphibole microstructures have been made, *e.g.* the five different varieties of the serpentine minerals (*i.e.* chrysotile, lizardite, polygonal serpentine, massive and fibrous antigorite) were not discriminated and characterized. For this aim, mineralogical studies have begun and detailed characterization of the main lithologies (serpentinites, metabasalts, ophicalcites) are being conducting by XRPD, SEM/EDS, XRF and spectrographic study. To do unambiguous identification of the serpentine varieties, TEM/EDS and micro-Raman investigations are in progress [5, 6].

Preliminary results have shown that serpentinite samples contain serpentine (dominated by antigorite), chlorite and clay minerals. Serpentine shows the pseudomorphic mesh texture and bastite replacing olivine and pyroxene respectively with some rare relicts of these structures. Intergrowths of fibrous serpentine (chrysotile may be) with bastite are frequently recovered. Metabasalts consist of amphiboles (dominated by asbestos actinolite), epidote, albite, muscovite, chlorite, titanite, calcite, magnetite and nimite. Ophicalcites contain calcite (mainly phase), serpentine (antigorite is the prevalent serpentine variety), Fe-actinolite, chlorite, talc and magnetite. These new knowledge could be used i) as markers of specific environmental conditions during asbestos mineral formation, ii) to identify eventually health hazard areas owing to asbestos fiber.

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HT-STUDY OF THE $P31c \leftrightarrow P6_3$ PHASE TRANSITION IN KALSILITE, $KAlSiO_4$

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Kalsilite, $KAlSiO_4$, occurs as different polymorphs in K-rich silica undersaturated volcanic rocks, and in metamorphic rocks. The low-kalsilite form has space group $P6_3$. The structure is an ordered three-dimensional framework of AlO_4 and SiO_4 tetrahedra forming six-membered rings pointing up (U) and down (D) alternately, in a tridymite-like framework topology (UDUDUD). The rings are di-trigonally distorted, and are stacked along the *c* direction, sharing the apical O atoms in a staggered configuration [1]. Na-free metamorphic twinned crystal of kalsilite from Punalur district in Kerala, India, has having $P31c$ symmetry [2]: individual sheets of $P31c$ kalsilite are essentially the same as those of the $P6_3$ structure but are stacked in an eclipsed manner, with the di-trigonal rings in succeeding sheets point in the same directions. Annealing of $P31c$ kalsilite results in the $P6_3$ form starting at 473 K and is complete at 773 K [3]. The transition is described as being irreversible and proceeds by tetrahedral rotation such that successive (001) sheets undergo opposite-sense rotations [3]. The process was previously studied by means of *ex situ* powder X-ray diffraction of annealed samples. The progress of the $P31c \leftrightarrow P6_3$ transformation was followed [3] by measuring the intensities of the 111 and 112 reflections: the intensities of reflections *hhl* type should be sensitive to the structural change, because those with l = even (*a*-type) would be expected to decrease in intensity, whereas those with l = odd (*b*-type) should increase from zero (*hhl*, l = odd are systematically extinct in space group $P31c$). The presence of the $P6_3$ phase was also confirmed by Rietveld refinement and after complete transformation annealing at 500°C for 14 days, by single crystal X-ray diffraction (SCXRD) [3].

We have performed an *in situ* high-T SCXRD study of twinned metamorphic kalsilite from the same sample studied by [2] and [3], with the aim of following the structure transformation *in situ* and of testing reversibility. We have collected data on lattice parameters each 25°C steps up to 923 K and the intensity of the (11*l*) reflections (with l = 1-6). Complete intensity data collections were made at 298, 373, 473, 573, 673, 773, 873 and then at room-T after cooling. Upon heating, the *a* cell parameter and cell volume increased up to 923 K, while the *c* lattice decreases showing a faint but neat collapse of ~ 1 ‰ at 473 K. This feature is accompanied by the increase of intensity of *b*-type reflections that were extinct, while *a*-type reflections become progressively weaker, and thus corresponds with the onset of the phase transformation. Structure refinement at 473 K confirmed $P6_3$ symmetry and the absence of twinning. The process saturates at 573 K [Ib/Ia = constant] and over such temperature both groups of reflections keep decreasing intensity keeping their averaged ratio constant, while structure keeps $P6_3$ symmetry. We ended the annealing experiment at 923 K in order to avoid the $P6_3 \leftrightarrow P6_3mc$ phase transition [4]. On cooling, the intensity of the *b*-type reflections increases down to 573 K. At that temperature we switched off the furnace to quench the $P6_3$ structural state. We collected intensity data during cooling and recorded a gradual decrease of *b*-type reflection intensity while the *c* lattice parameter slightly increased. Structure refinement showed the inversion of the structure back to $P31c$ space group, with {0001} twining again present in the same ratio as before annealing. The transformation is accompanied by a change in the bonding scheme of the K atoms while no disorder of Al and Si is observed in the tetrahedra.

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HIGH-PRESSURE STRUCTURAL EVOLUTION AND EQUATION OF STATE OF ANALBITE

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The volume and unit-cell parameters of analbite (*i.e.* $NaAlSi_3O_8$ with complete Al,Si disorder) have been determined by single-crystal X-ray diffraction to a maximum pressure of ~ 8.71 GPa. The volume variation with pressure is described by a 4th-order Birch Murnaghan Equation of State with $K_{0T} = 50.3(5)$ GPa, $K'_0 = 8.9(5)$ and $K''_0 = -2.4(3)$ GPa^{-1}. The value of the room-pressure bulk modulus is ~ 1.9% lower than that of low albite, and the on-set of volume softening in analbite is at ~ 6.7 GPa, some 1.7 GPa higher than the on-set in albite. The anisotropy of compression of analbite is less than that in albite.

Single-crystal structure determinations of analbite to ~ 9.4 GPa show that there is no significant detectable compression of the T-O bonds within the structure, and the compression of the framework of tetrahedra is therefore accommodated by changes in the T-O-T angles which result in significant compression of the "crankshaft chains" within the framework. No significant shear of the tetrahedral rings of analbite was detected, in contrast to the structural compression of albite. Overall, the structural changes that occur in analbite from 0 to 9.4 GPa resemble those seen in ordered albite over the pressure range 0-4 GPa. Analbite shows a significantly greater structural rigidity than low albite over the larger pressure range.

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$^{[4]}Fe^{3+}$-O DISTANCE IN SYNTHETIC KIMZEYITE GARNET

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In natural kimzeyite garnet and in its synthetics analogues trivalent Fe is known to be located in the tetrahedral site substituting for silicon and/or Al [1, 2, 3, 4]. Fe ionic radius is much larger than that of Al and Si in tetrahedral coordination; thus Fe substitution for Si and/or Al accounts for a large increase in both the kimzeyite cell parameter and <T-O> distance. However, as Fe and Si (and eventually Al) are located in symmetry equivalent sites, X-ray diffraction (XRD) cannot provide a direct measure of the Fe-O distance. As $^{[4]}Fe^{3+}$-O distances are not commonly reported in minerals, a synthetic sample has been studied by powder XRD and X-ray Absorption Spectroscopy (XAS) in order to get information on both the average structure and on the local environment around Fe tetrahedron.

Synthetic kimzeyite analogue has been prepared by mixing stoichiometric amounts of reagent grade oxides and holding the reagents at 1250°C for 36 hours. The products consist of $Ca_3Zr_2[Fe_2SiO_{12}]$ kimzeyite garnet and minor $CaZrO_2$ (< 5 wt.%). Powder XRD spectra have been collected by means of a Philips PW1830 diffractometer equipped with a graphite monochromatised Cu*K*α X-ray tube, whereas Fe *K*-edge XAS spectra have been collected in fluorescence mode at the GILDA beamline of the ESRF storage ring using a Si (311) monochromator. Structural refinement and EXAFS data analysis have been carried out by means of the GSAS code and GNXAS package respectively. Preliminary theoretical XANES spectra have been calculatd by means of the MXAN code.

The garnet cell parameter (a_0 = 12.625±0.001 Å) are consistent with those found in the literature for a synthetic sample of similar composition [2]. Also interatomic distances (<Ca-O> = 2.507 Å, Zr-O = 2.105 Å, <T-O> = 1.773 Å) are reasonably consistent with those of natural samples when taking into account chemical differences of the samples examined. The tetrahedral T-O distance is unusually long compared with garnets where tetrahedra are occupied solely by Si due to the large Fe content of this site.

XANES data display a pre-edge peak whose intensity and energy position are consistent with the presence of trivalent Fe in tetrahedral coordination. EXAFS derived Fe-O distance is consistent with extrapolation from literature data for garnets having different tetrahedral Fe occupancies (assuming full occupancy of the tetrahedral site by Fe^{3+}). Preliminary theoretical XANES spectra are presented in comparison to the experimental one.

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CRYSTAL-CHEMISTRY OF Ti-FLUOROPHLOGOPITE FROM PRESIDENTE OLEGARIO, ALTO PARANAIBA ALKALINE PROVINCE, BRAZIL

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Trioctahedral micas from kamafugitic lavas of Presidente Olegario (Brazil) turned out to be Ti-rich fluorophlogopites and have been investigated using a combination of Electron Probe Microanalysis (EPMA), Single-Crystal X-ray Diffraction (SCXRD) and Mössbauer spectroscopy. One specimen also underwent thermal treatment (*ex situ* heating at 700°C and 900°C). SIMS data on light elements were taken from previous investigation [1].

EPMA data yielded the following ranges: Al_2O_3 (8.72 ÷ 10.09 wt.%), MgO (19.62 ÷ 20.59 wt.%), FeO (5.68 ÷ 6.46 wt.%), TiO_2 (5.87 ÷ 7.46 wt.%), K_2O (8.91 ÷ 9.71 wt.%), Na_2O (0.39 ÷ 0.59 wt.%) and fluorine (3.44 ÷ 4.12 wt.%). The analyzed micas belong to the 1*M* polytype, with average cell parameters a = 5.333, b = 9.234, c = 10.139 Å, β = 100.176°. Structure refinements using anisotropic displacement parameters were performed in space group *C*2/*m* and converged to $2.01 \leq R \leq 3.51$, $2.00 \leq R_w \leq 3.51\%$. The Fe species as evidenced by Mössbauer investigation were: $^{VI}Fe^{2+} = 60\%$, $^{VI}Fe^{3+} = 10\%$, $^{IV}Fe^{3+} = 30\%$.

The mica has peculiar chemistry and cation distribution: it has no $^{VI}Al^{3+}$ and Na is very likely partitioned over interlayer and octahedral site. Na occurrence at octahedral site has been already documented [2]. Major substitutions are OH ↔ F, and Ti-oxy substitution, $^{VI}R^{2+} + 2\ (OH)^{-} \leftrightarrow {}^{VI}Ti^{4+} + 2\ O^{2-} + H_2\uparrow$. Accordingly these micas have structural features which have so far been found separately in fluorophlogopites [3] and in micas affected by Ti-oxy substitution [4].

Heating of one sample at 900°C results in shrinking of the *b*-cell parameter (Δb = 0.0213 Å), accounted for by a decrease of M1-O4 and M2-O4 bond distances, and compatible with an increase of $^{VI}Fe^{3+}$ concentration by about 0.10 a.p.f.u. with respect to the room temperature value. The results are consistent with previous works [5, 6].

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DEHYDRATION DYNAMICS OF B-LEVYNE BY *IN SITU* TIME RESOLVED SYNCHROTRON POWDER DIFFRACTION

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The thermal behaviour of microporous materials is of essential importance both for their characterization and for their industrial applications and varies significantly from one material to another. The isomorphous substitution of Al and/or Si by other tri- and tetravalent metal ions is considered a tool for tailoring the catalytic properties of zeolites. In recent years, much attention has been given to boron substituted zeolites (borosilicates) because their weaker acidity is suitable for certain catalytic reactions that require mild solid acids as catalysts. (*e.g.* toluene alkylation with ethanol [1]).

The thermal dehydration and template burning process of a boron substituted levyne (B-LEV), synthesized in the presence of quinuclidine (Q) ($[Na_3,H_2][B_5Si_{49}O_{108}]\cdot 6Q\cdot nH_2O$) [2], were studied *in situ* by synchrotron powder diffraction up to 900°C. Time-resolved diffraction data were collected at the GILDA beamline at ESRF (Grenoble). TG and DTG analyses carried out from 25 to 900°C indicated that the overall weight loss is about 27%. The evolution of the structural features monitored by full profile Rietveld refinements reveals that the decomposition and expulsion of organic molecules (at ~ 600°C) causes a dramatic change in the unit-cell parameters. At the same time, a sudden change in the slope of the TG analyses is reported.

At room temperature quinuclidine assumes two different orientations within the cage which are differently occupied. A sharp thermal expansion characterizes B-LEV when one of two possible orientations of the Q molecules is lost, whereas negative thermal expansion accompanies the expulsion of the second one. XRD diffraction patterns indicated that B-LEV maintains its crystallinity up to 800°C. At higher temperature it undergoes a partial structural collapse.

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THE INTRIGUING THERMIC STORY OF A NATURAL ZEOLITE: STRUCTURAL MODIFICATIONS, TOPOLOGICAL CHANGES AND STABILITY OF GMELINITE

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The thermal behaviour of gmelinite (GME), a natural zeolite, has been studied in the temperature range 100-1175 K by different X-ray diffractometric and thermal analysis techniques.

In situ single-crystal X-ray structure refinements were performed at room conditions and at increasing temperatures, in a hot nitrogen stream, up to the fragmentation of the crystals, which occurs at a temperature as low as 375 K, and afterwards the crystal was cooled down to room conditions. At room conditions, extraframework cations are located in two symmetrically independent positions, both of which are coordinated to either framework oxygen atoms or water molecules. When the mineral is heated at 90°C, and about 40% of H_2O is lost, one cation site splits over two positions, which are three-coordinated to the framework oxygen atoms. The dehydration process is completely reversible over a period of hours. X-ray single-crystal data has highlighted that gmelinite-Na when quenched at 100 K displays remarkable modifications in its extraframework content, resulting in a strong disorder in its extraframework ions. As in the case of heating, the mineral restores its structural features when brought back to room temperature.

Ex situ powder data showed that gmelinite is stable up to about 575 K. Over this temperature the mineral transforms into a new phase whose topology is the same as that of AlPO-5 (AFI) [1]. The new phase collapsed at 1160 K. Single crystal and powder data indicated that gmelinite rehydrates reversibly up to the temperature of phase transformation. A single crystal study showed that the new phase is really characterized by an AFI topology but small domains equivalent on symmetry planes orthogonal to the 6_3 axis cause a structural disorder. Synthetic precession images of the *hk*0, *h*0*l*, and *hk1* reciprocal planes showing very wide spread reflections with *l* odd, but absent with *l* even, provided useful information on the microstructure of the crystal. Near infrared diffuse reflectance spectra, showing the absence of hydroxyls in hydrated gmelinite and their presence in AFI-type phase confirmed the strong defectivity of the latter material.

The *in situ* time resolved diffraction data which allowed us to follow the structure modifications and phase transformations during their occurrence, *i.e.* far from equilibrium conditions, showed a very interesting feature. Gmelinite-AFI phase transformation does not occur directly, on the contrary, it takes place through the formation of a new metastable phase, whose unit cell parameters strongly differ both from those found in gmelinite and AFI-type materials, but are intermediate between them, and does not correspond to any phases known to date.

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$MgAlF_5 \cdot 1.5H_2O$: A NEW PHASE FROM ELDFELL VOLCANO, ICELAND

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A new fluorine-rich phase, with ideal formula $MgAlF_5 \cdot 1.5H_2O$, was found among fumarolic encrustations collected in April 1988 on the Eldfell volcano (Heimaey, Vestmannaeyjar archipelago, Iceland). Subsurface temperature during sampling was measured to be approximately 100°C. The new phase forms a fine-grained mass of 10-30 μm in size (Fig. 1), which was found on 2-3 cm crust on altered scoria of hawaiite [1] deposited after the eruption started on January 23th, 1973.

Associated minerals are ralstonite, $Na_xMg_xAl_{2-x}(F,OH)_6 \cdot H_2O$, and another potentially new phase with composition $CaAlF_5$ [2]. The new phase from Eldfell volcano is prismatic, colourless to white, transparent, non-fluorescent, has a vitreous lustre and a white streak. The calculated density is 2.10 g/cm^3. SEM-EDS quantitative chemical analysis shows the following range of concentrations (in at.%): Mg 10.43-12.55 (average 11.62, σ 0.63), Ca 0.29-1.99 (average 1.17, σ 0.55), Na 0.59-1.35 (average 0.77, σ 0.19), Al 12.03-13.27 (average 12.82, σ 0.28), F 51.45-52.94 (average 52.26, σ 0.43), O 19.76-22.81 (average 21.36, σ 0.78). The empirical chemical formula, calculated on the basis of 5 anions per formula unit, is $(Mg_{0.90}Ca_{0.09}Na_{0.05})_{\Sigma 1.04}Al_{0.99}[F_{4.03}(OH)_{0.97}]_{\Sigma 5} \cdot 0.68H_2O$ (mean of twenty-four point analyses), where $(OH)^-$ is calculated for change balance. Single crystal X-ray measurements showed orthorhombic symmetry for this new phase, space group *Imma*, with the following unit-cell parameters: a = 6.9107, b = 7.1589, c = 10.2958 Å, V = 509.355 Å^3, Z = 4. X-ray powder diffraction pattern closely resembles that for synthetic $MgAlF_5 \cdot 1.5H_2O$ [3]. Indexing was performed on the basis of lattice parameters reported for the synthetic analogue (PDF 039-0665). The strongest reflections in the powder diffraction diagram [d in Å, (I relative to 10)] are: 5.72, (10); 3.02 (5); 3.05, (4); 1.78 (3); 4.95 (3); 3.57, (3); 2.91 (2); 2.84 (2); 1.90 (2).

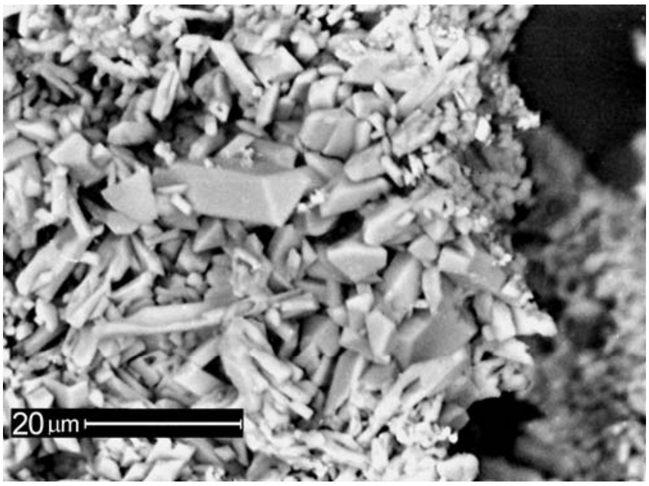

Fig. 1. SEM backscattered image of prismatic crystals.

The new species will be submitted soon for approval to the IMA-CNMNC.

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AMPHIBOLES FROM THE SUBCONTINENTAL LITHOSPHERIC MANTLE OF THE NORTHERN VICTORIA LAND (ANTARTICA): IMPLICATIONS FOR THE WATER ACTIVITY AND METASOMATISM

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Spinel-bearing lherzolites from Baker Rocks (Northern Victoria Land, Antartica) have pargasitic amphiboles as metasomatic phase. Amphiboles are both disseminated in the peridotite matrix (with modal contents up to 4%) or in veins mostly planar (0.1-1.5 mm wide) [1, 2].

We studied these amphiboles in order to define their conditions of formation and, combined with the H_2O content in coexistent pyroxenes, to estimate the total water budget of this mantle domain. The samples were analysed by Single-Crystal XRD, EMPA and XANES to have an accurate crystalchemical formula and to calculate the f_{H2} and ultimately the fO_2 or a_{H2O}.

The crystalchemical data (SCXRD and EMPA) showed that the studied amphiboles have similar composition, irrespective of the textural position, with only limited variation on TiO_2 (3.30-5.07 wt.%) and FeO_{tot} (4.5-7.8 wt.%). The presence of Ti at M1 site is suggested by the high equivalent thermal factor of M1 and cation off-centering. The high M3 site distortion and low M3-O mean bond distances suggest the presence of Fe^{3+} at M3 site in the samples with the highest FeO_{tot}. Crystallographic data allowed to used the Oberti *et al.*'s method [3] to calculate dehydrogenation, whereas Fe^{3+}/Fe_{tot} was measured by Fe K-edge XANES spectroscopy at GILDA beamline (ESRF). Our samples show O^{2-} values from 0.80 a.f.u. to 1.07 a.f.u., with the lowest dehydrogenation for samples with lowest Ti and Fe. The Fe^{3+}/Fe_{tot} measured and the crystallographic data (partitioning of Ti at M1) suggested that the Ti-oxy substitution is the main responsible for the dehydrogenation, with only a minor Fe-oxy component. These data were used to estimated the a_{H2O} and the fO_2 of the mineral assemblage, following Lamb & Popp [4] and Ballhaus *et al.* [5] methods, since our pargasites have a lower OH content compared to other amphiboles of mantle xenoliths (*e.g.* [6]). Pressure estimates indicate a relatively shallow lithospheric mantle (P 0.5-1.6 GPa) and T in the range of 800-1000°C, fitting the McMurdo geotherm [2], implying an a_{H2O} for the amphibole formation in the range of 0.01-0.02, considering the Mg, Na and Al end-members of the equilibrium: ol (Fo) + cpx (Di)-(Jd) + sp(Al-sp) + H_2O = amph (Pg) + opx (En). The calculated a_{H2O} values are low and very low, if compared with those reported for the stability field of the reaction in the T-a_{H2O} diagrams [5]. $\Delta\log fO_2$ values relative to FMQ buffer range from -1.4 to -0.4. This range perfectly overlaps that of anhydrous samples from the same locality, as well as those obtained from peridotite xenoliths from continental localities ($\Delta\log$ (FMQ) = –1.5 - +1.5; T = 900-1100; P = 1.0-1.5 GPa [7]). These data agree with the H_2O contents of coexisting pyroxenes, which are, on average, at least two times lower than those from other intraplate off-craton mantle xenolith [8], and discharging the hypothesis that their low H_2O contents may have resulted from the OH being preferentially partitioned in amphibole. This fact confirms the anomalously low whole-rock water content shown by the Antarctic sublithospheric mantle domain in a rifting setting.

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FIRST CRYSTAL-STRUCTURE DETERMINATION OF AN OLIVINE INCLUSION STILL TRAPPED IN A DIAMOND: A WINDOW TO THE INACCESSIBLE EARTH

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A novel experimental approach using single-crystal X-ray diffraction has been used to study an olivine inclusion still trapped in a Siberian diamond. The experimental procedure, typically used for *in situ* high-pressure studies (*i.e.* diamond-anvil cell), allowed us (i) to determine with high precision the remnant internal pressure at the inclusion, and (ii) to refine the crystal structure of the olivine without extracting it from the host diamond. The crystallographic data allowed us to refine the mean number of electrons at the M2 and M1 crystallographic sites of the olivine and to obtain a composition $Fo_{92.7(0.4)}Fa_{7.3}$. Knowing the P-V equation of state for such composition, we determined an internal pressure of 0.40(2) GPa. This pressure value was used to estimate the pressure of formation of the host diamond, taking into account elastic relaxation and using the most up-to-date compressibility and thermal expansion parameters for olivine and diamond. The estimated formation pressures ranged between 3.9 and 6 GPa for assumed temperatures of 800 and 1300°C, respectively. The data suggest formation at P-T conditions close to the diamond-graphite transition and are in excellent agreement with those determined by conventional thermobarometry for other olivine and clinopyroxene inclusions in peridotitic diamonds and diamondiferous xenoliths from Siberian kimberlites.

HT BEHAVIOUR AND DEHYDROGENATION PROCESSES IN MONOCLINIC AND ORTHORHOMBIC AMPHIBOLES OF PETROGENETIC RELEVANCE

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Understanding and modelling the HT behaviour of minerals is a fashionable issue in modern mineralogy. Indeed, these studies provide fundamental information not only on thermoelastic behaviour but also on the "reactivity" of the studied phase in response to increasing temperature conditions (cation disorder, phase transitions, and even dehydrogenation or dehydration in the case of hydrous minerals). Notably, all these processes significantly affect the molar volume and the thermoelasticity of the studied phase. Amphiboles are an important family of rock-forming minerals with a really intricate crystal-chemistry. They are known to store markers of petrological processes, and thus HT study of amphiboles under controlled conditions will also provide both a check of our present knowledge and a more detailed image of this petrogenetic information. As a matter of fact, HT studies on amphiboles may make available precious information on phase stability, on molar volumes and crystal-chemical markers to be used in thermodynamic modelling in upper-mantle geological contexts, as well as on the condition of water release and thus on the water budget in the Earth mantle.

In the last two years a team based in Pavia has accumulated data on the HT behaviour of a number of monoclinic calcic amphiboles with high Al contents [1, and still unpublished work], which are of relevance to upper mantle processes (pargasite, hastingsite and kaersutite with variable Fe^{2+}/Mg ratio); more recently, we have started working on orthorhombic amphiboles (anthophyllite and gedrite) [2, 3], the second of which is also of interest for "cold" subduction zones.

The study of the evolution of the unit-cell parameters (with the consequent analysis of the strain) has been coupled with a detailed study of the evolution of the amphibole structure and of site populations, providing good models for cation ordering processes and for the atomistic mechanisms accompanying and ruling dehydrogenation. The different behaviours observed will be commented, and the comparison will help to understand how the occurrence and extent of the dehydrogenation process, the nature of the B cation (Ca in monoclinic, Mg in orthorhombic amphiboles) and the symmetry (in this case, the different ways of piling up I-beams along *c* and the existence of two independent types of double-chain of tetrahedra) can affect thermoelastic behaviour and cation ordering in amphiboles.

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RE-INVESTIGATION OF THE CRYSTAL STRUCTURE OF ENSTATITE UNDER HIGH PRESSURE

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Orthopyroxenes (opx) have been intensively investigated since they are involved in a very wide range of geological environments, from magmatic to metamorphic rocks and meteorites. In particular, opx are significantly abundant in the upper mantle and the knowledge of their compressional and thermal behaviour is fundamental in understanding complex geodynamics processes occurring at that depth. It is important to determine the details of the crystal structure of the end-member $MgSiO_3$ orthoenstatite as a reference model for the behaviour of the opx component of mantle assemblages. Several investigations have been already performed at high pressure on pure synthetic $MgSiO_3$ in order to determine its elasticity and structural behaviour [1, 2, 3]. Angel & Jackson [3] obtained a best estimate of the EoS parameters for $MgSiO_3$ orthoenstatite combining the various results of single-crystal compression data. In this work we investigated the structural evolution as a function of pressure for the end-member orthoenstatite up to about 9.4 GPa by means of high-pressure single crystal X-ray diffraction. Aim of this study was to improve the quality of the crystal structure parameters at high pressures to the level obtained in similar studies for the orthopyroxenes characterized by different chemical substitutions [4, 5].

A fragment of $100\times150\times50$ μm^3 in size was cut from a large colourless single crystal of synthetic $MgSiO_3$ selected for the intensity data collection. The sample was loaded in an ETH-type diamond anvil cell and the measurements were performed using a Bruker-AXS four-circle diffractometer equipped with a SMART1000 CCD area detector. For the pressure calibration the EoS determined by Angel & Jackson [3] was used. Ten complete data collections up to about 9.4 GPa were carried out. As no violation in symmetry was detected with increasing pressure, all the refinements were performed in *Pbca* space group.

The obtained data show a significantly lower scatter than those from a previous study [1]. They allow us to compare better the mechanisms of compression among the sample studied and other orthopyroxenes with different composition. We will present a comparison of the crystal chemical parameters with results from studies on orthopyroxenes with different compositions [4, 5, 6] which now allow an accurate investigation of the real effect of Ca, Al and Fe substitutions in orthopyroxene.

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THE CONSTITUENT PHASES OF ULTRAMAFIC XENOLITHS FROM HANNUOBA REGION (NE CHINA), CRYSTAL CHEMISTRY AND PETROGENETIC IMPLICATION

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Several Authors described in the last decades the crystal chemistry of major mantle constituents, allowing the improvement of the knowledge of mantle mineralogy and inferring petrological constraints for evaluating the cooling history of the host rocks [1, 2, 3, 4].

In this work the crystal chemistry of coexisting phases in a suite of spinel peridotite xenoliths from Hannuoba region (North Eastern China) has been carried out by means of single crystal X-ray diffraction and electron microprobe to obtain site occupancies, and compare with other world while analogues.

The Hannuoba basaltic plateau, 200 km northwest of Beijing, large more than 1700 km^2, lies within the North China Craton and consists of inter-layered alkaline and tholeiitic basalts; the alkaline ones host deep-seated xenoliths while only very rare xenoliths have been found in the tholeiites. Volcanism is related to widespread Cenozoic rifting in the North China Craton. In the Damaping area, along a NE-trending tectonic belt, outcrops one “peridotitic body” characterized by abundant spinel peridotite xenoliths (approximately 85% of the outcrop) with large size (up to 80×60×45 cm), and coarse grain size and gem-quality olivine.

Clinopyroxenes: the Hannuoba cpx are characterized by high Ca (0.775-0.872 atoms for formula unit, a.f.u.) and Mg (0.791-0.962 a.f.u.) contents. V_{cell} varies from 433.34 to 436.44 Å^3 and parallels V_{M1} and V_{M2} increase. On the contrary, V_{T} decreases with increasing V_{cell}, due to Si content increasing, related to the increase of Mg# cpx and the general decrease of cpx modal content (*i.e.* increase of basalt component extraction). Mg and R^{3+} ($^{VI}Al + Fe^{3+} + Cr + Ti$) cations fill M1 polyhedron, while Fe^{2+} is present only in small amount. M1 volume increase is controlled by R^{3+} decrease. *Spinel*: within the suite, unit cell parameter a_0 ranges from 8.1291 to 8.2265 Å and Cr content increases from 0.1792 to 0.6191 a.f.u., whereas oxygen coordinate u remains virtually constant (0.26276-0.26310), therefore giving a quite constant ratio of octhahedral (M-O) and tetrahedral (T-O) bond distances. The increase in Cr causes progressive ordering of Mg and Al in T and M sites respectively. [5] evidenced how the cation partitioning and consequently the oxygen parameter (u) of Cr-spinels from peridotites is related to the cooling history of the host rock. Hannuoba spinels are characterised by higher u values (compared with analogues spinels described in literature), suggesting a slower cooling history. *Olivine*: Hannuoba investigated olivines have forsteritic compositions (Fo 89.2-90.6%) and V_{cell} varing from 291.6 to 291.8 Å^3. V_{M1} (11.876-11.907 Å^3) increases with decreasing Mg#, due to larger ionic radius of Fe^{2+} relative to that of Mg. No significant ordering of Fe^{2+} on M1 site has been detected (KD values near the unit).

The closure temperature of intracrystalline reactions for the three constituent phases provide a mean value of 700-750°C, suggesting a slow cooling rate and hence a thermal history consistent with the petrological environment (flood basalts). The pressure conditions estimated for Hannuoba xenoliths correspond to a dept of about 50-60 km, consistent with the Moho depth beneath the Hannuoba area, which is estimated by [6] at about 42 km.

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CRYSTAL CHEMISTRY AND GEOLOGICAL PROCESSES IN MICAS FROM MT. VULTURE (POTENZA, ITALY)

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The petrogenetic potential of trioctahedral micas of metamorphic origin has been explored in detail in a number of works [1, 2, 3]. For volcanic micas, instead, the search for crystal chemistry-petrogenetic relationships is often complicated by the fact that during or after their crystallization they undergo multi-step processes of non equilibrium/riequilibration [4, 5, 6]. This is the case of micas from Mt. Vulture, a Pleistocene composite volcano whose activity lasted about 550 ka. The micas so far analysed span the three main phases of the Vulture activity, *i.e.* the old (~ 700 ka), intermediate (~ 600-550 ka), and recent (~ 130 ka) activity. The crystal chemistry of the micas was studied in detail with a multi-analytical approach (EMPA, SIMS, SCXRD, FTIR, Mössbauer, XPS). The Vulture micas are very Fe^{3+}-rich (from ~ 30% to ~ 90% of the total iron) and have chemical and structural details compatible with the presence of at least two populations, the first characterized by the prevalence of Ti^{4+}-oxy and M^{3+}-oxy substitution mechanisms, the second by Ti^{4+}- vacancy and M^{3+}-vacancy substitutions. The occurrence of complex evolution, late/post magmatic events, phreatomagmatic phenomena are compatible with observed crystal chemical details of these micas [6, 7, 8, 9].

In recent works it has been proved that biotite may be used to estimate water fugacity (fH_2O) in any magmatic system where biotite-magnetite-sanidine is a stable assemblage [10, 11]. However the complexity of biotite solid solutions constitutes a major obstacle to the use of this geohygrometer. In the case of Vulture micas the biotite-magnetite-sanidine paragenesis is found in the basal Vulture pyroclastics (trachytic-phonolitic ignimbrites, old activity). The micas from Ignimbrite A and Ignimbrite B covers (Fara D'Olivo subsynthem) [12] were then selected. The results from Mössbauer investigation were: ${}^{VI}Fe^{2+}$ (%) = 42.3, ${}^{VI}Fe^{3+}$ (%) = 57.7 for mica from Ignimbrite A; ${}^{VI}Fe^{2+}$ (%) = 65.7, ${}^{VI}Fe^{3+}$ (%) = 34.3 for mica from Ignimbrite B.

To estimate the water fugacity (fH_2O) in the phono-trachytic magma of Mt. Vulture, the mica activity was derived using the partly ionic model of [13], that had been successfully used in previous studies [10, 11]. However the micas activities and water fugacity values calculated using the Mössbauer determined Fe^{3+} are up to an order of magnitude lower than corresponding ones calculated using the stoichiometric estimate of Fe^{3+}. The results show that the magmatic chamber of Mt. Vulture is localized at crustal depths as suggested by the geophysical investigation [14], and confirm the presence of a well developed hydrothermal system as hypothesized by other authors [7, 8, 15].

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ARMSTRONGITE: CRYSTAL STUCTURE DETERMINATION BY SCXRD INVESTIGATION

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Armstrongite, $CaZr[Si_6O_{15}]\cdot nH_2O$, ($2 \le n \le 3$), is a rare mineral usually occurring in schlieren of alkalic granite pegmatite, at the contact of arfvedsonite granite with xenoliths of felsic volcanic rocks. To date, it has been found in the core of granite pegmanite, alkaline granites in Mongolia [1] and in the Strange Lake complex, southeast of Lac Brisson, Quebec and Labrador, Newfoundland, Canada [2].

In paragenesis with quartz, microcline, albite, aegirine, arfvedsonite, monazite, synchesite, titanite and other titanosilicates, armstrongite crystals commonly form polysynthetic twins [3]. The first armstrongite twinned crystal was refined by [4] in space group $C2$ (R = 13%) using a De Jong-Bounman camera, but was lacking in the atomic displacement parameters and had a physically unreasonable overall scale factor. A more suitable model was obtained by [5] via a Rietveld analysis of an armstrongite (space group $C2$, R_{wp} = 2.75%) from Mongolia. The Rietveld refinement essentially confirmed both the space group and the model proposed by [4]. Polysynthetic twinning of armstrongite was due to the formation of elpidite, $(Na,Ca,\square)Zr[Si_6O_{15}]\cdot 3H_2O$, like modules at the border between the two parts of the twin (elpidite and armstrongite are correlated by a dimorphic transformation assuming the replacement $2Na^+ \leftrightarrow Ca^{2+} + \square$). Si-tetrahedra are formed by three bridging oxygen atoms (O_{br}) with a relatively low distortion, but a significant elongation along Si-O_{br} directions. Differently from the water ($2H_2O$) reported by [4], the occurrence of three water molecules in the armstrongite, one of which located along the 2-fold axis, was claimed by [5].

In this work, the results on a crystal collected from the same sample of [5] *via* a SCXRD investigation, is presented. The studied crystal is monoclinic [a = 10.14178(7), b = 14.1289(6), c = 7.8366(3) Å, β = 109.436(3)°] and twinned. It is constituted by two individuals rotated around a twin axis parallel to (100). The study of both the statistical tests and of the systematic absences have shown that the studied armstrongite crystallizes in the space group $C2/m$, in contrast with that reported in previous works [4, 5]. The structure was solved with the use of the SUPERFLIP program [6], and the space group $C2/m$ was confirmed by the analysis of the reconstructed electronic density. The investigated crystal was refined up to R = 3.3% (R_w = 3.8%). The result largely confirms the structural topology proposed by [5]. Armstrongite has a heterogeneous octahedral-tetrahedral framework formed by 8-membered rings interconnected to 6- and 4- membered rings. Zr and Ca coordinate 6-fold and 7-fold polyhedra, respectively, but Si-O distances result to be more regular with respect to those of [5]. In addition, the water molecule on the 2-fold axis was lacking. This contrasts with [5], but agrees with what was reported in the first structural study of armstrongite [4], where only two water molecules were localized.

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INVESTIGATION OF DIAMOND-FORMING MEDIA BY TRANSMISSION ELECTRON MICROSCOPY

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Natural diamonds represent an important and unique tool to study geochemical processes occurring in the Earth's interior. During their growth, diamonds may trap fluids and/or mineral inclusions, which are considered pristine witnesses of the surrounding diamond forming-media.

Further, the composition of these inclusions allows us to infer the chemical and physical conditions at which diamonds are stable in the mantle relative to graphite or carbonates.

In this study, TEM assisted by the Focused Ion Beam (FIB) technique were employed to investigate micro- to nano- inclusions in a cuboid fibrous diamond (BR5) from Brazil. The diamond, opaque in colour and 2 mm in size, was laser-cut from the center about 0.4 mm thick, parallel to the (001) cubic face (1). Several foils were prepared with dimensions of about 15×10×0.1 μm from the inner and outer part of the diamond using a Jeol 9310 Focused Ion Beam instrument with an ion beam generated from a gallium (Ga) liquid-metal ion source. The foils were then placed on a standard TEM copper grid with a carbon film.

Structural and mineralogical information about inclusions in diamond foils were obtained using selected area electron diffraction (SAED) that provides diffraction patterns from very small volumes. Qualitative analysis of chemical composition was obtained by EDX analysis.

Bright-field images of films recovered from the outer part of the diamond show inclusions (20-200 nm in size) as well as dislocation features widely distributed compared to foils from the inner part.

Many crystalline and fluid inclusions are chemically complex, containing Ti, P, K, Si, Fe, Mg, Ca and O as shown by EDX analysis. These inclusions are similar to that found in diamonds from Congo (2). Electron diffraction patterns on these inclusions demonstrate the coexistence of carbonate + mica + apatite minerals that likely represent the "fluid-forming assemblage" in agreement with multiple reports on occurrence of these phases.

Our first results of FIB/TEM studies of BR5 diamond have confirmed the gradual evolution of growth medium: the inner part grew from silicic fluid while the outer part grew from carbonate-rich fluids.

The identified dominant assemblage of high-Si micas, crystalline Ca-Mg-Fe carbonate and apatite pointed towards carbonatitic melt as the best analogue of the fluid in the studied diamond.

Carbonatitic melts equilibrated with fibrous diamonds may also be interpreted as potential metasomatic agents in the upper mantle.

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THE SECOND OCCURRENCE OF KUDRIAVITE, (Cd,Pb)Bi_2S_4: CHEMICAL AND STRUCTURAL CHARACTERIZATION

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Kudriavite, (Cd,Pb)Bi_2S_4, is a recently discovered new sulfosalt from the high-temperature fumarole incrustations of the Kudriavy volcano, on Iturup Island, in the Kurile arc, Russia [1]. Together with tazieffite, it represents a rare case of natural sulfosalt containing both Cd and Bi as essential constituents. Kudriavite is the natural analogous of the synthetic phase $CdBi_2S_4$ of the system Cd-Bi-S, carefully investigated in recent times [2] owing to the potential of Bi-chalcogenides as thermoelectric materials [3]. The structure investigation of kudriavite [1, 4] showed an atomic arrangement equivalent to that of the synthetic phase $CdBi_2S_4$ and indicated that this mineral is a pavonite homologue, N = 3 [5].

In this study we describe the second occurrence of kudriavite. The investigated crystals were collected from the high-temperature fumarole deposits of the Mutnovsky volcano (Kamchatka Peninsula, Russian Federation). Microprobe data on crystals from this second occurrence showed a significant enrichment of Cd with respect to the type specimen, as well the lack of In, which is instead particularly abundant in the type material (up to 3.5 wt.%). The average composition obtained on 28 point analyses is: $(Cd_{0.75}Pb_{0.19}Fe_{0.03})_{\Sigma=0.97}Bi_{2.00}(S_{3.80}Se_{0.22})_{\Sigma=4.02}$. Single crystal X-ray data were refined in the space group $C2/m$ to R = 6.61%. The unit-cell parameters are a = 13.1910(19), b = 4.0233(7), c = 14.8648(31) Å, β = 116.28(1)°. The structure arrangement of kudriavite from Mutnovsky is the same as that of the type specimen and of the synthetic $CdBi_2S_4$. It is built of three-octahedron-wide columns of (311)PbS-like slabs combined by "unit-cell twinning" in a quasi mirror-glide succession. The slabs, which are intrinsically of the same topology, differ in the coordination state of bordering cations because of the relative positions of adjacent layers [4]. In the slab of the type I (the "non accreting" slab common to all pavonite homologues) the central columns of octahedral coordinated site *Me*4 are flanked by half-octahedral coordinations *Me*2. The central columns of octahedral sites *Me*3 in the slabs of type II (of varying thickness, *i.e.* "accreting" in pavonite homologues) are flanked by octahedral sites *Me*1 involving a S atom from the adjacent slab. The structure refinement of kudriavite from Mutnovsky shows that the cation sites *Me*1, *Me*3 and *Me*4 incorporate Cd, whereas *Me*2 is an almost pure Bi site. This is in agreement with the situation observed in the synthetic material, although the refined occupancies of Cd in each site are different in the two structures (*Me*1 = 88% Bi and 12% Cd, *Me*3 = 76% Bi and 24% Cd, *Me*4 = 10% Bi and 90% Cd in kudriavite from Mutnovsky; *Me*1 = 82% Bi and 18% Cd, *Me*3 = 40% Bi and 60% Cd, *Me*4 = 100% Cd in synthetic $CdBi_2S_4$). The discrepancy is due to the occurrence of Pb in the investigated samples according to substitution Pb ↔ Cd. Our structure analysis suggests that Pb enters all the Cd-bearing sites of the kudriavite from Mutnovsky and, probably, also the Bi site *Me*2. Sites populations of kudriavite from Mutnovsky resulting from the present study are also significantly different from that of the holotype owing to the very different chemistry of these kudriavite occurrences, which is related to the simultaneous action of Pb ↔ Cd and Bi ↔ In substitutions in the type specimen.

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SESSION 1.8

Magmatic chamber processes

Convenors:

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^{238}U-^{230}Th-^{226}Ra DISEQUILIBRIA IN THE PRESENT-DAY MAGMAS OF STROMBOLI VOLCANO: INSIGHTS IN THE VOLCANO FEEDING SYSTEM

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Over the last several hundred years, the steady-state activity of Stromboli has been characterised by persistent mild explosive eruptions, ejecting black scoria bombs. Periodically, lava flows and different-scale paroxysms, also ejecting light-coloured pumices, interrupt the "normal" activity. A degassed and highly porphyritic magma (HP-magma), with a basaltic shoshonitic composition, is erupted by the normal activity and by the lava flows, whereas a slightly more mafic and volatile-rich magma with low phenocryst content (LP-magma) is also erupted as pumices by the paroxysms. In the last 15 years few episodes have been characterized by production of both LP and HP magmas. We selected samples of HP and LP magmas from these eruptions for measurements of U-series disequilibria.

The long-lived U and Th isotopes (^{238}U, ^{235}U and ^{232}Th) decay to stable Pb isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb, respectively) through a series of short-lived radiogenic and radioactive isotopes (*e.g.*, ^{231}Pa, ^{226}Ra, ^{228}Ra). The various geochemical properties of U-series isotopes cause nuclides within the chain to be fractionated in different geological environment, whereas their half-lives, ranging from days to few tens of thousand years, allow investigating processes occurring at timescales from days to 10^5 years. This makes U-series disequilibria a useful tool to investigate the dynamic and timescales of magmatic processes such as magma generation and storage before eruption. The variation of U-series activity-ratios [*i.e.* (^{230}Th/^{238}U), (^{230}Th/^{232}Th), (^{226}Ra/^{230}Th) where parentheses denote activity] during the history of a volcano related either to change of magma input or to processes occurring during storage at different level in the crust.

In this study we measured HP and LP samples (pumice-scoria pairs) from 1996, 1998, 1999, 2000 small-scale paroxysms, and 2003, 2007 intermediate-scale paroxysms for (^{230}Th/^{238}U), (^{230}Th/^{232}Th), (^{238}U/^{382}Th) and (^{226}Ra/^{230}Th), plus (^{228}Ra/^{232}Th) in a subset of LP samples.

LP and HP samples are clearly separated by most of the abovementioned isotope ratios. In particular, they group apart in a (^{230}Th/^{232}Th) *vs.* (^{238}U/^{382}Th) *equiline diagram*, with LP magmas showing comparable (^{230}Th/^{232}Th) but lower (^{238}U/^{382}Th) than HP magmas. This suggests the occurrence of recycled crystals from previous activities within HP magmas, in agreement with *in situ* micro-Sr isotope data [1].

Significant variations of the activity-ratios with time, especially (^{230}Th/^{232}Th), are present within LP-magmas from different eruptions. This can be interpreted either as the response of the shallow reservoir to a change in the magma input or as the instantaneous response of the system to variation of the magma input related to small changes in the mantle partial melting regimes beneath the island.

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TEMPORAL EVOLUTION OF THE PLEISTOCENIC RHYOLITIC SYSTEMS OF MILOS ISLAND (GREECE)

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Rhyolitic magmatism has characterized the younger volcanic history of Milos Island (Cyclades, Southern Aegean Sea). Two main rhyolitic complexes were built during the last 400 ka: Trachilas, in the northern sector of the island, and Fyriplaka to the South. The age of the first is about 0.38 Ma [1], while Fyriplaka is younger, being dated between 90 ka [1] and 19 ka [2]. Both centres were built by an alternance of effusive and explosive phases, these lasts leading to the formation of tuff ring. A common feature of both complexes is the presence of enclaves in the lava flows. These enclaves have dacitic composition in the Fyriplaka lavas, while those in the lavas of Trachilas are rhyolitic. Petrography and geochemistry of lavas, pyroclastic products and enclaves of the two centres have been carried out in order to study the younger volcanic system of Milos Island.

Several petrographic and geochemical similarities have been found between the upper rhyolites of Fyriplaka and the enclaves in the Trachilas lavas. They both are characterized by a mineralogical paragenesis of plagioclase, quartz, biotites, ilmenite, and magnetite. The composition of mineral phases is very similar: in particular biotite Mg# is around 0.60 and 0.65. The potassium content of the whole rock is relatively low (K_2O about 3 wt.%) and the N_2O/K_2O ratio is slightly above 1. The equilibrium between the two oxides allowed the simultaneous determination of pre-eruptive temperature, which resulted about 720°C, and the oxygen fugacity ($\log_{10} fO_2$ = NNO+1).On the other hand Trachilas lavas show many similarities with the rhyolitic lavas outcropping at the base of the Fyriplaka complex. The main petrographic difference with the previous group of rocks is the presence of K-feldspar and the absence of ilmenite in the mineralogical assemblage. Biotites of both rhyolites have Mg# lower than 0.6. The rocks are more potassium-rich than the previous group and their Na_2O/ K_2O ratio is lower than 1. Also the trace elements of the two groups of rocks are different, with the Trachilas and basal Fyriplaka rhyolites more enriched in Nb, Rb and Y. The pre-eruptive temperature of the magmas, calculated on the basis of the plagioclase-K-feldspar equilibrium, resulted about 710°C for a pressure of 5 kbar. The calculation of oxygen fugacity was not possible, but the comparison of the biotites with those occurring in similar rocks (Upper Pollara eruption, Aeolian Islands, [3]) suggests that it was close to the Ni-NiO buffer.

The data suggest that two different rhyolitic reservoirs were active under the island of Milos during the last 400 ka. The oldest, more K-rich, was responsible for the eruptions building the Trachilas complex in the North of the island and produced the basal lava flow outcropping in the Fyriplaka area. During its ascent toward the surface this “old” rhyolite intercepted a different rhyolitic magma batch, K-poor, mingling with it. Later on, this more superficial rhyolitic reservoir fed the Fyriplaka eruptions. The pre-eruptive conditions of the two rhyolitic magmas were probably different with the “young” rhyolitic magma characterized by more oxidizing conditions.

No hypothesis can be done on the origin of these two different rhyolites (crustal anatexis *vs.* evolution of a more mafic melt), even if the presence of less evolved enclaves in the “young” Fyriplaka lavas seems to suggest an origin of these magmas by AFC processes.

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MAGMA MINGLING AND CRYSTAL RECYCLING INSIDE A SHALLOW MAGMA CHAMBER DURING THE LAST ACTIVITY OF NISYROS VOLCANO, GREECE

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Interactions between different magmas are common processes during the evolution of a volcanic system. One of the best evidence is the presence of mafic enclaves inside evolved host, like lava flow or domes, caused by immiscibility condition between different magmas.

Nisyros volcano shows many evidences of mingling/mixing processes all along its volcanological evolution, especially during the last phase of activity, when six lava domes rich in mafic enclaves are emplaced, after a caldera collapse (probably < 24 ka) [1, 2, 3]. Field observation and a clear compositional gap between dome lavas and enclaves ensure that generation of hybrid magmas did not really occur. The presence of chilled margins in the enclaves suggests their sudden crystallization when intrusion in the cooler, more evolved host took place [4, 5], thus preventing chemical interactions.

Lava domes are porphyritic (up to 20-30 vol.%, mainly plagioclase) with criptocrystalline to glassy groundmasses. Magmatic enclaves have hypocrystalline dictytaxitic textures, with low porphyritic index (~ 5 vol.%) and groundmasses characterized by elongated plagioclase and amphibole microlites. Many phenocrysts and macro-phenocrysts, especially plagioclase, show disequilibrium textures which are commonly ascribed to mixing [6]. Accurate observations reveal the occurrence of mineral phase transfers from the host lavas to the enclaves (mainly macro-phenocrysts of plagioclase) and vice versa (crumbling of enclave groundmasses releasing microlites of pyroxene, olivine, amphibole and plagioclase). This generates a micro-scale mingling, which increases from the oldest to the youngest domes. Many micro-enclaves and femic micro-aggregate are also commonly scattered inside dome lavas, thus enhancing mingling. Mineral chemistry results well support the evidence of single phase exchange processes between the two magmas: femic phases show compositions clearly out of equilibrium conditions and plagioclase crystals reveal a double composition, which is mainly correlated with their size and textures. Furthermore, *in situ* ^{87}Sr/^{86}Sr analysis gives evidences that macro-plagioclase are antecrysts probably recycled from the previous magmatic system (*Upper Pumice* activity). The compositions of amphibole in the enclaves allow supposing a slight pressure decrease with time, probably caused by the uprise of contact surface level between the two magmas.

These results suggest that new batches of mafic magma intrude into a shallow, evolved magma chamber, developing convective motions and complex mingling interactions among the two magmas, together with recycling of old crystals. Thus, a highly heterogeneous system is generated from an originally rhyolitic magma chamber.

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EUROPIUM IN SILICATE GLASSES AT DIFFERENT OXYGEN FUGACITY

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Synthetic silicate glasses corresponding to compositions relevant for the Earth sciences were used to study the dependence of the redox states of a Rare Earth Element (Eu) on the bulk melt composition and at different values of oxygen fugacity (from air to IW-2). Rare Earth Elements (REE) have demonstrated to be important geochemical indicators; in fact, the distribution of REE in igneous rocks is frequently used to constrain the mineralogy of the source materials, the degree to which magma composition has been modified by crystal fractionation, and to identify the mineral phases removed from the magma during differentiation. The variation of the $Eu^{2+}/(Eu^{2+} + Eu^{3+})$ ratio can be also used as oxygen fugacity indicators. As the Eu^{2+}/Eu^{3+} buffer is located at very low oxygen fugacity, the $Eu^{2+}/(Eu^{2+} + Eu^{3+})$ ratio can be used to constrain the formation conditions within a very large range of oxygen fugacity down to few log units below the Fe/FeO buffer. The $Eu^{2+}/(Eu^{2+} + Eu^{3+})$ ratio is therefore very useful in the study of meteoritic material and in studying planetary evolution.

The samples were analyzed by X-ray Absorption Spectroscopy (XAS) to obtain the Eu oxidation state and local geometry. Eu L_{III}-edge XANES peak analysis allowed also a quantitative assessment of Eu redox ratio; literature data report a difference of 7-8 *e*V between Eu^{2+} and Eu^{3+} in the experimental spectra and this energy shift is evident enough to well differentiate between the two valences and to determine the Eu oxidation state in the glasses under investigation. Moreover, EXAFS data analysis allowed to determine the Eu-O bond distances and the structural environment around divalent and trivalent europium in the studied glasses.

A complete understanding of transition and REE elements is important for the geochemical and petrological interpretations of magmatic processes and partition properties between melt and crystals.

THE VOLATILE-INDUCED DIFFERENTIATION OF THE ETNEAN MAGMAS FROM THE ELLITTICO TO THE PRESENT-DAY ACTIVITY

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Mount Etna volcano (3340 m a.s.l.) located in eastern Sicily (Italy) is one of the most active volcanoes of the world with a continuous degassing through the summit craters and frequent eruptions occurring mostly from its flanks and from the two sub-terminal (NE and SE) craters. The scientific literature regarding the petrology of Etnean volcanics has pointed out that after 1971 eruptions produced mostly lavas with a trachybasaltic to trachyandesitic compositions, characterized by higher K content than lavas of comparable compositions erupted pre-1971 (K_2O from ~ 1.5 to ~ 2.2 wt.%). Moreover K increase is accompanied by a progressive Rb, Cs, and $^{87}Sr/^{86}Sr$ increment.

The origin of this geochemical feature, not explainable with ordinary crystal fractionation, and its emergence at one definite moment of the volcano evolution has puzzled for years the volcanologists, causing them to provide more than one paradigm to explain it, and all existing hypotheses formulated for the post-1971 K enrichment do not explain satisfactorily the phenomenon leaving the question still open.

Here is presented a critical re-examination of published data for major element (598 whole rock analyses), trace element (341 whole rock analyses) and isotopic ratios (55 $^{87}Sr/^{86}Sr$ analyses), relative to historical and pre-historical lavas. This critical appraisal has evidenced that K increment is not limited to the products of the last 35 years. A comparable increase in K is noticed in lavas emitted during the pre-historic phase of the recent Mongibello (K_2O max ~ 2.5 wt.%) and in lavas related to the early phase of the ancient Mongibello (K_2O max ~ 3 wt.%). Moreover data from melt inclusions in olivines of 2001 and 2002 eruptions (64 major element analyses), reveal that K contents remain constant for melts with entrapment pressure between 490 to 100 MPa to increase significantly in melts entrapped at pressures below ~ 100 MPa.

We advance the hypothesis that supercritical fluids coming from deeper magma and carrying alkali Cl-complexes migrate through basic to intermediate magmas residing in the shallow feeding system. As Cl exsolves and departs from the system alkali are released contributing to the observed K enrichment of the shallow magma. Fluctuations of this geochemical parameter could be associated to changes throughout time of volatiles influx and therefore to magma supply. Considering that the amount of magma entering a plumbing system is determined by the rate of regional extension, this geochemical parameter might be associated to an extensional regime acting in the past over the Etnean area.

PETROLOGICAL AND TEXTURAL FEATURES OF PLAGIOCLASE AS A KEY FOR UNDERSTANDING THE FEEDING SYSTEM PROCESSES: THE MT. ETNA 2002-2003 BI-LATERAL ERUPTIVE EVENT

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Plagioclase textural features and *in situ* major and trace element analyses of its zoning patterns have been investigated in the products of the 2002-2003 eruption of Mount Etna. SEM imagining has been used to sort plagioclases in different textural groups and chemical profiles across major resorption surfaces have also been performed.

The 2002-2003 eruption of Mt. Etna, which occurred on both southern (S) and northern (N) flanks of the volcano, was the last bi-lateral event since 1971. Distinct magmas (Low-K Oligophyric - LKO and High-K Oligophyric - HKO) have been emitted at different times along distinct fracture segments of the NE Rift on the north. On the southern flank and on the lowermost section of the NE Rift High-K Porphyritic (HKP) lavas were erupted.

Petrological data support a common origin for S and N HKP lavas, with the most primitive magmas erupted on the southern flank of the volcano, as also testified by the presence on both flanks of the volcano of quartz-rich xenoliths. Mass balance calculation models indicate that the most differentiated HKP lavas from the NE Rift can be obtained by fractionation of about 13% of cumulitic material starting from the least differentiated HKP lavas emitted on the southern flank. On the other hand LKO lavas, erupted only on the northern flank, can be linked fractionating about 11% of material, without a significant contribution of Plg. Noteworthy the same modeling does not allow to obtain the most differentiated LKO lavas starting from HKP lavas or the opposite, that is the most differentiated HKP lavas from high Mg# LKO magmas.

The compositional profiles of crystals revealed that plagioclases of HKP lavas shows dissolved or partially dissolved rounded cores, characterized by abrupt An decrease after the resorption event. Cores are often in equilibrium with the whole rock, becoming less anorthitic with time. Plagioclase rims are different between S and N HKP lavas: in the former, the occurrence of dusty rounded partially resorbed rims is frequent, and characterized by an abrupt increase in An content. In the latter, rims present alignments of melt inclusions, associated with a decrease in An content. Plagioclases embedded in LKO and HKO magmas, shows highly An_{85-90} cores.

A MELTS model of plagioclase stability indicates that crystals from both HKP have cores with An_{75-80}, suggesting a crystallization pressure ranging from 2000 to 900 bars, thus dissolution of the cores is generated under decompression regime in water under-saturated conditions. This data suggest a common origin of the magma between 6.6 to 3.3 km depth. Instead, highly An cores, embedded in oligophiric magmas, are consistent with a nucleation at very shallow depth in water-saturated conditions. The occurrence of dusty rims, associated with An increase in S HKP lavas, indicates that several refilling has interested the S Rift, as also suggested by progressive increase of Mg# of erupted lavas. Plagioclase textures indicate that this magma, which has feed the second part of 2002 eruption, has also been erupted in the first period of 2004 eruptive event. The absence of any refilling texture, recorded in plagioclase of N HKP indicates that the eruption was passive triggered by seismic swarm and that S Rift is the main magma ascent pathway in recent period, since 1971.

ISOTOPES OF NOBLE GASES FROM FLUID INCLUSIONS IN MAFIC PHENOCRYSTS FROM EXTRUSIVES AND ULTRAMAFIC XENOLITHS OF STROMBOLI (AEOLIAN ISLANDS, ITALY)

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We present a study of noble gases abundance (He, Ne, Ar) and isotopic ratios (He, Ar) in olivine- and clinopyroxene-hosted fluid inclusions from basaltic Low Porphyritic (LP) pumices and High Porphyritic **(**HP**)** scorias, respectively of paroxysms and mild explosions of the Stromboli present activity [1] and from ultramafic xenoliths of the 2 ka ago San Bartolo lavas [2]. New petrologic studies on such ultramafic xenoliths show that they are mostly wherlites (subordinately lherzolites), with slightly protogranular to porphyroclastic texture. Thermo-barometric estimates on the mineralogical assemblage indicate that ultramafic xenoliths equilibrated at depth well below the crust-mantle transition of Stromboli.

While Ar isotopes are dominated by a clear atmospheric signature in all the samples, $^{3}He/^{4}He$ from LP pumices and S. Bartolo ultramafic xenoliths converge to a value of 4.2-4.7 Ra, with relatively high gas content. Conversely, the low gas content of the HP scorias allowed us to measure chemical concentrations but not their $^{3}He/^{4}He$ ratio. Inferences found out from gas content are therefore in full agreement with previous knowledge about differences in volatile content between HP and LP magmas. The $^{3}He/^{4}He$ measured values are much lower than those of most primitive mantle terms of the Sicilian volcanism (7±0.6 Ra [3]), due to contamination at mantle level beneath Stromboli, operated by the Ionian subducting slab.

On the basis of the measured $^{3}He/^{4}He$ in the LP pumices and ultramafic xenoliths, helium in thermal waters from the Stromboli basal aquifer is a mixing of a mantle-derived and an atmospheric term. The $^{3}He/^{4}He$ values measured in the rocks constitute the upper limit that should be expected in thermal fluids in case of effusions and/or paroxysms.

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MANTLE TO SURFACE DEGASSING OF EREBUS VOLCANO

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Continental intraplate volcanoes, such as Erebus volcano, are associated with extensional tectonics, mantle upwelling and high heat flow. Erupted magmas have an alkaline nature and are rich in volatiles, especially CO_2, inherited from fluid-rich mantle sources. Here, we report high temporal resolution measurements of gas emissions from the active lava lake of Erebus volcano, obtained by open-path Fourier transform infrared (FTIR) spectroscopy. Remarkably different gas signatures are associated with passive and explosive gas emissions, representative of volatile contents and redox conditions that reveal contrasting shallow and deep degassing sources. Using further constraints from a suite of melt inclusion analyses, we show that this unexpected degassing signature provides a unique probe for magma differentiation and transfer of CO_2-rich oxidized fluids from lithospheric roots up to the surface, and evaluate how these processes operate in time and space. Extensive crystallisation driven by CO_2 flushing is responsible for isobaric fractionation of parental basanite magmas close to their source depth. While Magma deeper than 4 kbar equilibrates under vapour-buffered conditions, shallower magmas allow deep, CO_2-rich fluids to accumulate prior to release either via open-system degassing conditions with reduced oxidation states, or as slugs that ascend as a closed-system preserving the deep, oxidized signature, and explode at the surface in Strombolian fashion.

RELATIONSHIP BETWEEN MONOGENETIC MAGMATISM AND STRATOVOLCANOES IN WESTERN MEXICO: THE ROLE OF LOW-PRESSURE MAGMATIC PROCESSES

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A large Quaternary monogenetic volcanic field is present in the western part of the Trans Mexican-Volcanic Belt. It is constituted by mafic-intermediate scoria cones and silicic domes arranged in two NNW-SSE alignments which mark the north and south borders (Northern Volcanic Chain and Southern Volcanic Chain respectively) of the San Pedro-Ceboruco graben. The products of this monogenetic field span a large range of compositions (from basalt to rhyolite) and magma affinities (from sub-alkaline to Na-alkaline), defining different magmatic groups. Mafic and silicic monogenetic centres from the north alignment, also coexist with two stratovolcanoes (Ceboruco and Tepetiltic) sometimes punctuating their flanks.

All data suggest the existence of 4 different types of primitive magmas (Na-alkaline, High-Ti, Low-Ti/SVC and sub-alkaline) which evolve independently subjected to low-P evolutionary processes characterised by different conditions. Despite the relatively small size and simplicity of monogenetic magmatism trends of major elements variations with silica contents for High-Ti and SVC series indicate that fractional crystallization controls the liquid line of descend, though each monogenetic centre underwent slightly different conditions and magmatic processes. The positive correlation between Sr isotope ratios and silica contents observed for SVC and High-Ti groups point to crustal interaction via AFC processes. Source processes + fractional crystallization and AFC processes can act at the same time giving complex geochemical and isotopic characteristics. A tectonic control is also suggested by geochemical data. AFC processes mainly modify monogenetic magma outpoured between the two stratovolcanoes and on the southern border of the graben, whereas minor crust interaction seems to affect scoriae cones and domes located SE of Ceboruco and N-NE of Tepetiltic. In addition, Na-alkaline magma is outpoured only N-NE of Tepetiltic.

A limited magma interaction between monogenetic and polygenetic magmatism has been recognised at Ceboruco. Nevertheless the mafic magma feeding High-Ti monogenetic systems might represent one of the possible end-member which triggered the Ceboruco caldera-forming eruption. This can have important implication on other explosive system in which monogenetic magmatism is associated with stratovolcanoes.

MAGMA FLOW IN LACCOLITHS (ELBA ISLAND): RESULTS FROM FABRIC ANALYSES

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Shallow igneous intrusions are the link between plutonic and volcanic processes. The detailed study of the emplacement of intrusive bodies can help to explain the evolution of felsic magma chambers [1, 2]. The aim of this study is to test current understanding of feeding and growth mechanisms of shallow-level intrusions (less than 3-4 km deep) from magma flow markers. The study area includes the Late Miocene San Martino multilayer porphyry laccolith and its large subvertical feeder dykes [3] (Elba island, Italy). These intrusive bodies are composed of monzogranite and are characterized by prominent sanidine megacrysts set in an aphanitic groundmass. Emplacement depth was roughly 1900 m with an estimated filling time on a scale of < 100 years [4, 5]. Magma flow can be studied by the analysis of flow markers such as the preferred orientation of K-feldspar megacrysts and biotite phenocrysts. Orientation of K-feldspar megacrysts can be measured directly in the field while the biotite phenocrysts attitude can be reconstructed using anisotropy of magnetic susceptibility (AMS) measurements. Petrographic studies, SEM-EDS analyses and heating experiments have shown that biotite is a significant iron-bearing phase and may carry the magnetic signal. The preliminary K-feldspar on 25 sites (1500 measurements) reveal a well defined foliation with no discernible lineation. AMS data on 40 sites (400 measured cores) reveal a foliation, that is parallel with the feldspar data, but in addition also reveals a well defined lineation. Both sets of data show local variability of lineation and foliation, probably reflecting local variations of flow direction (perhaps magma lobes or magma fingers [2, 6]?). Foliation-lineation markers and their interpretations are strong constraints to the feeding and filling model we are building up for the San Martino laccolith.

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SESSION 1.9

Eruption dynamics and mid-long term volcanic hazard

Convenors:

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PYROCLASTIC DENSITY CURRENTS AT MOUNT ETNA: HAZARDS AND AN UPDATE

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Mount Etna is generally considered a non-explosive volcano, although recent eruptions have underscored its capability of generating significant ash plumes that represent a threat to air traffic. Another facet in the repertoire of the volcano, pyroclastic density currents (PDCs), has until now received little attention. Large-scale pyroclastic flows last occurred during the caldera-forming Ellittico eruptions of Etna, 15-16 ka ago [1], and the risk of them occurring in the near future is negligible. However, minor PDCs can affect much of the summit area and portions of the upper flanks of the volcano. During the past 25 years, small pyroclastic flows or base-surge-like vapor and ash clouds have occurred in at least 10 cases during summit eruptions of Etna [2, 3, 4].

Four different mechanisms of PDC generation have been identified during these events: (1) collapse of pyroclastic fountains (as in 2000, 2008, 2010, and possibly in 1986); (2) phreatomagmatic explosions resulting from mixing of lava with wet rock (2006); (3) phreatomagmatic explosions resulting from mixing of lava with thick snow (2007); (4) disintegration of the unstable flanks of a lava dome-like structure growing over the rim of one of the summit craters (1999). All of these recent PDCs were of a rather minor extent (maximum runout lengths were about 1.5 km in November 2006 and March 2007) and thus no they represented no threat for populated areas and human property around the volcano. Yet, events of this type pose a significant threat to the lives of people visiting the summit area of Etna, and areas in a radius of 2 km from the summit craters should be off-limits anytime an event capable of producing similar PDCs occurs.

The most likely source of further PDCs in the near future is the Southeast Crater, the youngest, most active and most unstable of the four summit craters of Etna, where 8 of the 10 documented recent PDCs originated. It is likely that similar hazards exist in a number of volcanic settings elsewhere, especially at snow- or glacier-covered volcanoes and on volcano slopes strongly affected by hydrothermal alteration [3, 4].

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THE WELDED DEPOSIT OF THE ONANO PYROCLASTIC FORMATION (WESTERN VULSINI, ITALY): DEPOSITIONAL AND STRATIGRAPHIC FEATURES

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The Onano Pyroclastic Formation, closely linked to the genesis and evolution of the Latera Caldera, is one of the largest deposits of the Latera Volcanic Complex (LVC), developed in the western sector of the Vulsini District between 0.3 and 0.1 Ma. The LVC was formed from a central building, originated after the migration of the eruptive activity that had initially characterized the pre-existing Bolsena Volcano.

The Onano eruption, dated 0.17 Ma on the basis of geochronological data of the underlying and overlying deposits, is the final step of the most volumetrically important period of volcanic activity during which a series of large pyroclastic flows were emplaced around the caldera. The eruptive dynamics and the depositional mechanisms of the Onano Formation are still subject to different interpretations, because of its stratigraphic and compositional peculiarities.

The Onano deposits were field surveyed and sampled in order to: 1) identify the various facies of the deposit, 2) reconstruct the mechanisms of emplacement, 3) hypothesize the eruptive dynamics. Sixteen samples from proximal to distal facies were analyzed for density and porosity, in order to determine the degree of welding of deposit.

The considerable variability of density (ranging from 0.64 to 1.83 g/cm^3) and porosity (ranging from 31 to 74 WP%) has allowed to recognize three different facies (F1, F2 and F3). The typical appearance and structure of the deposit, characterized by coarse grain, lack of fine fractions and varying degrees of welding and agglutination, as well the accumulation on high terrain up to 6-7 km far from the centre of emission, may suggest the hypothesis of an origin by a lava flow to be reconsidered. We can therefore suggest that the Onano Formation can be regarded as a ballistic origin triggered by intense fissural lava fountaining occurred on the NE edge of Latera Caldera. This mechanism could in some cases have generated a secondary remobilisation of the accumulated pyroclasts (reomorphic process).

Further and more detailed field surveys are nevertheless necessary to support this hypothesis.

THE GAS-PARTICLES CONDUIT FLOW DURING EXPLOSIVE ERUPTIONS: AN INTEGRATED EXPERIMENTAL AND NUMERICAL APPROACH

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Explosive volcanic eruptions are the most dangerous events that can affect the areas surrounding active volcanoes. It is well known that conduit exit conditions play a major role in determining the rate and style of explosive eruptions, and these in turn determine how the eruption can impact on the areas subjected to volcanic risk [1, 2]. For these reasons many researchers tried to develop models for the forecasting of conduit exit conditions. Theoretical [3, 4] and numerical [5, 6] modelling are the most widespread approach in volcanology. Experimental models are not common because of the difficulties to set-up large-scale experiments [7]. For this reason theoretical and numerical models always lack in the experimental validation. The first large-scale experiments on the mechanics of explosive eruptions where designed by CIRISIVU and proved to scale well to natural cases [8, 9]. From these experiments an experimental model for the forecasting of exit velocity of eruptive mixtures and the conditions of stability of the main eruptive styles was developed [10].

Numerical models that reproduce the large-scale experiments were developed with the aim to apply them to the real eruptions, as the experiments showed to scale well to real cases. This would be the first time that numerical models are validated against large-scale experiments in volcanology. The models simulate the pyroclastic flows created in the experiments and the gas-particles flow along the conduit.

Here a steady 1-D two-phase numerical model of the gas-particles flow in the conduit is presented. The equations of conservation of mass and momentum for gas and volcanic particles are solved via the Runge-Kutta scheme with an adaptive stepsize. The model takes in account the real shape of volcanic particles and uses a well established law for the calculation of particles terminal velocity [11]. The pressure gradient in the conduit, which is the main driving force of the vertical two-phase flow, is obtained by the conduit flow experimental model [10]. Finally the interphase drag force and the friction between the phases and the conduit wall are included by using the empirical laws for wall-particles and wall-fluid frictions developed in industrial engineering and classic fluid dynamics. All the experimental runs have been simulated and the model results in mixture exit velocities that are consistent with the ones measured in the experiments, with a mean relative deviation ranging from 0.044% to 20% depending on the particle-wall friction law used. Therefore the numerical model is promising and can be improved and used for the simulation of real cases and used to provide initial and boundary conditions for simulations starting from conduit exit.

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DUAL EXPLOSIVE ACTIVITY OF FEW THOUSANDS YEARS AGO AT STROMBOLI AS RECORDED BY THE *PIZZO SOPRA LA FOSSA* PYROCLASTIC SEQUENCE

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The *Pizzo Sopra la Fossa* tuff cone of Stromboli volcano was emplaced in the depression following the 6 ka Neostromboli-collapse (*Fossetta* crater), by the most explosive events of the Recent period of activity. A precise age of this activity, however, was still unknown [1]. Based on the stratigraphic, petrographic, mineralogical, geochemical and isotopic data performed on the *Pizzo Sopra la Fossa* deposits by the present study, together with the correlation to other deposits of known ages [1, 2], this activity has been dated between 2-3 ka ago.

The *Pizzo Sopra la Fossa* deposits now represent the remnant of a collapsed tuff cone formed by a thick pyroclastic sequence of unconformably cross-bedded fallout and surge levels of mainly lapilli and ash. The main outcrop, strongly altered by fumarolic activity, is located above the active craters, but minor outcrops are found both on the south flank, near *Le Croci* and on the north, along the uppermost part of the old pathway. Due to its location, the *Pizzo Sopra la Fossa* sequence was poorly studied, although it represents a key point for recognising the recent evolution of Stromboli, being the linking phase between the Neostromboli and the present-day period of activity.

We focussed our studies mainly on *Le Croci* outcrops characterized by a 6 meters thick sequence of mainly fall deposits. Different types of analysis on the juvenile components of the pyroclastic deposits (scoria and bombs) followed to a detailed stratigraphic reconstruction.

Geochemical and isotopic data reveal the presence of two distinct groups: Group-1 (bombs and one scoria) are high-K basaltic-andesites, whereas Group-2 (all scoria) are shoshonitic basalts. Group-1 rocks have lower incompatible trace element contents and Sr isotopic ratios, but displays higher ^{143}Nd/^{144}Nd values, than Group-2. They also show some petrographic differences.

Different evolutionary processes also characterised the two groups of magmas: Group-1 evolved by fractional crystallization plus crustal assimilation, whereas Group-2 by magma mixing. The fact that such different magmas were erupted almost contemporaneously, suggests the presence of two distinct magma chambers, possibly located at different depth, which were feeding two coeval and distinct explosive activities.

These data also show that Group-1 rocks are similar to the composition of both the *Lower Sequence* found in trenches by Rosi *et al.* [2] and the *S. Bartolo lavas,* whereas Group-2 scoria have affinity with the *Post Pizzo Series*, which afterward evolved to the present-day activity [3]. Based on these correlations, it has been recognised that this dual explosive activity forming the *Pizzo Sopra la Fossa* tuff cone occurred only few thousands years ago.

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PETROGRAPHIC AND TEXTURAL FEATURES OF SPATTER DEPOSITS FROM HISTORICAL PAROXYSMS AT STROMBOLI VOLCANO (AEOLIAN ISLANDS, ITALY)

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Normal strombolian activity fed by a crystal-rich (HP ~ 50 vol.%) degassed magma (HK to shoshonitic basalt) which resides in the upper part of the plumbing system is sporadically interrupted by more energetic short-lived explosive eruptions, with various intensity and magnitude, named "paroxysms" [1], during which a deeper crystal-poor (LP ~ 10 vol.%) and highly vesicular gold-coloured pumices are erupted together with crystal-rich scoriae [2, and references therein]. According to recent paleomagnetic studies, large scale paroxysms, emplacing spatter deposits on the rims of the Sciara del Fuoco down to the coast, occurred into two time windows, during XX Century and between 1400-1600 AD [3, 4, 5]. These events are the most powerful and hazardous activity of the volcano in the past centuries.

This study is has been focused on a spatter deposit cropping out on the N rim of the Sciara del Fuoco at elevation of ~ 500 m a.s.l., likely associated with an event dated 1400-1600 AD. In particular, whole rock chemistry, textural study, microprobe analyses of minerals and glass, were carried out to shed light on the nature of these products, and asses correlation between petrochemistry and eruptive dynamics. The sequence start with a preserved basal tephra layer (fine to coarse ashes and lapilli of both HP and LP products) followed by decimeter-sized intensely flattened dark crystal-rich scoriae. The *spatter deposit s.s.*, cropping out at the top, consists of an accumulation of weakly agglutinated pyroclasts with a maximum thickness of 50 cm with flattened shape. The lower part of the spatter deposit is made up of dense, HP clasts, while the upper part is characterized by clasts with a glassy, yellow-olive coloured outer margins and a highly vesicular (spongy-like) and LP dark grey core. The microlites-free groundmass of the quenched outer margins of the spongy-like clasts have a basalt-shoshonitic composition and belong to the compositional field of LP magma erupted in the past years (MgO > 5.5 wt.%, K_2O < 2.6 wt.% and $CaO/Al_2O_3 > 0.58$). While, glassy matrices from LP lapilli from the basal layer is slightly more evolved (MgO < 5.5 wt.%, K_2O = 2.6-3 wt.% and CaO/Al_2O_3 = 0.5-0.6). The HP and LP products have the typical texture and mineral composition of the HP and LP magmas erupted from Stromboli. In particular, the mineral assemblage of the LP products record open system magmatic processes as magmatic recharge and mixing with a mushy body. The compositional zoning of the deposit suggests that two mechanisms controlled the eruption dynamics during this paroxysm: (i) the destabilization of the deep LP reservoir induces degassing and formation of a foam layer in the lower part of the shallow HP reservoir. The collapse of the foam layer forces the expulsion of the crystal-rich, degassed magma. Possibly only the upper part of the deep magma column is involved in this phase; (ii) the rapid rise and degassing of deep, volatile-rich magmas (without decoupling liquid/gas) trigger a fire fountain resulting in the emplacement of the upper part of the spatter deposit.

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EXPERIMENTAL EVIDENCE LINKS VOLCANIC PARTICLE CHARACTERISTICS TO PYROCLASTIC FLOW HAZARD

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Pyroclastic density currents (PDC) are the most hazardous events of explosive volcanism, and their devastating power is mainly related to flow velocity, particle volumetric concentration and the temperature. One of the main parameters used in the literature for expressing the impact of PDC is the dynamic pressure, $1/2\rho u^2$ (ρ is flow density and u is velocity along flow direction).

Recently, we introduced a new method for reconstruction of physical parameters (density, velocity and dynamic pressure) of PDC, starting from deposits of past eruptions. The model links turbulent boundary layer theory, the transport mechanism of pyroclastic particles and their physical characteristics.

In order to validate our model, experiments for the generation of large-scale, multiphase, gravity-driven currents were designed and engineered.

The experimental apparatus consists of a cylindrical conduit that is filled with samples of natural volcanic products. This material is expelled from the conduit as a two-phase mixture by means of a system that supplies highly pressurized gas.

The currents generated during the experiments are large enough to allow both scaling of the main macroscopic fluid-dynamics parameters of natural pyroclastic flows and sampling of their experiment. Particle transportation processes, grain size, video sequence and sensor analysis show that several similarities emerge between our experimental runs and natural PDC. The experiments replicated both the lobate dispersion and the three major transportation modes (concentrated undercurrent, bed load at the base of turbulent flow and continuous suspension of fine-ash particles) of actual PDCs. Our model was therefore applied for the reconstruction of the physical characteristics of PDCs of the experimental deposits. The system of equations of the model was implemented using data of particles, which come from two different transport regions. The first one represents the zone where the particles are entrained at the base of the current and the second is the region where the particles are sedimented by settling from turbulent suspension.

The solutions of our model fit with data recorded by video sequences and sensors. Therefore our model can be considered as validated by data of large-scale experiments.

HYDROUS SPECIES IN VOLCANIC GLASSES FROM THE POSTA LUBRANO TEPHRA (ISCHIA IS., ITALY): IMPLICATIONS ON WATER-MAGMA INTERACTION

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Understanding the state and motional properties of water in volcanic glasses is of particular interest in the study of explosive eruption dynamics. In the case of interaction between magma and external water fluid instabilities are created, giving rise to the collapse of the vapour film which forms at the interface with the melt, causing explosive fragmentation. The exsolution of volatiles from the melt during uprising and decompression allows the development of supersaturation conditions and the expansion of hydration bubbles which, in non-equilibrium conditions, increase magma fragmentation by pore steam explosions and pose the conditions for an explosive burst. It is commonly assumed that water speciates into the silicate melt structure of a bubble-free silicate glass through a heterogeneous reaction with the oxygen of the silicate network to form OH groups according to the reaction:

$$H_2O + \text{-O-} = 2OH^-$$

where the relative proportion of molecular water and OH groups depends on the total water content and on temperature conditions at the glass transition. Deviations from the apparent equilibrium constant for the above reaction eventually observed in natural glasses may hence give information on the interaction of the melt with external water during the explosive burst that generated pyroclastic deposits. In the present study the water speciation has been determined in volcanic glasses from the Posta Lubrano eruption (Ischia Is.) by ^1H MAS NMR spectroscopy, in addition to major element chemistry and Sr isotope ratio. The Posta Lubrano eruption represents the second phase of growth of the Montagnone_Maschiata volcanic complex, which, together with Mt. Rotaro, is the only example at Ischia of a long-lasting activity in a quite limited vent area, likely fed by magmas that rose through the same conduit system. The eruption was mainly phreatomagmatic, with the emplacement of pyroclastic density currents, intercalated with subordinate thin fallout beds, which followed the emplacement of a lava dome. The tephra is exposed in the northern part of the island, overlying a paleosol developed above the dome and underlying the Cretaio tephra. The age of the deposit is bracketed between the fourth Century BC and the second Century AD. Glasses from the different members in the stratigraphic sequence have a quite homogeneous trachyte-phonolite chemical composition; however, the $^{87}Sr/^{86}Sr$ ratio of glasses ranges between 0.70601 and 0.70650, well above the experimental uncertainties and partly overlapping the Sr isotopic composition reported for the Cretaio volcanic glasses. The deconvolution of the ^1H MAS NMR spectra accounts for isolated H_2O molecules and OH groups, yielding a highly variable H_2O/OH molar ratio throughout the eruptive sequence, in some cases deviating towards exceedingly higher H_2O content with respect to what expected considering the water-melt speciation equilibria of undissociated molecular water, OH and anhydrous oxygen. Glasses with the highest water content also show the highest ^{87}Sr enrichment, which is attributed to open-system behaviour. The geochemical, isotopic and speciation data are interpreted in terms of a new magma input from depth, triggering the eruption, followed by a variable interaction with external water or hydrated sediments at crustal level during the different phases of the eruption.

THE DEGASSING STYLE OF MT. ETNA VOLCANO (ITALY) BETWEEN JANUARY 2009 AND JUNE 2010 INFERRED FROM CRATER PLUME AND SOIL GAS MEASUREMENTS

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In 2009, Mt. Etna (Italy) activity was characterized by the end of a long-lasting flank eruption started on May 2008 and by the opening of a new summit degassing vent on the E flank of the South-East crater on 6th November. Near-daily SO_2 flux measurements, calculated HCl and HF fluxes obtained by combining FTIR measurements with daily SO_2 flux, and periodic measurements of soil CO_2 emissions, allowed to observe a sequence of significant anomalies that preceded a followed the opening of the 6th November vent. Thanks to the differential release of magmatic gas species from an ascending magma body we tracked the magma transfer process in the volcano plumbing system from depth (< 5 km) to the surface. Over the period investigated soil and crater gas emissions indicate two distinct degassing behaviours: the first between April-November 2009 was characterized by an increase in soil and crater gas emissions; conversely, the second started in late February 2010 and is still going on, and is characterized by a steady decrease in SO_2, HCl and HF emission rates, and by intermittent but generally high rate of diffuse CO_2 efflux. Our results combined with volcanological evidences indicate a first stage of efficient gas-magma ascending and degassing regime via the central conduit system that culminated with the opening of the new degassing vent. Conversely, a second phase of deficiency of gas-rich magma in the shallow feeding system of the volcano occurred since late February 2010, which would reflect the possible migration of magma from the main feeder conduit into lateral portions of the volcano edifice.

THE OPENING PHASE OF A LARGE MAFIC EXPLOSIVE ERUPTION: THE CASE OF THE VILLA SENNI ERUPTION (COLLI ALBANI VOLCANO, ITALY)

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This work is concentrating on the basal surge and fallout sequence of the Villa Senni Eruption Unit as they may answer questions regarding the beginning of this large mafic ignimbrite eruption. Our work is based on a detailed field description associated with the juvenile microtextures analysis.

The Villa Senni Eruption Unit (350 ka) represents the youngest large caldera-forming eruption of the Colli Albani volcano near Rome (Italy). The Colli Albani magma is marked by very undersaturated chemistry (tephritic to K-foiditic) and low viscosity. The total volume of the Villa Senni Eruption Unit is estimated at > 50 km^3 and 30 km^3 DRE [1]. The unit includes a sequence of a basal fallout/surge deposit, two main ignimbrites emplaced during the same eruptive event, a series of breccia deposits positioned between the two ignimbrites, and a rarely preserved final fallout.

The entire surge and fallout deposit is 190 cm thick at the caldera wall, consisting of 19 individual, parallel to faintly cross-stratified layers. The deposit distally thins to 25 cm at 18 km east of the caldera and to 2.5 cm at 21 km NW of the caldera.

The eruption started with fine ash surges showing cross-stratification at proximal locations and being vesicular distally. The deposit consists mainly of juvenile clasts, which are angular, poorly vesicular, and rich in leucite microlites (~ 80 μm). Clasts around 100-150 μm show signs of magma-water interaction: quench fracturing: conchoidal and step fractures, smooth surfaces, adhering clasts and melt film. These features are present in several thin alternating surge and fall sequences at the base of the deposit. The lithic clasts in these first deposits are concentrated in layers, indicating pulsatory behaviour of the eruption. Upward, the deposit consists of thicker, coarse ash to lapilli fallout layers from more sustained columns. The juvenile clasts in these deposits are more irregularly shaped, with higher vesicularity (but less than 50%) and smaller leucite microlites (~ 60 μm). The uppermost part of the basal fallout/surge deposit shows features transitional to the first large ignimbrite: fallout deposits alternate with poorly sorted flow units, with an increase in free leucite crystals and lithic content, with more abundant deep lithic clasts and a further leucite microlite size decrease (~ 20 μm), which could indicate an accelerating magma in the conduit.

We think that external factors, such as magma-water interaction and consequent gas explosions, triggered the highly explosive Villa Senni Eruption. Low vesicularity of the early juvenile clasts suggests the magma was relatively low in volatiles at the outset and did not start as a gas-driven eruption. Later in the eruption, the high ascent rate and fast decompression of the magma sustained a large explosive eruption.

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SESSION 1.10

Volcanic monitoring and short-term hazard evaluation

Convenors:

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THE ITALIAN MEROMICTIC VOLCANIC LAKES OF MONTICCHIO (MT. VULTURE) AND ALBANO (COLLI ALBANI)

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The Albano (Colli Albani, Lazio, max. depth 167 m), Monticchio Grande (max. depth 35 m) and Monticchio Piccolo (max. depth 38 m) (Monte Vulture, Basilicata) volcanic lakes are the only meromictic volcanic lakes in Italy, being characterized by stable chemical and thermal stratification of water and presence of significant amounts of dissolved gases at depth.

In the present study, the chemical, physical and biological processes that control the water isotopic and compositional stratification in these three systems were investigated. The main, minor and trace compounds were determined in the aqueous phase along with the isotopic ratios of oxygen, hydrogen and carbon (inorganic) in water molecule and DIC (Dissolved Inorganic Carbon), respectively, and those of carbon in CO_2 and carbon and hydrogen in CH_4.

The Na-HCO_3 composition depends on both interaction of lake water with volcanic rocks and the presence of dissolved CO_2. The vertical profiles of temperature, *p*H, dissolved O_2 and anionic and cationic species (HCO_3, Ca, SO_4, NH_4) indicate a clear separation between *epilimnion*, where oxygen is available as dissolved phase, and *hypolimnion*, dominated by reducing conditions. This is also confirmed by the vertical distribution of concentrations and isotopic characteristics of CO_2 and CH_4.

The total gas pressure (P_{tot}) of dissolved gases is lower than the hydrostatic pressure, indicating that a gas release able to produce “limnic eruption”, like those occurred at the Cameroonian Lakes of Monoun and Nyos in 1984 and 1986, respectively, has to be considered unlike.

The $\delta^{13}C_{CO2}$ values are consistent with a deep-seated source of dissolved CO_2 that is likely produced by i) thermometamorphism of carbonate formations and ii) mantle degassing. The $\delta^{13}C_{CH4}$ values are consistent with a biogenic source of CH_4, being similar to those typically related to carbonate reduction by bacterial activity. The distribution along the lake vertical profile of the isotopic composition of two main gaseous carbon species can be related to: 1) CO_2-CH_4 isotopic exchange; 2) reduction of CO_2 to CH_4 at reducing conditions; 3) oxidation of CH_4 to CO_2 at oxidizing conditions; 4) direct CH_4 and CO_2 production by bacterial activity.

In conclusion, these results have shown that, although the morphometric features (water volumes of Monticchio Grande, Monticchio Piccolo and Albano lakes are $3.3 \cdot 10^6$, $4 \cdot 10^6$ and $450 \cdot 10^6$ m^3, respectively) and the relatively low gas concentrations (max. 19.4 mmol/L at a depth of 38 m in the Monticchio Piccolo lake) suggest that the gas reservoirs of these lakes cannot presently represent a serious hazard for limnic eruptions, the vertical patterns of the CO_2/CH_4 ratio and the $\delta^{13}C$-CO_2 and $\delta^{13}C$-CH_4 values may represent promising tools to evaluate the recharge rate of CO_2-rich fluids into these lakes. The calculated value of $\delta^{13}C_{DIC}$ can also be considered a useful parameter to trace the processes regulating the carbon cycle within the lake waters.

DEGASSING OF MONTICCHIO MAAR LAKES (MT. VULTURE VOLCANO, ITALY): MAGMATIC ORIGIN OF THE FLUIDS AND EVIDENCES OF GAS BURST RECURRENCE

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Two gas-rich lakes fill the Monticchio maar craters situated on Mt. Vulture volcano (Southern Italy) a complex strato-volcano, whose activity began in the middle Pleistocene and which represents the easternmost expression of the Quaternary Italian volcanism. Lago Piccolo of Monticchio and Lago Grande of Monticchio (hereafter called LPM and LGM respectively), are located in two maar craters, created during the last activity of the volcano (~ 13,000 years ago). It was an intense explosive volcanic activity where a relatively small volume of erupted magma sprayed out over a large area that is now partially urbanized.

According to Chiodini *et al.* [1], our investigation ascertained that the most abundant dissolved gases are carbon dioxide and methane displaying a strong increasing concentration with depth in both lakes and in some cases their pressure dangerously approach the hydrostatic one. Our results further show that the methane isotopes have a typical biogenic signature, whereas the carbon isotopes of CO_2, indicates a main inorganic origin, contrary to previous hypothesized, which falls within the range of Italian volcanic emissions. Helium abundances of are up to two orders of magnitude above the equilibrium with air, while the helium isotopic ratio, up to 6.1 Ra (where Ra = $1.4 \cdot 10^{-6}$ is the $^3He/^4He$ ratio in the atmosphere), is in the same range of that measured in olivine-hosted fluid inclusions of the explosion ejecta of the Monticchio maars. This indicates an active inflow of mantle derived fluids into the lakes [2].

Taking into account the volume of water in the two lakes and the abundance of dissolved gases, we calculated that about 9 tons of CH_4 and 386 tons of CO_2 are dissolved in the mixed waters of LGM, whereas 83 tons of CH_4 and 814 tons of CO_2 are dissolved in the stratified waters of LPM.

We then estimated the equivalent volume of gases that a hypothetical sudden release of all the dissolved gases (CH_4 plus the lethal CO_2) could generate a volume of $2.3 \cdot 10^5$ m^3 for LGM and of $5.8 \cdot 10^5$ m^3 for LPM, at atmospheric pressure. Those volume are respectively equivalent to layers of this lethal gas mixture up to ~ 0.6 m thick over the entire surface of LGM (427,000 m^2), and up to ~ 3.5 m thick over the entire surface of LPM (172,000 m^2) [2].

Although the amount of gases dissolved in the waters of these lakes is only a fraction of that to be found in Lake Nyos, nevertheless both the Monticchio lakes must be considered hazardous sites, as the release of the dissolved lethal carbon dioxide could be triggered by an overturn of the waters, or by other external causes, in a touristic area which attracts about 30,000 people every Sunday throughout summertime [2]. Indeed, historical reports clearly describe catastrophic gas release from both lakes that has occurred several times during the last two centuries. Therefore, the result we gained can be considered as the ground for a regular monitoring plan of these two maar lakes.

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HYDROTHERMAL PROCESSES GOVERNING THE CHEMICAL COMPOSITION OF FLUIDS EMITTED BY THE CRATER FUMAROLES AT MT. ETNA

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The geochemistry of gas discharges located at the top of volcanic edifices is receiving upward consideration as it critically constrains models and schemes of fluid circulation below crateric areas. The fumarolic system at the crater area of Mt. Etna volcano represents an interesting case study from this point of view.

Mt. Etna is one of the most-active volcanoes in the world. It is characterized by major eruptions, frequent Strombolian activity, and ash emissions. The volcano summit consists of the central crater of Voragine surrounded by the three active cones of the North-East Crater, Bocca Nuova, and the South-East Crater. They are characterized by very fractured and unstable edges. Under these conditions most of the fractures represent preferential degassing pathways for volcanic fluids, so that the main fumarolic fields develop in such fractured areas.

The geochemistry of the fumaroles at the summit area of Mt. Etna was investigated. Fumarolic samples were collected between June 2008 and August 2009. Gas samples were usually collected as "dry gas" and analyzed for the concentrations of He, H_2, O_2, N_2, CO, CH_4, and CO_2. Fumarolic gases were also sampled a few times using the classical Giggenbach bottles and Giggenbach-type bottles filled with ammonia and silver nitrate in order to determine the SO_2/H_2S ratio. In addition a novel method was employed in order to sample fumaroles characterized by high content of atmospheric gases.

Two types of fumaroles were identified: low-temperature fumaroles, which are dominated by CO_2 with minor amounts of SO_2 and H_2S, and negligible halogen contents, and high-temperature fumaroles, which are strongly air-contaminated and characterized by appreciable amounts of volcanogenic carbon, sulfur, and chlorine. Our data clearly indicate that secondary processes modify the composition of the fluids once they leave the magma body.

A model based on thermodynamic data is proposed to explore such postmagmatic processes. We computed the equilibrium composition of magmatic gases that cool starting from magmatic temperatures under several pressure conditions. The model, which uses Etnean plume geochemistry as starting composition of fluids exsolved from magma, shows that SO_2 and H_2S control the redox conditions of the gas mixture during the cooling, until the reactions involving CO/CO_2 and H_2/H_2O ratios are fully quenched. The scrubbing processes occurring subsequent to condensation and gas–liquid water interaction allow total removal of HCl and partial removal of sulfur species. During the ascent toward the surface, the concentration of CH_4 increases in all fumaroles due to a modest contribution from hydrothermal fluid. A geochemical model for the interaction of pristine magmatic fluids with shallower systems is proposed. The model explains geochemical changes at the crater fumaroles in terms of variable hydrothermal and magmatic contributions, and modified thermodynamic conditions.

DEEP AND SHALLOW SOURCES OF MAGMATIC DEGASSING AT CAMPI FLEGREI CALDERA (SOUTHERN ITALY) AND THEIR RELEVANCE FOR UNDERSTANDING UNREST EPISODES

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Volcanic calderas are affected by unrest episodes usually dominated by hybrid magmatic-hydrothermal system dynamics. Unrest episodes can evolve to eruptions of variable intensity, up to Plinian. Campi Flegrei caldera (CFc) is a type-location for this kind of activity escalation. CFc offers unique opportunity to join volcanological information to a long record of geochemical parameters. This allows understanding the role that magmatic degassing plays on variations displayed by the hydrothermal system. We model uneruptive unrest episodes as driven by i) the shallow emplacement (~ 4 km depth) of one volatile-rich magma batch ascending from a deep (≥ 8 km) magmatic body of regional extent, ii) subsequent gas separation with degassing driven by crystallization, and iii) concomitant fluxing from the deep magmatic body. Our model matches three decades of geochemical constraints from fumarole discharges, as well as data from melt inclusions of past CFc eruptions. Besides, magma physical properties demanded for modelled degassing conditions are in good agreement with existing geophysical data. Our results open new perspectives to the definition of unrest scenarios at highly-populated CFc, as well as other resurgent calderas.

GEOCHEMICAL RELATIONS BETWEEN PERIPHERAL AND CRATERIC DISCHARGES OF GASES AT MT. ETNA: INFERENCES ON COMPLEX DEGASSING PROCESSES

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Geochemistry of gas emissions along flanks and summit of volcanoes provides key information about the magmatic sources and dynamics of the feeding system, once effects of secondary shallow processes have been recognized and removed. Especially, abundance and isotopic composition of noble gases help to this aim thanks to their unreactive nature.

At Mt. Etna, several studies have been performed on peripheral emissions, whose geochemistry has allowed to recognize degassing processes of the Etnean magmas at relevant depth (> 5-6 km) [1, 2, 3]. These sites have provided information on the episodes of deep recharge of the magmatic system and on the importance of these events in terms of involvement degree of the system. Nevertheless, information on magma degassing at shallower levels of the feeding system has been prevented, up to now, due to the location of the sampling sites at no more than 300 m above to sea level and far (> 20 km) from the active volcanic conduits.

Here we display the results of two-year long geochemical survey of some fumaroles at Voragine crater of Mt. Etna. Such monitoring has been coupled to a synchronous monitoring of the well-studied peripheral emissions, to reveal the possible genetic relations of the released gases. For the first time at Mt. Etna, the geochemical study has included abundance and isotopic composition of Ar, coupled to He, Ne and CO_2 concentrations and carbon isotopes.

Our study has displayed that the peripheral gas discharges are fed by magma that degases in the range of 300-400 MPa by an open system mechanism, in agreement with previous studies [2, 3]. The summit crater fumaroles are aligned along the identical degassing paths in terms of He/Ar and Ar/CO_2 ratios, but they highlight minor pressure/depth of exsolution. Interestingly, the carbon isotope composition, coupled to noble gases, puts into evidence that a part of the magmatic gases exsolved at high depth interacts with the magma batches stored at shallow levels and modifies the compositional ratios of the main geochemical indicators of magmatic degassing. The crater fumaroles therefore result from a two-endmember mixture of magmatic gases coming from high and shallow depth in the plumbing system, revealing a complex evolution of the magmatic fluid phase that agrees with recent petrologic studies.

The resolution of the composition of these two endmembers also allows to understand when the deep magmatic term becomes more important, providing information on increasing activity in the middle or long term.

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STUDY OF GROUND MOTION POLARIZATION ON MT. ETNA TO INFER THE RELATION WITH BRITTLE DEFORMATION FIELD

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Seismic anisotropy and its variations are investigated in volcanic areas to infer eruptive dynamics and for prediction purposes. The conventional methodological approach is based on the S-wave splitting. It has been extensively applied to earthquakes on Mt. Etna volcano [1, 2, 3]. The goal of this presentation is to discuss the suitability of a different approach to get comparable information. This approach is based on the study of ground motion horizontal polarization both in ambient noise and earthquake waveforms, mostly in the long coda. Applications are performed in the frequency domain through the technique H/V and in the time domain through the covariance matrix diagonalization method. The advantage of our approach is the high stability of results, independently of the nature and location of the source of seismic signals. We have found that ground polarizations are not isotropic and reflect the brittle deformation pattern associated to the main tectonic structures of Mt. Etna. In particular, we have focused our attention on the Pernicana Fault. We have applied the package FRAP3 [6] to model the brittle deformation field expected in the damage zone of the Pernicana Fault, where more than 200 sites where investigated in previous studies [4, 5] to compute the local polarization azimuths. We have found a satisfactory consistency between observed polarizations and the orientation of the predicted fracture systems. These show a consistent orthogonal trend with respect to the polarization direction. A model is proposed to explain the found relation.

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INSTALLATION OF A TILTMETRIC STATION ON THE STROMBOLI CRATER

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Stromboli is located in the Tyrrhenian Sea, in the northernmost part of the Aeolian Islands; it is an active strato-volcano characterized by continuous strombolian activity and by predominantly fractured in a SW-NE direction [1].

In this paper we present a new tiltmetric station called STR installed from OV-INGV at the end of October 2009 at about 740 m altitude, 200 m SW from the vents of the volcano.

This station is equipped with a bi-axial, bubble-type, short baselength platform tiltmeter, manufactured by Applied Geomechanics (A.G.I.) mod. 702, that allows measurement of the tilt variations along 2 orthogonal directions X and Y aligned to West-East and North-South axes. The tiltmeter is placed and leveled on a plate of leucitite in turn surrounded by a cement matrix at the base of a hand-dug hole 1 m deep, 1 m wide and isolated from the surrounding soil from aluminum panels (Fig. 1). The tiltmetric signals are acquired with a sample rate of 0.333 Hz; the data transmission to Monitoring Center at Osservatorio Vesuviano in Naples is performed by a RS232-WiFi converter that interfaces the datalogger Handi-logger mod. 798 A with the INGV Stromboli's wireless network [2]. Data collected through the program LOG-AC are downloaded every 2 hours on the server localized in Naples by the program PC208W and here processed using graph-analytical procedures implemented through software Dadisp [3].

The ground inclination field for the last two months of 2009 at the STR station, shows six permanent tilts related to explosive events of the volcano recorded respectively on November 8th (1.3 μrad to WSW) and 24th (32.6 μrad to SW) and to other phenomena recorded on December 8th (8.9 μrad to W), 12th (1.3 μrad to NW), 13th (2.1 μrad to WNW), and 19th (5.5 μrad to NNE) (Fig. 2).

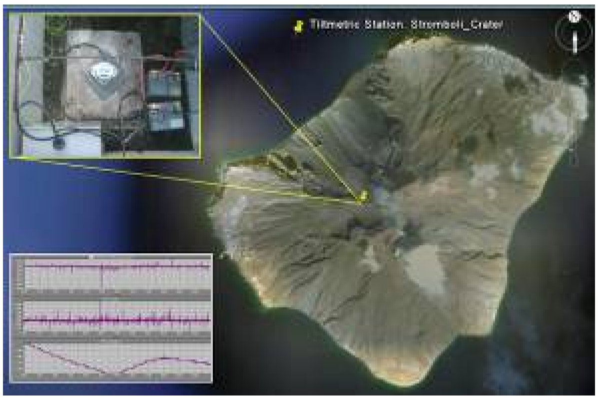

Fig. 1

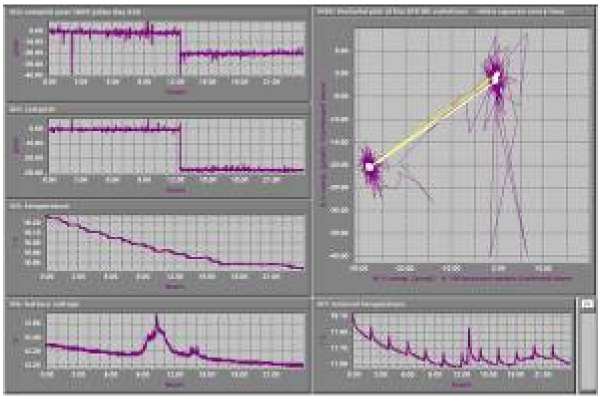

Fig. 2

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STROMBOLI CRATER: GROUND DEFORMATION MEASURED BY A TILTMETRIC STATION

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Stromboli volcano, located in the Tyrrhenian Sea, is the northeastern most part of the Aeolian Islands and has one of the world's longest recorded periods of activity. From submarine investigations has been identified a predominant regional NE-SW structural trend [1], lied along the regional volcano-structural trend of the Aeolian arc, displayed in the subaerial part of the edifice by preferential dyke orientation. Geological surveys [2] show that the subaerial evolution of Stromboli Island began 100 ka ago and can be divided into seven phases, separated by erosional deposits or by collapses of calderas or flanks. In the last phase, *ca.* 5,000 years BP, the northwest sector of the volcano collapses and the huge landslide left a depression horseshoe shaped (called Sciara del Fuoco) that starts from the summit area.

Monitoring of the ground tilt related to explosive processes from broadband seismic sensors [3] and from tiltmeters [4] is being already carried out for several years, but the height of the devices has never reached the craters. We present here new ground deformation data acquired from OV-INGV by a tiltmetric station (called STR), installed at the end of October 2009 at about 740 m altitude, 200 m SW from the vents of the volcano (Fig. 1). The tiltmetric signals are acquired with a sample rate of 0.333 Hz; the data transmission to Monitoring Center at Osservatorio Vesuviano in Naples is performed by a RS232-WiFi converter that interfaces the datalogger with the INGV Stromboli's wireless network. The ground tilt recorded over the last two months of 2009 at the STR station, shows a tilt toward W modulated by long-term variation in soil temperature; indeed, a thermal decrease of 3.2°C recorded by tiltmeter from 28/10 to 31/12 caused a fictitious tilt of 53 μrad to W and of 2.6 μrad to N. This effect is almost entirely caused by temperature changes that expand and contract the ground in an unpredictable way because of its heterogeneity; however, this influence has been evaluated and then subtracted by using a statistic approach (called thermal decorrelation) [5]. The ground inclination field thus calculated still shows a significant tilt to W, although smaller (37.2 μrad), but a tilt of 11.9 μrad to N. Most of this deformation is due to six permanent tilts related to explosive events of the volcano recorded respectively on November 8th (1.3 μrad to WSW) and 24th (32.6 μrad to SW) and to other phenomena recorded on December 8th (8.9 μrad to W), 12th (1.3 μrad to NW), 13th (2.1 μrad to WNW), and 19th (5.5 μrad to NNE) (Fig. 2).

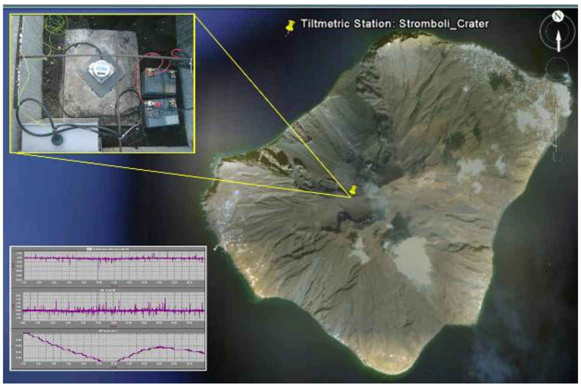

Fig. 1

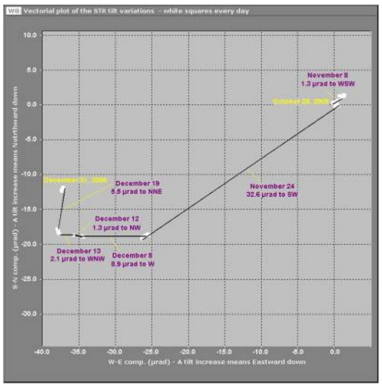

Fig. 2

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SESSION 2.1

The resource Air: natural and anthropic air pollution, nanoparticles, impact of human activities, and climatic changes

***Convenors*:**

G. Rampazzo (*Univ. "Ca' Foscari", Venezia*)
G. Valdrè (*Univ. of Bologna*)

PRESENCE OF Fe^{3+} ON FIBROUS ZEOLITE OFFRETITE: POSSIBLE TOXICOLOGIC IMPLICATION

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Fibrous minerals are of extremely interest for their implications on human health. Among the large number of papers devoted to the crystal chemical characterization of fibrous minerals a few recent works have focused their attention on erionite, a mineral belonging to the zeolite group, due to its involvement on malignant mesothelioma [1, 2]. Chemical analyses of various samples from different localities have consistently indicated the presence of variable amounts of iron that has been located by previous authors inside the cages of this zeolite. However, a recent work has indicated that Fe^{3+} occurs as nanoparticles located at the mineral surface of an erionite sample from Rome Oregon [3]. According to this finding, it is currently under investigation the possible role of such nanoparticles on the toxicity of erionite by combining full crystal chemical and spectroscopic characterizations with *in vitro* and surface reactivity experiments. In fact, it is of great importance to establish the location of iron inside the zeolite structure (framework sites or external surface) in order to determine its bioavailability and activity. Offretite is a natural zeolite structurally related to erionite *via* a different stacking sequence …ABAB… instead of …ABAC… and two polytypes have been reported to occur in association. This study is aimed to the crystal chemical characterization of a sample of fibrous offretite to be used as background for the investigation of its potential toxicity. The sample under investigation was labelled as erionite and came from Chase Creek, Falkland-British Columbia, Canada (Mineralogical Museum of "La Sapienza" Rome). However, a careful scrutiny of X-ray powder diffraction data indicated that the sample consisted of a mixture of both polytypes. Therefore, a structural analysis was made by the Rietveld method indicating that the mixture contained prevailing offretite (~ 87%) and minor erionite (~ 13%). Unit cell parameters were of $a \sim 13.27$, $c \sim 7.55$ Å for offretite and $a \sim 13.26$, $c \sim 15.04$ Å for erionite. A full structure analysis was carried out on the prevailing offretite only. ^{57}Fe Mossbauer Spectroscopy was used to define iron speciation for offretite sample. The Mossbauer spectrum was characterized by a single broad peak of absorption with an isomer shift of ~ 0.15 mm/s, attributed to the presence of superparamagnetic Fe^{3+}.

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REMEDIATION OF FLY ASH AND HEAVY METAL PARTICLES BY JOULE HEATING VITRIFICATION

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The Joule heating vitrification is a thermal remediation treatment consisting in a progressive heating by high power currents up to reach the melting temperature of the material, then followed by rapid cooling to form a monolithic glass. The vitrification process was successful applied to various inorganic toxic wastes [1, 2, 3] and here are reported the results relative to the application of the process to remediate fly ash of civil waste combustion and heavy metal-rich particulate.

The vitrification plant can be roughly described consisting of the main following parts: a current generator of high power made up by a three-phase Scott transformer; four identical graphite electrodes to deliver the current into the material to remediate; a gas-effluent capture system; a gas-effluent treatment system consisting of filtration and scrubber units. The Joule heating vitrification process is characterized by the following main phases: the initial electrical conduction into the material by a conductive path; a progressive decrease of the electrical resistance due to the formation of highly conductive melted zones; a progressive increase of the temperature up to complete melting; a final phase characterized by the cooling and formation of a glassy monolith.

The progressive heating and melting up to temperature higher than 1800°C leads to the destruction of the organic component and removal of volatiles and semi-volatiles compounds, which are collected and treated by a suitable gas-treatment plant. The complete melting of the waste materials (fly ash and heavy metals) and the rapid cooling of the melt leads to the immobilization of inorganic contaminants (such as Pb, Zn, Cu, S, etc.) in a glassy monolith.

SEM-EDS analyses showed a chemically and morphologically homogeneous glass and macroscopic and microscopic vacuoles were observed only in the uppermost part of the monolith, due to the release of gas components during the melting process. XRD data showed a broad pattern in the range 20-30° (2θ) in all zones of the monolith indicating mainly the presence of amorphous material. Minor microcrystalline phases were found only in the lowermost part of the monolith where the slow cooling rate allowed crystal growth.

The hazardous metals were completely immobilized in the glass matrix and the leaching test performed both in the monolith and in little glass blocks showed the absence of metal ions in the eluate fluids assuring a high chemical stability of the monolith after the remediation treatment. The presence of microcrystalline phases should not represent a chemical weakness of the material but rather assure an improvement of the produced glass.

The remediation by Joule heating vitrification process resulted a highly effective technology to reclaim inorganic contaminated particulate in an off-site configuration, however, the easy removal and handling of the vitrification plant allows to implement the technology to remediate contaminated soils also *in situ* and on-site configuration, leading to enlarge the possible applications of the process.

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MONITORING OF SOLID PARTICULATES ARIBORNE SAMPLES FROM MOUNTAIN SNOW IN SOME SITES OF THE ALPS – ITALY

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In the last decades, few days a week, several city centres in Italy are closed at vehicular traffic. This precaution has been decided in order to limit the presence of particulate matter, that usually affects the air in a significant amount, often exceeding the limits set by law [1, 2]. The particulate matter has an impact not only on human health [7, 8], but also in the cultural heritage and natural environment deterioration [9, 10].

Understanding the origin of these particles, both anthropogenic and natural, is now a urgent demand for human health.

Thanks to the Autonomous Province of Trento it has been possible to sample the snowpack in some ski areas, such as Passo Tonale, Alpe di Pampeago, Passo Rolle, during stratigraphic profiling. During the analyses of last snow samples (winter 2010) it has been observed the presence of volcanic ash particles rich in quartz. This feature is typical of certain types of orogenic volcanoes Andean type [3, 4]. Calculating natural origin levels and removing from those the natural contribution, it is possible to assess the human impact. Natural contribution is strictly related to winds and currents movement for this reason a deep knowledge of these factors can help in the determination of the prevalent trajectories during the year [5, 6]. During a recent penetrometerical and stratigraphic profile on Presena glacier, at an altitude of 2750 meters, the main nivo-meteorological features, together with the air temperature and temperature inside the different layers of the snowpack (at intervals of 20 cm) have been measured with great detail. Moreover the shear strength and density of each layer, thicker than 6 cm for the entire snowpack estimated at about 4 meters have been defined. Subsequently, through a DEC analysis of the climatological data, it has been possible to discriminate what event are characterized by volcanic ashes or desert sands. During the stratigraphical profiling some snow samples has been collected and analysed by SEM and ICP-MS in the laboratories of the Earth Sciences Department of Ferrara University. These qualitative and quantitative analyses allow to obtain chemical and mineralogical composition, together with trace elements content, of these samples enabling to define the emitting source.

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UNEVENNESS AND HIGH SPECIES RICHNESS OF BACTERIA IN URBAN AIR PARTICULATE MATTER

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Current knowledge about both microbial communities associated with airborne particulate matter and their relations with environmental and atmospheric conditions is limited. In particular, only few studies have focused on the characterization of the total air microbial community in urban areas. The present study aims at describing the microbial community associated with coarse (PM_{10}) and fine ($PM_{2.5}$) particulate matter during different seasons in Milan (Italy) urban area using parallel massive pyrosequencing. Particulate was sampled on teflon filters over three months during summer and winter seasons and the hypervariable region V3 of gene 16S rRNA was amplified from the DNA extracted from the filters [1]. Operational Taxonomic Units (OTUs) were obtained by clustering the sequences into groups of sequence variation from 99 to 70% identity cut-off values. The results showed large variations in the microbial community associated with PM both in terms of seasonality and size. Plant-associated bacteria species dominated summer particulate while spore-forming bacteria predominated during winter. Both summer and winter communities were characterized by very high richness while they were dominated by few OTUs (low evenness). The richness values are comparable to those obtained by pyrosequencing approach for soils which are considered the most biodiverse environments for bacteria [2]. According to recent ecological theories, very uneven communities like ours have both very low functionality and a very low stability that, in turn, may explain the dramatic changes in the bacterial community composition from summer to winter we observed. Our results suggested that not only can the sources of the particulate influence the presence of specific bacterial groups, but also that the environmental factors and stresses can shape the bacterial community.

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ENVIRONMENTAL AND HEALTH ASPECTS RELATED TO HEAVY METALS IN PARTICULATE MATTER: DETERMINATION AND RELEASE TESTS IN BIOLOGICAL ENVIRONS

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The particulate matter (PM) is a suspension of solid and liquid particles in the air, with aerodynamic diameter < 10 μm, and specifically indicated as PM_{10}, $PM_{2.5}$, and PM_1. A large concentration PM in the air can represent a strong environmental emergency because of its claimed toxicity. Because of its composition, the PM presents an intrinsic toxicity, amplified by its capacity to host various carcinogenic substances, in particular the heavy metals. Different pulmonary pathologies are generally attributed to the inhalation of PM, and the pleural calcified plaques seem to be directly correlated to the malignant pleural mesothelioma [1].

The recent directive 2008/50/EC regulates the quality and enhancement of the air in the European countries [2], establishing the concentration limits for PM_{10}, and $PM_{2.5}$, in 50 and 25 $\mu g/m^3$/day, respectively. Some previous works already reported data on the Italian situation, and some paper was specifically published concerning the city of Rome [3, 4].

In the present work preliminary data on $PM_{2.5}$ collected from the urban central area of Rome are reported. The study focuses on 1) chemical characterization, and 2) tests of release of heavy metals in physiological solution. The principal aim of this new study is to assess the environmental and health risk of a determined area on the basis of the content and quantitative release of the metals present in the original particulate material.

The $PM_{2.5}$ sampling was performed on polytetrafluoroethylene (PTFE) filters (47 mm diameter, and 2 μm pore sizes). Morphological, mineralogical, and chemical characterizations were carried out by XRPD, SEM-EDS, and ICPMS analysis. The tests of release of heavy metals (Cd, Cu, Cr, Ni, Pb, and Zn) were executed in physiological solution, at constant temperature (37°C). Solution samplings were made for 30 days in order to better define the kinetic of release of the heavy metals. The quantitative chemical characterization of PM, coupled with the study of release of heavy metals in physiological solution is the key to better define environmental and health risk for in the investigated areas.

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COMPARISON OF GEOCHEMICAL COMPOSITION OF FINE PARTICULATE MATTER ($PM_{2.5}$) IN THE VENICE AREA

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Atmospheric aerosols constitute a multi-component system of material in solid or liquid state (excluding pure water) that could enter in air by natural or anthropogenic sources.

The chemical composition and size of the particles are strongly linked to their sources and formation processes. In view of the impact on health, fine and coarse particles are differentiated by the 2.5 µm threshold. Mass concentrations of particulate matter ≤ 10 µm (PM_{10}) and ≤ 2.5 µm ($PM_{2.5}$) are known as 'inhalable' and 'fine' fractions, respectively.

In the last decades, particulate matter pollution has become an important environmental risk factor having adverse effects on human health, climate and ecosystems. In particular during cold periods, $PM_{2.5}$ levels in Venice area frequently exceed the target value of 20 $\mu g\ m^{-3}$ fixed by the Directive 2008/50/CE.

Venice area is affected by several potential PM sources: (i) the medium size urban area of Mestre; (ii) the industrial zone of Porto Marghera; (iii) a crowded road-network; (iv) the artistic glass-making area of Murano; (v) the shipping traffic; (vi) the Marco Polo airport.

The main goals of this study are: (i) to highlight the relationship between $PM_{2.5}$ levels and micro-meteorological conditions, (ii) to investigate the relationship between the chemical composition in sites with different emissive scenarios, (iii) to identify site-specific elements and principal PM sources in each site.

Based on different environmental conditions, three sites of Venice have been selected: a coastal site, Punta Sabbioni; an urban background site, Via Lissa - Mestre, an industrial site, Malcontenta - Porto Marghera.

From 26th February to 3rd April 2009, 90 $PM_{2.5}$ samples were collected according to EN 14907:2005 using a low volume sampler (2.3 $m^3\ h^{-1}$) on pre-conditioned quartz fiber filters. Samples were then cut in two portions. First portion was dissolved in MilliQ® water in ultrasonic bath and then analyzed by ion chromatography to determine water soluble inorganic ions (Na^+, NH_4^+, K^+ Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-}). Microwave acid digestion was applied to second portion to determine elemental composition by ICP-OES (S, Na, Fe, K, Ca, Mg, Al) and ICP-MS (As, Cr, Ni, Cu, Cd, Pb, Co, Mn, V, Zn, Ba, Se, Ti, Sr).

Average $PM_{2.5}$ concentrations are 28.9 $\mu g\ m^{-3}$, 32.0 $\mu g\ m^{-3}$, 22.0 $\mu g\ m^{-3}$ in Via Lissa, Malcontenta and Punta Sabbioni respectively.

First results show high levels of PM correlated to low wind speed, constant pressure, low temperature and low mixing height. These conditions prevent the dispersion of air pollutants, allowing the accumulation of particulate matter.

In these days an increase of major ions - main nitrates - was observed. On whole periods major ions (NH_4^+, NO_3^-, SO_4^{2-}) represent 26.2%, 32.4%, 36.6% of $PM_{2.5}$ total mass in Via Lissa, Malcontenta and Punta Sabbioni respectively.

Typical crustal elements (Al, Ca, Mg) present higher concentrations in Via Lissa and Malcontenta than Punta Sabbioni, probably linked to resuspension processes cause by vehicular traffic. Between trace elements, Zn and Pb present higher concentration in all three stations.

Compositional data will be analyzed by discriminant analysis to identify common elements in the three sites, and by factor analysis to identify $PM_{2.5}$ sources.

MATERIALS SCIENCE MEETS MINERALOGY: VOLCANIC ASH AND AEROENGINES

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The recent volcanic activity of Eyjafjallajökull in southern Iceland has highlighted the need to be able to assess accurately the effect of relatively low levels of volcanic ash particulates in the atmosphere of the order of a few mg m^{-3} on the performance of both commercial and military aircraft engines. Of particular concern is the degradation of the turbine blades in these engines as a result of exposure to volcanic ash. In the hottest part of aircraft engines temperatures reach up to 1200°C. Therefore, metallic components such as turbine blades, discs and nozzle guide vanes operating in such temperatures are protected by thermal barrier coatings (TBCs) some 200 μm thick [1]. Typically these coatings are made of yttria-stabilized zirconia (YSZ) [1, 2].

In the literature, the effect of volcanic ash and other particulates on turbine blades is assessed experimentally from observations of the degradation behaviour of the TBCs when exposed to calcium magnesium aluminosilicate (CMAS) [*e.g.*, 1, 2, 3, 4]. Critical to the response of the TBCs is the melting point of the CMAS – the literature suggests a value of 1240°C is not unreasonable for CMAS compositions close to eutectic composition found in minerals ingested into aircraft engines in both sandy and volcanic ash environments. Research clearly shows that, once in molten form, CMAS is able to infiltrate the YSZ TBCs relatively easily because of the columnar nature of the coating microstructure. This in turn stiffens the TBCs and causes their spallation, thereby exposing the underlying nickel-based metallic alloy components to higher temperatures than they would normally see, and thus reducing their performance life. This is a more subtle effect than the blocking of cooling passages in turbine blades leading to engine shutdown at very high levels of ash concentration in the atmosphere of the order of 1 g m^{-3} adjacent to erupting volcanoes [5]. Clearly, it is in the interests of aircraft engine manufacturers to set as low a limit of weight of volcanic ash particulates per unit volume as possible in the atmosphere when flying through volcanic ash, on the grounds that *any* exposure to such material is life-limiting for critical components in aircraft engines. However, this has to be balanced against the disruption to air travel when volcanoes emit ash at relatively low levels into busy air lanes hundreds of kilometres away from the volcano, as happened in April and May in 2010 in Western Europe [5].

In this presentation I will first describe the materials science underlying turbine blade technology and demonstrate how highly engineered these components are in aircraft engines to withstand creep, thermal fatigue and oxidation in the hottest part of the engines. I will then review the current state of knowledge in the literature on the effect of CMAS on these components at both low and high concentration levels per m^2 of surface. Finally, I will pay attention to what checks and balances need to be in place for monitoring any long-term deleterious effects of relatively low levels of volcanic ash in the atmosphere on aircraft components.

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SURFACE POTENTIAL OF MINERAL PARTICLES BY SCANNING PROBE MICROSCOPY

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The interaction of micro and nanoparticles between themselves and with extended surfaces is driven by several forces, among which for instance, adhesion, hydrophilicity/hydrophobicity, magnetic forces and surface-related electrostatic potential.

The use of spatially resolved techniques to characterize the local chemical and physical properties of microsized particles is of paramount importance to know their reactivity to the surrounding environment.

Besides surface morphology, recent advancements of Scanning Probe Microscopy (SPM) have made available a wide range of surface investigations at the nanoscale. These include for example rheological, magnetical and electrical properties of the surface.

In this paper we present new SPM methodologies to characterize the surface electrostatic potential of mineral particles. Several Kelvin Probe Force Microscopy (KPFM) techniques have been used.

The dual-pass lift mode performs sequentially a topographic measurement and an electric potential detection some nanometres above the sample surface. The single-pass mode performs, simultaneously, topographic and potential measurements by using very high modes of flexural vibrations of the cantilever. In the latter case, the Kelvin feedback can be set-up in amplitude or in frequency modulation to optimize the electric potential resolution. An electrostatic (EFM) mode was also used to cross-correlate the surface potential results.

The SPM observations were conducted at RT (22°C), atmospheric pressure and relative humidity of about 40%. Chlorite was used as a mineral standard for EFM and KPFM study because is a layer silicate where a positively charged octahedral layer, about 0.5 nanometre thick of brucite is sandwiched between two negatively charged TOT layers by means of weak electrostatic forces. A Nanonis (SPECS Zurich, Switzerland) SPM Controller with two oscillators connected to a MultiMode head (Digital Instruments, Santa Barbara, California) was used. In static-mode EFM, specifically FIB-machined Si_3N_4 gold-coated tips ($k \sim 0.06$ N/m) were used and the probe-deflection *vs.* tip-surface voltage difference V was calibrated by using a cleaved graphite standard. In dynamic-mode, NCHPt NanoWorld (Switzerland) Pt/Ir-coated silicon tips ($k \sim 2.8$ N/m, working frequency ~ 70 kHz) were employed. After cleavage, chlorite presented simultaneously on the same specimen surface zones of brucite and zones of siloxane with lateral sizes ranging from a few nanometre to microns [1]. Kelvin and EFM allowed us to measure the thickness of the brucite layers and to experimentally verify the layer polarity [2]. In static EFM we have acquired the probe deflection versus tip-sample distance at constant V. In this mode of operations the electrostatic interaction forces resulted of the order of some tens of pN in agreement with a theoretical model [3]. In Kelvin force microscopy we measured a voltage difference ranging from about 50 mV to 500 mV between the brucite-like and the TOT layer. It was finally observed that the two layers presented adhesion and shear force contrast because of the different hydrophilic/phobic property.

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ELABORATION OF A NEW METHODOLOGY FOR THE DETECTION OF INORGANIC PARTICLES/FIBRES IN THE PM$_{10}$

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The increase of air pollution is one of the most important issues due to its effect on human health and the European laws require a steady monitoring of suspended Particulate Matter (PM) [1]. Thus, the investigation of the mineral component in the PM$_{10}$ (particles with aerodynamic diameter less than 10 μm) is essential to obtain information about their chemical/physical properties, including how they interact with other aerosol species and gases in the atmosphere, and their principle effects on human health [2]. Recent studies on PM$_{10}$ emphasize that the airborne fine particles are a multiphase system, which undergo many chemical-physical modifications especially because of its heterogeneous composition. PM$_{10}$ is usually monitored by high volume device, collecting the suspended material onto specific membrane made either in quartz or in glass fibres [1] and measuring the concentration by the gravimetric method of the suspended PM$_{10}$, that is defined as the total mass of the PM$_{10}$ per cubic meter of air within 24 hours [3]. This type of analyses provides only the weight of suspended materials without information about the ratio between organic and inorganic portions. Moreover, the European Community is recently showing an increasing interest in assessing the chemical characterization of the different components occurring in the PM.

The presented study aims to elaborate a quickly and not expensive new methodology in order to perform the chemical and the morphological characterization by SEM/EDS of potential toxic inorganic compound (*e.g.* asbestos and metals) occurring in the PM$_{10}$. A procedure was elaborated for removing the solid components of the particulate matter from the sampling filters - that are routinely used by the environmental protection agencies to determine the air quality- and then deposit them on a polycarbonate support, more suitable for the SEM/EDS analysis. Thanks to the developed procedure, it was possible to:

a) distinguish easily particles/grains/fibres from the original support from those in the PM$_{10}$;

b) ascribed the different observed particles to the inorganic/mineral phases, on the basis of the EDS chemical analyses;

c) propose an apportionment of the detected phases to different sources, natural or anthropogenic, in the different analyzed samples and in each sample to define the percent weight of each of them;

d) exclude the presence of breathable fibrous phases ascribing to the minerals defined "asbestos" by law [4].

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AIR POLLUTION MODEL SYSTEM TO SIMULATE $PM_{2.5}$ DISPERSION IN VENICE AREA

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Understanding air pollution dispersion is difficult but essential to estimate air quality and health impacts. To this purpose specific measurement devices for sampling are required which entail high costs and involve a consistent number of people. The use of mathematical models, despite their limitations, enables to study regions of different sizes and to provide information when there is a shortage of data in non-controlled areas. These models describe the causal relation between emissions, atmospheric concentrations, and deposition. In fact they provide quantitative information about concentrations and deposition and they can give a more complete and consistent description, including an analysis of the causes and emissions sources, meteorological processes, physical and chemical transformations that led to these concentrations/deposition.

With this view, it was decided to use a model chain in a project which studies both primary and secondary $PM_{2.5}$ particulate in the Venice area as complementary device to experimental researches carried out between January 2009 and February 2010.

The model system, distributed by ARIANET S.p.A., consists of three main components: a diagnostic meteorological model (*MINERVE*) [1], a turbulence model (*SURFPRO*) [2] and a photochemical-eulerian dispersion model (*FARM - Flexible Air quality Regional Model*) [3].

Minerve is a 3*D* wind field model for complex terrain. It produces a mass consistent wind field using data from a dispersed meteorological network. Temperature and humidity fields can also be interpolated. Surfpro produces dry deposition velocities and turbulent diffusivities fields needed by the eulerian model. FARM is used to calculate concentration and deposition of reactive emissions including photochemistry gases and particles, it calculates dispersion using either a one or two way nesting within multiple grids.

The model chain has been used to simulate principal pollutants dispersion in Venice area with specific attention to $PM_{2.5}$ fraction.

Four periods has been considered during different seasons for which both organic and inorganic measured data was available. Emissions used as model input have been referred to EMEP/CORINAIR Emission Inventory Guidebook [4] groups in Venice area during year 2005. Even though experimental period refers to 2009-2010, 2005 emissions are the only data guaranteed by public administration. A work in progress is focusing on calculating 2009's emissions for principle sources in Venice area. These data will be used to simulate air pollution dispersion during measurements periods so to compare calculated results with experimental data.

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PGE ACCUMULATION IN SEDIMENTS AND ROAD DUSTS: ANALYSIS OF THE ALBINEA (REGGIO E., ITALY) DISTRICT

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The present research is aimed at studying the presence of Pt, Pd and Rh (PGE) in both sediments and dusts sampled either on construction works or in different sites of the Albinea City, as a result of the emissions from high traffic pollution. The measurement of total concentration of PGE was performed by mass spectrometry, using an internal standard and software elaboration in order to correct recombination and interference effects between elements. In particular, the interference estimate was pondered on the base of Cu, Sr, Pb, Rb, and Zn contents. Besides element concentrations, also the mineralogical composition of the matrix (sediment or dust) was evaluated by powder diffraction.

The results of our study were compatible with those of other previously studied cities; in addition sediments and dusts compositions parallel those of autochthonous sediments and building materials, respectively. The highest PGE concentrations were found in the zones of highest traffic, in particular where a start/stop flow was induced by the presence of traffic lights.

Schäfer & Puchelt [1] argued that when PGE are of anthropic origin, Rh and Pt show a direct correlation. This trend is clearly observable in our samples, both sediment and dust (Fig. 1). As Pd is concerned, Tsogas *et al.* [2] demonstrated that a steady Pd increase, both absolute and comparable with Pt, is to ascribe to catalytic converters of the last generation, which use higher Pd content. For the studied zone, however, no comparison data exist, since our data are the first ones even collected. It is however worth noting that our data are on average higher than those from literature, referred to urban and civil complexes (roads, highways, tunnels).

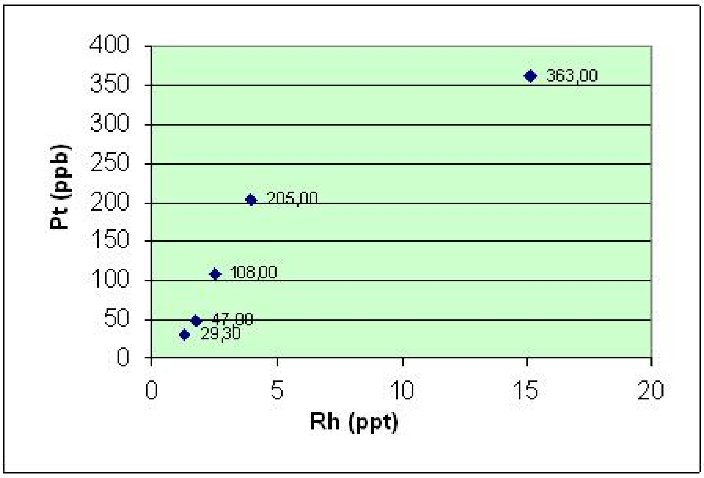

Fig. 1. Pt (ppt) *vs*. Rh (ppt) plot for the Albinea district.

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SEASONAL VARIATIONS OF FINE PARTICULATE MATTER ($PM_{2.5}$) AND MAJOR INORGANIC IONS IN THE VENICE AREA

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Fine particle ($PM_{2.5}$, $D_a < 2.5$ µm) result mainly from gas-to-particle conversion processes and carbonaceous exhaust emissions. Particles derived from gas-to-particle conversion are identified as secondary aerosol.

Major water soluble inorganic ions consist in ammonium (NH_4^+), calcium (Ca^{2+}), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-) and chlorine (Cl^-). They are mainly present as sodium chloride (NaCl), potassium chloride (KCl), ammonium nitrate (NH_4NO_3), ammonium sulfate ($(NH_4)_2SO_4$) and secondly as calcium nitrate ($Ca(NO_3)_2$), sodium sulfate (Na_2SO_4) and calcium sulfate ($CaSO_4$).

Ammonium nitrate and ammonium sulfate derived from gas-to-particle processes and form Secondary Inorganic Aerosol (SIA). The concentrations of these components are related to the transfer time scale between gas to particle phase, which is a function of ambient temperature, relative humidity, and their gas phase constituent concentrations in the atmosphere (NO_x, SO_2, NH_3, VOC's).

The aims of this study are to: (i) investigate $PM_{2.5}$ and major ions concentration in different atmospheric conditions; (ii) characterized secondary inorganic aerosol on $PM_{2.5}$.

A $PM_{2.5}$ sampling campaign started on December 2008 and finished on February 2010 in three different sites of the Venice area: (i) an urban background site (Via Lissa - Mestre); (ii) an industrial site (Malcontenta, near Porto Marghera); (iii) a coastal site (Punta Sabbioni).

Samples have been collected by low volume sampler (2.3 m^3 h^{-1}) on pre-conditioned quartz fiber filters, according to EN 14907. Ultrasonic method was used to extract all filters for determination of inorganic ions by ion chromatography (Na^+, NH_4^+, K^+ Mg^{2+}, Ca^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-}).

Monthly average concentrations show a typical pattern with maximum values in cold season and minimum in warm season. Four periods had been selected for ionic components analysis: (i) spring, 26th February - 3rd April; (ii) summer, 11th June - 16th July; (iii) autumn, 20th September - 31st October; (iv) winter, 22nd December - 31st January.

Ammonium, nitrate and sulfate result to be major ions in $PM_{2.5}$ in all seasons. Nitrate highest values have been detected in spring and winter. Sulfate presents maximum concentration in summer and autumn. SIA amount (SIA = $[NH_4^+] + [NO_3^-] + [SO_4^{2-}]$) shows highest values in Punta Sabbioni in all seasons.

To compare average concentration One-way ANOVA test has been applied. Tests show no-significant differences (p value > 0.05) in $PM_{2.5}$, NH_4^+, NO_3^- and SO_4^{2-} concentrations between the three stations in summer, autumn and winter. Moreover, Pearson correlation coefficients highlight a similar temporal pattern.

ANALYSIS AND MODELLING OF ASBESTOS FIBRE DISPERSION IN URBANIZED CENTRES

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In the 70's and 80's asbestos-containing materials were widely used in building construction, for this reason today they are very common in every city all around the world.

Often this material is in poor state of repair and when released in to the air, these fibres can cause serious consequences for the health of exposed people.

The purpose of this study is to define and quantify the presence and the dispersion of respirable asbestos fibres in the air of some highly urbanized centres in the Umbria region, Central Italy, combining air concentration measurements and numerical modelling.

The sampling was made with instrumentation designed for monitoring of air quality in terms of PM modified with express polycarbonate filters with 25 mm of diameter and porosity of 0.8 µm. The air flow rate was 16 l/min and we collected 2 samples corresponding to a volume of 1500 l for each measurement.

Measurements of fixed stations were used to obtain the values of fibres concentrations in different areas of the region and some "natural" background values. Then we used mobile stations to measure the fibre concentration in areas characterized by the presence of suspicious buildings pointed out by local people, or by health authority.

The locations of sampling stations where chosen in areas close to some old industrial centres in order to obtain significant concentrations. The identification and the counting of airborne asbestos fibres were made by SEM analysis of the filters.

The measured values of wind and airborne fibre concentrations were used to test and validate a numerical model that describes the dispersion of this kind of fibres in urban environments. The numerical model is based on the solution of the advection-diffusion-sedimentation equation. Wind field is calculated coupling the dispersion model with a mass consistent wind model whereas turbulent diffusivity is estimated in accord to the similarity theory inside the atmospheric surface layer. Settling velocity accounts for effect of the particle shape. The inputs to the model are the topography, wind measurements from meteorological stations, atmospheric stability information, mass flow rate from the sources and aspect ratio and density of the fibres.

The results obtained using the dispersion model can help to understand the mechanisms of transportation of these particles inside the atmospheric surface layer and to provide a hazard assessment of the investigated urbanized areas.

DEFINITION OF QUANTITATIVE CHEMICAL ANALYSIS PROCEDURE FOR AIRBORNE PARTICULATE MATTER (PM_{10} AND $PM_{2.5}$)

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In the last decades the quality of the air has been object of several studies, as concern in particular atmospheric particulate matter [1]. Pollution due to the presence in the atmosphere of minute particles is one of the most important factors affecting the human health, together with effects related to climatic changes. The dimension of the fine particles in the atmosphere, predominantly constituted by PM_{10} and PM $_{2.5}$ [2], are so small that is very difficult the analyses them using the standard quantitative chemical techniques.

The aim of this project is to better define the particulate matter present in the atmosphere adopting analytical methods able to evaluate the quality and the quantity of the particles.

A test area in the ENEA Centre of Trisaia (Rotondella Borough), located 4 km far from the sea and close to the boundary between Basilicata and Calabria Regions, has been identify. Some samples of solid particulate matter have been collected from this study site in order to create a reference dataset. Sampling has been carried out from 11 p.m. of 7/07/09 to 11 p.m. of 8/07/09 (sample 1) and from 11 p.m. of 8/07/09 to 11 p.m. of 9/07/09 (sample 2) using quartz fibre support Pallflex® Air Monitoring Filters, Tissuquartz™ Filters, 2500 QAT-UP.

Chemical analysis of metals has been carried out using a multi-elemental analytical methodology suitable for the determination of trace elements such as ICP-MS [3]. Samples treatment and chemical analysis have been performed in the laboratories of the Earth Sciences Department of the Ferrara University. Samples analysis has been execute using a Thermo Electron Corporation Xeries spectrometer, equipped with a collision/reaction (cell CCT^{ED}) for the reduction/exclusion of main polyatomic and isobaric interferences. This technique is suitable for revealing in solutions most of the elements present in the periodic table, and between them to distinguish the natural contribution indicators, deriving for outcropping lithologies (Na, Al, K, Ca, Mg, Mn, Fe) and anthropic contribution markers (Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Zn). The distribution of these elements enabling to define local backgrounds and give a potential instrument for identifying possible long range contributions. In the fine tuning of the procedure for the samples treatment for ICP-MS analysis it has been necessary to decide for one of the two possible approaches: extraction of particulate matter from filters or dissolution of particulate matter with the filter. In the preliminary tests the latter method has shown the better results influencing the choice of the same support (quartz filter) for all the samples. Reproducibility and accuracy of the method have been tested through several analysis repeated on several sub-samples at different dilution. The activities of this project, through a monitoring of the particulate matter, will enable to give a support for the identification of air solid particulate matter provenance. This will be helpful for suggesting strategies able to contrast the pollutants emission in the sources, allowing the accomplishment of effective reduction of local, national and international emission (paragraph 2 Directive 2008/50/CE) [4, 5]. This European Directive ask detailed measurement of fine particles in the atmosphere in rural sites for better define the impact of these pollutants, this in order to formulate suitable actions. Moreover these measurements, as cited by EMEP [6] will enable to discriminate between natural local contributions in rural areas and long range atmospheric pollutants.

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VERTICAL PROFILE TO MONITORING PARTICULATE MATTER IN PO VALLEY AND FRIULI PLAIN

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Po Valley and the Friuli Plain in Italy are areas with the highest concentration of solid particulate matter in Europe [1]. This implies that those areas does not respect the limits imposed by European Parliament in 2008 [2, 3]. The aim of this study is to contribute in the characterization of the particulate matter, through direct flying sampling in atmosphere to define physical properties and sources of this particulate.

Object of these investigations were PM nature from two different sites characterized by different environmental features: a) a rural area in the Po Valley; b) an urban area in the Friuli Plain close to Trieste city. Sampling has been carried out in June-July 2009 in the Po Valley and in June-September 2009 in the Friuli Plain using a small aircraft (CESSNA 172P), collecting samples with constant speed (about 175 km/h) for assuring a continuous air flow.

Particle concentration has been measured for five aerodynamic equivalent diameters (0.5, 1.0, 2.5, 5.0, 10.0 microns) using a laser counter (LIGHTHOUSE HH 3016), direct collection of particles has been carried out by means of double glued tapes as well as filters. The acquisition has been carried out vertically profiling the atmosphere from 150 to 2400 metres [4]. In addition SEM analysis, from Center for Electron microscopy in Ferrara University, has been carried out on single particles to obtain detailed dimensional and morphological information helping to hypothesize their origin and the toxicity [5], has been complemented with SEM-XVP analysis useful to define the origin and the nature of organic matter [6].

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MONITORING OF SOLID PARTICULATES AIRBORNE SAMPLING FROM MOUNTAIN SNOW IN FERRARA – ITALY

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The effects on health, environment, monuments and cultural exposure to airborne particulate solid can be estimated through chemical and mineralogical analysis and the observation of morphological data to enable identification of source. To date, most scientific documents describe physical and meteorological models [1, 2, 3] to describe the trajectories of the wind and the paths of pollutants at globally (transboundary contributions) and local scale [4] in order to assess short and long term climate change. Only recently attention has focused on particle analysis, not only quantitative but also qualitative. For technology problems, however, the results concern only on micro particles and are extremely rare information on behavior, morphology and composition of natural and anthropogenic nano particulate [5, 6, 7].

This project, focused on the study of micro and nano particulate inorganic - natural, wants to define the analysis procedures and the composition and morphology of local and cross-border geological contributions, valuable for the development of realistic models as a basis for abatement strategies. Since few studies are available in the literature related to natural particulate less than 2.5 microns, for sampling and analytical limitations [8], we decided to investigate the aqueous solution derived from dissolution at room temperature of snowfall occurred in Ferrara city during last winter. It is well known that extreme heavy snowfall can remove particulates in the atmosphere, and create good conditions for the collection of this pollutant, to better define the contribution.

Po Valley and Friuli Plain in Italy and Belgian Plain in Europe, are areas with the highest concentration of solid particulate matter in all the world [9]. For this reason one of the sites chosen for investigation is the province of Ferrara.

Samples were taken in the city, subject to anthropogenic pollution by particulate matter, and in Codigoro country in Ferrara province, far from anthropogenic sources.

Was done with a double sampling: a first in the final stages of snow, which aims to characterize natural contributions after several hours of snow and so the removal of anthropogenic contribution; a second in about a day away from the end of snow to collect natural and anthropogenic contributions in terms of reduction of particles for a longer period. The sampling strategy provides several samples in three different times when it snowed (December 2009, February and March 2010).

Department of Earth Sciences and Centre for Electron Microscopy University of Ferrara have made qualitative and quantitative studies on samples of melted snow through analysis on plasma mass (ICP-MS), ion chromatography and scanning electron microscopy (SEM).

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EMISSIONS MONITORING OF "MARCO POLO" AIRPORT (TESSERA – VENICE)

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Aviation activities are included in the Community Scheme of Allowances of Greenhouse Gases by the 2008/101/CE Directive of European Parliament and the Council of December 19th, 2008, amending the 2003/87/EC Directive. The airport major emission sources are aircraft engines fueled by petroleum products, activities directly related to the passengers and luggage movements, as well as the airport structure operations (heating, fuel storage, etc.).

Ca' Foscari University (in collaboration with SAVE S.p.A. and Ente Zona Industriale) has been studying the Marco Polo emissions since June 2009, by processing the main atmospheric variables and the major pollutants concentration revealed in the study area. Specifically, the chemical species monitored every hour by Ente Zona mobile unit are: SO_2, PM_{10}, O_3, NO, NO_X NO_2, CO, methane and non-methane hydrocarbons, while meteorological variables sampled are wind speed and direction, solar radiation intensity, precipitation rate, and temperature. The sampling site (a parking area near the airstrip) was chosen estimating the main relapse points of aircraft emissions below 1000 m and neglecting the other sources. This was done by processing the air traffic data provided by SAVE S.p.A., by using a Lagrangian model SPRAY [1] that is part of the SCAIMAR modeling system, managed by Ente Zona Industriale.

The study of airport pollutants dispersion in the Venice area is extremely important because: i) Marco Polo air traffic is among the highests in Italy, and ii) the airport is located near the Venice lagoon, a complex and delicate ecosystem.

Principle aim of this collaboration is at estimating the emission contribution of Marco Polo airport, as well as informing the public opinion spreading the results of this research.

During this first year (June 2009 - May 2010), overtakings of the law limits were recorded only for NO_2, NO_X and PM_{10}. These species, together with CO and volatile organic compounds, are major pollutants associated with fossil fuels combustion. Based on the data currently available, we may claim that near the monitoring area there are several sources of these pollutants, and that the airport is not the dominant source because: i) concentration values of the above mentioned pollutants exhibit a low correlation coefficient; ii) their concentration values and (as well as the values of the correlation coefficients) do not increase significantly when the wind direction is favourable to the monitoring of airstrip, iii) the estimated concentration values are on the average lower than those revealed by the mobile unit. Presently, it is not possible to estimate the contribution of airport to the concentration of NO_2, NO_X and PM_{10}, but we can assess that their increased concentration in winter is likely due to the emissions growth from part of several different sources, as well as by the changes in climatic conditions that favour their concentration.

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IBIL ANALYSIS OF ROAD DUST FROM THE "TRAFORO DEL SAN BERNARDO" TUNNEL

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The objectives of this work are: i) to characterize the road dust from the "Traforo del San Bernardo" tunnel and some materials taken as the possible sources of the particulate matter at issue, and ii) to assess the potential application of Ion Beam Induced Luminescence (IBIL) for the characterization of complex environmental matrices. This research is innovative since IBIL has never been used so far to probe this kind of matrices.

Road dust is composed of natural and anthropogenic particles to be collected on surface and along roadsides, and this material contributes significantly to atmospheric particulate matter by resuspension of finer particles. Samples were collected in the ventilation air shaft of Traforo del San Bernardo highway tunnel (Italy-Swiss border), that is an ideal sampling area to study the particulate emitted from the vehicular traffic. Samples were dried and sieved (1000, 500, 250, 63 μm); sub-samples with particle size between 250-63 μm and < 63 μm were pressed in pellets and analyzed. IBIL spectra were obtained by irradiating the samples with a 1.8 MeV He^+ beam at the AN2000 accelerator of the INFN Laboratori Nazionali di Legnaro.

Concerning the matrices which are the possible sources of particulate matter that constitute the samples described above, we analyzed: i) washcoat samples collected from different types of catalytic converters; ii) particles collected in the expulsion plant of exhaust gases and ventilation system of various motor vehicles; iii) fragments of brake pads and tires. Moreover, the standard reference material of road dust (BCR-723) was also analyzed.

The spectra for all road dust samples exhibit a comparable asymmetric luminescence peak. For those ones collected inside the Traforo del San Bernardo, there is a maximum located in the 610-630 nm range, whereas the standard BCR-723 exhibits a peak at about 655 nm. The different peak positions and its asymmetry suggest that the samples contain two different organic compounds, probably produced by the petroleum combustion. The different concentration ratios between them give rise to the spectra difference for wavelengths longer than 650 nm.

Study of luminescence degradation under ion beam irradiation has shown that the two compounds have different radiation hardness. The more resistant species is responsible for the asymmetry of the peaks, emitting mainly at λ longer than 620 nm. On the other hand, the peak shape in the region with λ shorter than 630 nm is related to the photoemission of the less resilient species. It was shown that washcoat is not present in significant amounts in the analyzed road dust samples; nevertheless, due to the low luminescence of the other samples, their possible contribution to the formation of the samples may not be ruled out.

To test the reliability of IBIL technique, a further series of measurements have been performed on the possible sources of artifacts specific of the technique. In particular, the analyses have pointed out the similarity of the road dust spectra with that from graph paper, which was therefore analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) along with the samples, in order to identify the possible luminescent species. The tests have shown that both samples contain 2.4-bis (1.1-dimethylethyl)-phenol and diisobutyl phthalate, which the luminescence features can be ascribed to.

Work is in progress to characterize the luminescent species identified in the road dust samples. These could be used as an indicator to quantify the contribution of traffic source to this kind of matrix. In conclusion, this work has demonstrated that IBIL is a useful tool to characterize complex environmental matrices like road dust.

ANALYSIS OF AIRBORNE PARTICULATE MATTER: APPLICATION OF FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY AND SELECTED GEOCHEMICAL TECHNIQUES

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Air particulate matter includes mineral dust, metals, metalloids, sea salts, nitrate and sulphate of ammonium, organic compounds, elemental carbon as well as organic and inorganic pollutants residing almost exclusively in the gas phase. The relative abundance of these atmospheric components is temporally and spatially highly variable. Some of them are directly emitted into the atmosphere either by natural and anthropogenic sources (primary particles), while some others are the result of homogeneous or heterogeneous nucleation and condensation of gaseous precursors (secondary particles). These latters have a great affinity for water, thus contributing to acid rain, which promote, as well known, a faster decay of buildings.

In this work we report the results about the molecular species, concentrations and size distributions of the main water-soluble ion species in atmospheric aerosols under the polluted urban conditions existing in Palermo. PM_{10} and $PM_{2.5}$ filters from a sampling site exposed to heavy traffic were collected and examined. Water-soluble ions were extracted by ultra-pure water and each extract was analysed for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+} Cl^{-}, SO_4^{2-} NO_3^{-} and F^{-}. To obtain qualitative bond and functional group information for PM samples ATR-FTIR spectra of exposed and unexposed filters were also examined. Subtraction of the blank from the filter sample was performed for each sample. Ions contributed an average of 29 and 31% to $PM_{2.5}$ and PM_{10} mass, respectively. The water-soluble ions Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, NO_3^{-}, and Cl^{-}, were predominant in PM_{10}, whereas sulphate and ammonium were mostly predominant in $PM_{2.5}$, likely in the form of $(NH_4)_2SO_4$. The molar concentration ratio of ammonium to sulphate (NH_4^{+}/SO_4^{2-}) was found to be about 0.4 and 0.25 in $PM_{2.5}$ and PM_{10}, respectively, indicating an ammonium poor ambient atmosphere. Thus, ammonium ions are not so abundant as to totally neutralise sulphuric and nitric acids. $CaCO_{3(s)}$ resulted to be the most important neutralising agent. Fig.1 shows the ATR-FTIR spectra of PM_{10}, $PM_{2.5}$ and blank filter, with the functional groups identified along with their corresponding absorption frequencies. The peaks marked were assigned as follows (from left to right) SO_4^{2-} (616 cm^{-1}), CO_3^{2-} (878 cm^{-1}), SiO_4^{4-} (1045 cm^{-1}), NO_3^{-} and NH_4^{+} (1365 and 1414 cm^{-1}), C=O (1587 cm^{-1}), C-H aliphatic (2849, 2914, 2921 and 2986 cm^{-1}).

Specific organic molecules could not be confirmed, however, organic functional groups like carbonyls and aliphatic chains were assigned.

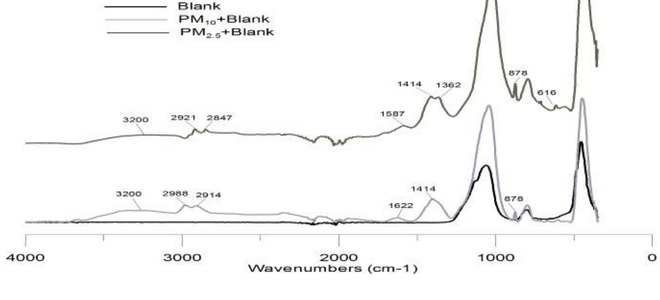

Fig. 1. ATR-FTIR spectra of PM_{10}, $PM_{2.5}$ and blank filter. Tensor 27 (Bruker Optics) FTIR spectrometer operating in the infrared (370-7500 cm^{-1}) region.

SESSION 2.2

Soil and Water resources: natural systems and anthropic impact

***Convenors*:**
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GEOCHEMICAL AND ISOTOPIC CHARACTERIZATION OF THE MONFALCONE THERMAL SPRINGS (FRIULI-VENEZIA GIULIA REGION, ITALY)

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The Monfalcone thermal springs represent the most important outflow of thermal waters in the Friuli-Venezia Giulia Region. The hydrothermal system was known for therapeutical use since Roman time and it was cited by Plinius Secundus in his *Naturalis Historia*. The history of the water captions is complex and thermal buildings were repeatedly destroyed and reconstructed. At present, thermal springs are surrounded by the industrial area of the town of Monfalcone. The thermal spring outlets are confined within carbonatic lithologies, mainly constituted by bioclastic limestones and breccias deposited during Cretaceous.

The first documented chemical analyses, which date back to the XIX Century, show a major ion composition similar to what measured at present day, suggesting that the geothermal system remained mostly unchanged. The present study reports on chemical and Sr-O-H isotopic data obtained on thermal waters sampled monthly during 2006-2007 surveys. The emergence temperature varies between 32.6 and 39.8°C; the total salinity is around 13,000 mg/L for the hotter samples. Waters are classified as Na-Cl-SO_4-type, with elemental ratios similar to those of modern seawater except for ratios involving Ca^{2+} ions. In particular, Ca excess is attributed to equilibrium with limestones, which constitute the main lithologies of the aquifer as suggested by the Sr isotopic composition. Waters are saturated with calcite and supersaturated with respect to dolomite. Oxygen and hydrogen isotope-ratios are in the relatively narrow range between -5.04 and -6.36 for $\delta^{18}O$ (‰ *vs.* SMOW) and between -33 and -40 for δD (‰ *vs.* SMOW), respectively, and plot close to the meteoric water line reported for northern Italy. The lack of a positive $\delta^{18}O$ shift indicates that waters were never heated enough to react with the reservoir of oxygen in the rocks during their flow. A direct correlation between temperature, salinity and chloride content is observed, suggesting that a thermal end-member of marine origin underwent dilution by low-temperature and low-salinity components. This is supported by the $\delta^{18}O$ data, showing that the isotopically lighter waters are characterized by the lower outlet temperature, consistently with admixing of a low-temperature end-member; whole ^{18}O-^{2}H isotopic signature is consistent with that of the karst aquifer. The estimated temperature of the geothermal reservoir, as inferred by speciation and mass-balance calculations, approaches 70°C. The proposed model requires that seawater underwent a 35 vol.% dilution by a low-salinity water before interacting with the shallow secondary karst aquifer. Considering the typical geothermal gradient of the area, a depth of about 2 km for the thermal aquifer may be estimated. In summary, the proposed semi-quantitative model for the Monfalcone hydrothermal system includes: (1) paleo-seawater infiltration at depth and dilution by low-salinity waters; (2) heating to about 70°C due to the local geothermal gradient; (3) upward migration of the thermal waters along fractures possibly related to the intense deformational regime of the area; (4) variable surface mixing with Ca-bicarbonate, karst-type cold waters; (5) discharge at a favourable spot.

RELATIONSHIPS BETWEEN SOIL COMPOSITION AND PHYTO- AND MYCO-DIVERSITY IN A WASTE-ROCK DUMP OF THE LIBIOLA SULPHIDE-MINE (EASTERN LIGURIA, ITALY)

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The research was carried out in an open air waste-rock dump of the abandoned Libiola sulphide mine (NW Italy) in order to study the relationship between soil composition and phyto- and myco-diversity and to assess the possible bioaccumulation of specific ecotoxic metals. The waste-rock dump (about 2 ha) is located close to an open-pit and several mine adits; it is highly heterogeneous due to the presence of lateral and vertical lithological variations of the deposited materials. In particular, it is possible to distinguish two main types of waste-dump sites: S1) mainly characterized by serpentinic and basaltic host rocks, and S2) with significant enrichments of pyrite-rich sulphide mineralizations.

S1 site is characterized by minor amounts of pyrite ($\leq$ 5%) showing various degree of oxidation. Clasts of serpentinite, basalts and ophiolitic breccias are the main components ranging from 50 to 80 wt.%. As a consequence, the mineralogical assemblage is dominated by serpentine-group minerals, chlorite, plagioclase, magnetite and other spinels. Secondary minerals (5-10 wt.%) are mainly represented by Fe-rich smectites with minor amount of goethite and hematite.

Serpentinite and basalt mineral assemblages are the main constituents (40-60 wt.%) also of S2 site that instead is characterized by significant enrichment (10-30 wt.%) of sulphide minerals (pyrite ± chalcopyrite ± sphalerite). The remaining mineralogical fraction (10-30 wt.%) is mainly represented by goethite and hematite with minor Fe-smectites.

Although both S1 and S2 sites highly exceed residential and industrial limits for a number ecotoxic metals, such as Cr, Co, Ni, Cu, Zn, and Cd, according to Italian law (D.M. 471/1999; D.Lgs 152/2006), they are significantly different in their chemical composition. In particular, S1 site is enriched in Ca, Mg, Mn, Ni and Cr. Conversely, the S2 site is enriched in Fe, Cu, Zn, S, Ag and Au: these elements are not only related to the high amounts of Fe-Cu sulphides, but also to the Fe-bearing secondary minerals that are able to efficiently scavenge the heavy metals released during sulphide oxidations.

As concerns the mycoflora, the most isolated microfungi species are tolerant to a wide range of pH and there is a remarkable mycodiversity in spite of heavy metal concentrations in native soils that exceed 2400 mg kg^{-1} Cu and 1500 mg kg^{-1} Cr. The macrofungal sporomata of *Scleroderma polyrrhizum* (J.F. Gmel.) Pers. and *Thelephora terrestris* Ehrh. have highlighted the capability to accumulate Ag (> 50000 μg kg^{-1}) and Cu (> 1000 mg kg^{-1}), respectively.

Among plant species *Alyssoides utriculata* (L.) Medik has showed more than 1000 mg kg^{-1} Ni in leaves, suggesting a preferential metal allocation and a Ni-hyperaccumulation.

The selected plant species could be fruitfully employed for future phytoremediation, while fungi could help the natural recolonisation of the surrounding vegetation. This multidisciplinary approach can help to fully characterize complex ecosystems, such as those related to highly contaminated mine soils, and establishes the basic knowledge to develop experimental protocols for future bioremediation and habitat restoration.

Fe-RICH STALACTITES AND STALAGMITES FORMED BY COLLOIDAL DEPOSITION WITHIN MINE GALLERIES

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Underground and superficial waters of Libiola Mine area are mostly ASW (Acid Sulfate Waters) due to active AMD (Acid Mine Drainage) processes triggered by oxidation of pyrite and chalcopyrite mineralizations. Ore minerals are still abundant as relics in the underground workings and in outcropping rocks and as non-economic pyrite-rich blocks in the waste rock dumps. Precipitation of solid phases extensively occurs elsewhere when abrupt changes of the physico-chemical parameters are encountered by the contaminated solutions. Of particular interest are the concretionary Fe-rich precipitates that form in underground open voids related to the mine workings (such as mine-galleries and -chambers). At the Libiola mine, stalactites and stalagmites occur on the walls, ceilings, and floors of two galleries (S. Barbara and Castagna), showing several moprhological and chromatic features (from yellow to orange, to brown to black).

The aim of this work is to characterize the mineralogy of the different occurrences of these Fe-rich stalactites and stalagmites as well as to investigate the physico-chemical parameters of the related mine and drip waters.

The mineralogy has been investigated by means of reflected and transmitted light microscopy, X-ray powder diffraction (XRPD), scanning electron microscopy (SEM-EDS), and electron microprobe analysis (EPMA-WDS). Mine and drip waters have been sampled for chemical analyses. Water temperature, electrical conductivity, alkalinity by acidimetric titration, *p*H, *E*h, ferrous and total iron concentrations were determined in the field during sampling. In the laboratory, waters have been analyzed for major chemical composition and trace metal content.

The samples, selected for this study, are representative of two types of stalactites ("soda straw" and "deflected" stalactites) and one type of stalagmite. The soda straw stalactites range from 1 to 50 cm in length and from <1 to 3 cm in diameter. They are characterized by a hollow core that allows the water flow; in cross-section, this central cavity is surrounded by concentric bands that are apparently representative of the various growth rings. The deflected stalactites range from 10 to 30 cm in length and from 5 to 10 in maximum width; they are curved along their length and characterized by a submillimetric layering marked by alternation of fine-grained materials separated by empty layers. Also in this case the layering is presumably representative of different growth stages. Finally, the stalagmite sample measures 6 cm in length and 2 cm in diameter and shows similar features to those observed in the soda straw stalactites.

XRPD result shows that all the samples consist of goethite in association with variable amounts of amorphous minerals. SEM-EDS analyses and EPMA-WDS maps evidence that all the concentric and curved bands are characterized by a variable contents of Fe_2O_3 (52.37-68.2 wt.%), SiO_2 (0.60-1.56 wt.%), Cu (0.14-0.58 wt.%), Ni (0.01-0.13 wt.%), Co (0.34-1.12 wt.%) and Zn (0.25-0.88 wt.%). The waters have intermediate Electrical conductivity (about 2200 µS/cm), with low iron content and a *p*H around 5.9 which is significantly higher than the extremely acidic waters found elsewhere in the mine The mineralogical and minerochemical characterization of these Fe-rich assemblages could make it possible to estimate the spatial and temporal variations of the contaminated mine seepage and to evidence the possible scavenging capacities of the precipitating minerals towards several ecotoxic metals.

GEOCHEMISTRY AND ISOTOPIC COMPOSITION OF COLD AND THERMAL WATER DISCHARGES AT MT. AMIATA

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Mt. Amiata (southern Tuscany) is the most recent volcanic apparatus of the Tuscan magmatic Province. The shallow aquifer of Mt. Amiata is the most important resource of drinkable water in southern Tuscany and northern Lazio, and an active geothermal field is present at depth. The main purpose of this work is to investigate the isotopic and geochemical features of inorganic and organic gas species in naturally discharged fluids to evaluate the influence of deep geothermal fluids in the shallow aquifer. In this context, a geochemical survey of the complex hydrological system feeding the numerous cold and thermal springs of the area has been carried out on the basis of the existing data integrated by a new dataset of water samples collected from January to March 2009.

Mt. Amiata area is characterized by the presence of two geothermal reservoirs: the shallower one, having a temperature of 200-230°C, is at a depth of 500-1000 m in the carbonate-evaporite formations, whereas the deeper one (depth > 3000 m) is within the metamorphic basal complex where temperature are up to 350°C [1, 2]. Moreover, in the NE area of the volcanic structure the relatively shallow hydrothermal system of the Bagni S. Filippo is located. The latter is hosted in Mesozoic formations and the discharged waters have temperature of about 60°C [3]. A shallow aquifer, within the fractured volcanic sequences above the Ligurian Units, feeds numerous springs, mainly located at the contact between the two formations. This aquifer is separated from the deep geothermal system by the low-permeable Ligurian Units. Thermal and cold springs related to the hydrothermal reservoirs are in the eastern and southern sectors of the Mt. Amiata volcanic edifice and are chemically characterized by: i) Ca-SO_4 composition, ii) relatively high TDS (total dissolved solids) values, iii) relatively high concentrations of minor compounds, such as B, Li, NH_4, As, HS and aromatic organic compounds. Cold and thermal springs fed by the shallow aquifer show a Ca-HCO_3 composition and low TDS values. The concentrations of VOCs (Volatile Organic Compounds) in most the Ca-HCO_3 waters are almost negligible, whereas Ca-HCO_3 springs emerging in the proximity of villages and cultivated areas present halocarbons and light alkanes likely related to anthropogenic activity. The springs fed by shallow volcanic aquifer has values of δ^2H and δ^{18}O corresponding to the isotopic features of meteoric water. On the contrary, waters from the shallow and deep geothermal reservoirs show δ^{18}O values enriched in the heavy isotope likely due to water-rock interactions.

The distribution of both inorganic and organic geochemical tracers and isotopic data suggests that contribution of deep fluids can only be recognized in the Ca-SO_4 waters, whereas the shallow volcanic aquifer is apparently not contaminated by the deep geothermal systems, being the two systems isolated by the low permeable Ligurian Units.

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GEOCHEMICAL MODELING TO CONSTRAIN THE PARAMETERS INFLUENCING AMMONIUM EXCHANGE FROM NH_4-RICH SOLUTIONS AND NATURAL ZEOLITES MIXTURES

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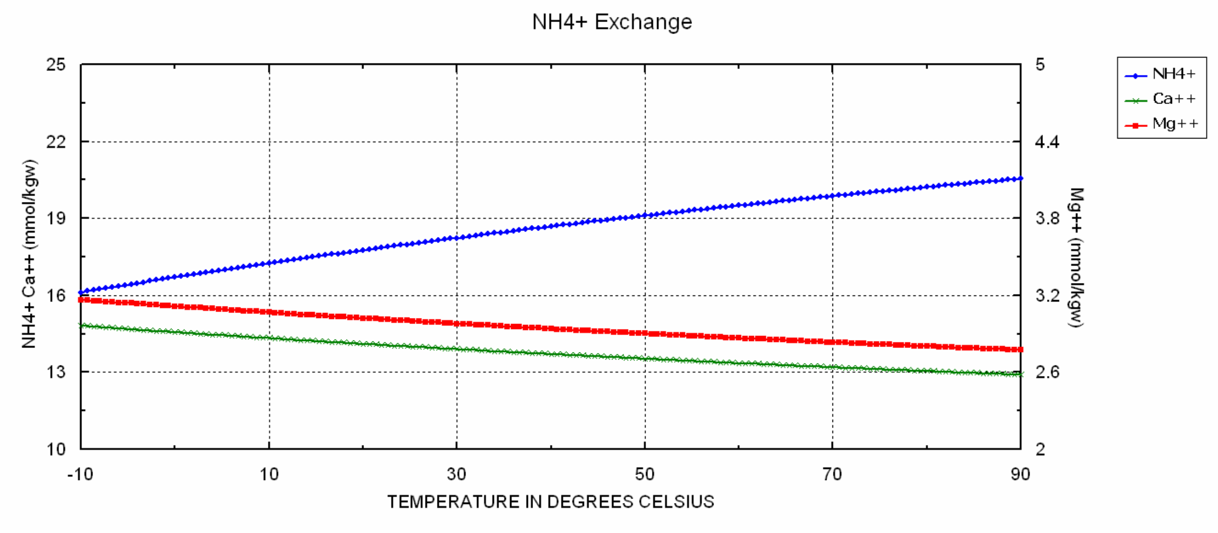
Natural zeolites are more and more frequently employed to remove excess ammonium in wastewater [1], since their capital cost is not excessive and their cation exchange capacity is elevated. Recently, natural zeolites have been also applied as fertilizer in orthoculture [2], after an exchange step within a ammonium rich solution. Despite of all this applications, many are the unknown parameters which can affect the cation exchange capacity of natural zeolites from an ammonium rich solution. For this reason a series of numerical scenarios have been performed to quantify possible side effects. The geochemical code PHREEQC-2 [3], was used in batch mode to evaluate the variation of the equilibrium exchange between ammonium and other cations (present onto the exchanger site of natural zeolites) induced by selected master parameters. The master parameters which were varied in a range of two order of magnitude, are: temperature (-10 to 90°C), ammonium concentration (2 to 200 mM/L), bulk cation exchange capacity of the matrix (1 to 100 meq/100g) and the composition of the exchanger sites. The latter two parameters are dependent from the type and amount of zeolites present in the original rock/sediment matrix.

Results are important to understand what is the best parameters combination to enhance ammonium exchange onto natural zeolites, and to provide optimal ammonium concentrations for agricultural purposes.



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METHYL *TERT*-BUTYL ETHER ADSORPTION ON HIGH SILICA FAUJASITE: AN EXPERIMENTAL AND COMPUTATIONAL MODEL STUDY

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Methyl *tert*-butyl ether (MTBE) is one of the fuel oxygenates which is voluntarily added to gasoline as substitutive of lead tetraethyl to raise the octane number. Owing to the high solubility in water (*ca.* 50 $g \cdot L^{-1}$ at room temperature), MTBE has been found to easily pollute large quantities of surface and groundwater when gasoline is spilled or leaked at gas stations or at refinery plants [1]. To restrict downward movement of contaminants, the use of physical barriers made of a continuous synthetic layer of low permeability materials constructed as the base of a land cell can be used [2]. In this context, the interaction between MTBE and a high silica faujasite was monitored in this study by infrared spectroscopy augmented by computer modelling.

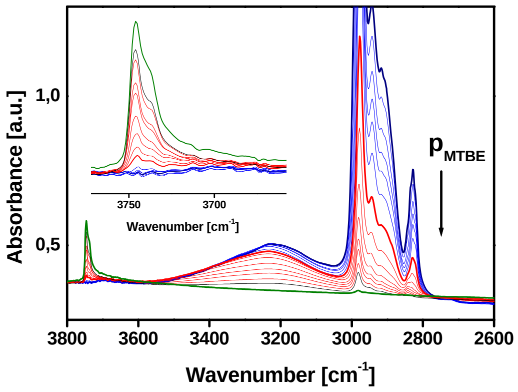

Fig. 1. IR spectra of progressive dosage of MTBE (p_{max} 120 mbar) on zeolite-Y pre-outgassed at 400°C.

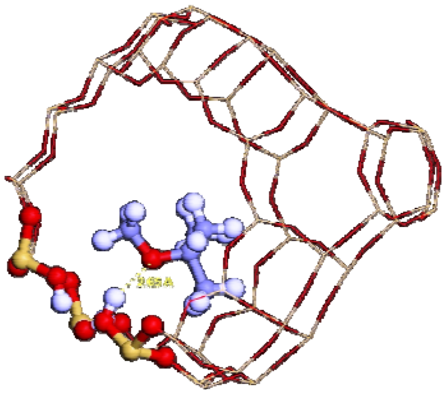

Fig. 2. Modelling of the interaction between the MTBE molecula and the cage of zeolite-

The infrared spectra show two characteristic bands at 3743 and 3730 cm^{-1} (Fig. 1, inset) due to isolated silanols located at the external surfaces of the zeolite crystal and in internal defects of the zeolite cage respectively. Upon MTBE adsorption (Fig. 1) both silanols are shifted to *ca.* 3230 cm^{-1}, thus suggesting the formation of H-bonded complexes of medium strength between silanols and organic pollutant. This interaction is reversible at room temperature: as a matter of fact the MTBE/silanols complexes are not stable upon progressive reduction of the MTBE pressure. The geometry of MTBE included in a zeolite-Y cage has been optimized at the DFT level with the hybrid functional B3LYP and a double-zeta basis set (Fig. 2). A defect was created in the cage wall removing a silicon atom to create three silanol groups: MTBE oxygen binds to one of such silanols through an H-bond of medium strength (O···O distance 2.65 Å), clearly revealed by the downshift of silanol -OH stretching frequency predicted by the calculation and measured in FTIR experiments.

Acknowledgements: Research co-funded by Research Center for Non-Conventional Energy, Istituto Eni Donegani - Environmental Technologies.

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SEASONAL VARIATION OF SOIL NATURAL RADIOACTIVITY IN THE COSENZA-RENDE AREA, CALABRIA (SOUTHERN ITALY)

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The subject of radioactive contamination gained considerable public importance because of his potential risk for causing health detriment. Naturally occurring radionuclides (uranium and thorium series, etc.) are the largest contributors to radiation doses received by human beings [1]. The concentrations of natural radionuclides in soils can vary in a wide range, depending on their content in the soil-forming rocks, but they also related to effects of meteorological variations [2, 3, 4].

This study was carried out to determine the variations of the natural radioactivity concentration in the Cosenza-Rende urban area (southern Italy) during two seasons (winter and summer). The reason for this selection was that January and July are the wettest and the most arid months, respectively. Determination of the natural radioactivity (^{40}K, ^{238}U, ^{232}Th) was carried out, by means of gamma-ray spectrometry system, in 181 surface soil samples representative of the same geological formations outcropping in the studied urban area. The descriptive statistics of results was reported in Table 1. The interpretation of the seasonal variations was conducted using geostatistical techniques.

Table 1. Descriptive statistics of radionuclides in summer (a) and in winter (b).

(a)	Total radioactivity (Bq)	K (Bq)	U (Bq)	Th (Bq)
N. Samples	181	181	181	181
Min	328.05	0.62	0.36	0.05
Max	476.15	7.86	5.32	2.96
Mean	365.90	2.57	1.58	0.59
Median	361.99	2.49	1.45	0.56
St. Dv.	20.95	0.79	0.67	0.31

(b)	Total radioactivity (Bq)	K (Bq)	U (Bq)	Th (Bq)
N. Samples	181	181	181	181
Min	0	0	0	0.01
Max	0.17	11.23	2.54	0.12
Mean	0.085	5.11	0.11	0.04
Median	0	4.93	0	0.03
St. Dv.	0.02	2.7	0.34	0.02

It has been observed that spatial and temporal variability of soil gamma-ray spectra was caused by the combined effect of geological and meteorological variations. The results indicate that the specific levels of terrestrial environmental radiation were related to the geology and lithology of each area, and to the thorium (Th), uranium (U) and potassium (K) content of the bedrocks. Especially they were controlled by the occurrence of mineral such as monazite or zircon in soils. Furthermore it has been observed that there is a seasonal variability in the same sample sites which was probably related to the condition of water saturation and moisture retention. During the winter water tends to be confined in a saturated surface soil which reduces radiation permeability. Conversely during the sunny summer the soil became drier and more permeable and the total radioactivity increases. Other causes of this seasonal variation could be temperature and atmospheric pressure variations, which, particularly during cold season, were essential due to stack effect.

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NOBLE GAS IN THE STRIMON BASIN (GREECE-BULGARIA): EVIDENCES OF KARSTIC AND THERMAL WATER MIXING

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The Strimon (or Struma) basin is an active, post-orogenic graben located at the Greece-Bulgaria border. The graben is contoured by the Serbo-Macedonian Massif to the West and by the Rhodope massif to the East. Marbles, gneisses and micaschists constitute the eastern margin of the basin. In this area, marble formations host the major karstic hydrosystem of Drama-Aggitis (Greece), whose main discharging points are the cold springs of Mara-Aggitis, Kéfalari and Drama.

Due to the occurrence of sparse granite bodies of Tertiary age related to the active extensional tectonics of the region, an anomalous heat flow is estimated all over the study area. A geothermal development program was carried out over the last few decades in the area, and low enthalpy fluids with temperatures in the range 27 to 60°C are currently utilized for greenhouse heating, fish farming, drying of vegetables, spas and bathing.

In an attempt to investigate water sources and deep circulation paths, free and dissolved gases were analyzed for their He and Ne contents and He isotopic composition in sixteen samples from Drama karstic springs, and in nine Strimon basin thermal waters samples.

The dissolved gases were extracted from sampled water by means of the space head method. The abundance of He and Ne was measured using a quadrupole mass spectrometer (VGSX200) after separation in a suitable all metal high vacuum line. The He isotopic composition [expressed as $R/R_a = (^3He/^4He)_{SAMPLE}/(^3He/^4He)_{AIR}$] was obtained by means of a magnetic mass spectrometer for rare gases (MAP 215-50).

All the available samples reveal the existence of a positive linear correlation between He/Ne ratio and temperature of the manifestations. This trend is indicative of a binary mixing between a He-enriched, thermal component and a He-depleted, cold component of meteoric origin. The karstic springs clearly separate from all the other samples, plotting close to the atmospheric end-member.

The He isotopic ratio (R/R_a) ranges from 0.26 to 1. Based on karstic springs R/R_a values ranging between 0.2 to 0.6, we estimated an atmospheric fraction close to 90% for the Drama well and the Aggitis spring, and a lower value between 50 to 30% for the Drama and Kefalari springs. As expected, the thermal springs combine the lowest R/R_a with the highest He/Ne ratio, supporting the hypothesis of a predominantly crustal origin of the sampled He.

The addition of radiogenic He accounts for the observed R/R_a ratios generally below the air reference value. However, the presence of some mantle-derived He is also evident, as traced by the occurrence of concomitant R/Ra values close to 1 and high He/Ne ratios. The presence of Alpine magmatism in both the northern part of the Strimon valley and at the Bulgaria-Greece border could account for the occurrence of ^{3}He enriched fluids in an area otherwise dominated by crustal melting.

Noble gas isotopic composition emerges as a very useful tool to trace mixing processes during underground water circulation in the Strimon basin. The He isotopes, in particular, revealed the mixing of two aquifers: a cold shallow one related to karstic circulation of air saturated water, and a thermal one, deeper, related to water circulation through granite bodies.

WATER DETERIORATION OF THE MAZARRÓN-GAÑUELAS AQUIFER (SE SPAIN) BY DEEP-SEATED CO_2-RICH SALINE WATERS AS EVIDENCED BY GEOCHEMICAL AND ISOTOPIC INVESTIGATIONS

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In the south-eastern part of the Iberian Peninsula, the Betic Cordilleras are characterized by many hydrothermal features, such as CO_2-enriched groundwaters, that are related to the complex tectonic setting. Higher CO_2 concentrations and saline waters than those expected in ordinary groundwater systems indeed occur at many localities and severely affect water usage.

In this framework a geochemical survey on about 20 waters (sampled in September 2009 and March 2010) and dissolved gases collected in the Mazarrón-Gañuelas Valley at different depth (> 50 ÷ 300 m) was carried out with the aim to i) geochemically and isotopically characterize the effects of the deep-seated CO_2-rich saline aquifer with the shallower ones, and ii) assess the geochemical processes deriving by this mixing in terms of water quality.

The Mazarrón-Gañuelas Tertiary basin (Murcia, central-southern Spain), part of the Alto Guadalentín Valley, is located in the SE part of the Iberian Peninsula and lies within the Betic Cordilleras (SE Spain) pertaining the eastern sector of the Alborán Domain. This area is mainly characterized by successive overthrust sheets of Paleozoic and Triassic rocks that were later broken by a series of large faults, including the Carboneras, Palomares, and Guadalentín sinistral strike-slip fault systems, which may be the surface representation of the zone of crustal thinning and magmatism. To be remarked it is the presence in the Mazarrón-Gañuelas basin of shoshonitic (13.7 Ma), ultrapotassic (11-6 Ma) and alkaline (4-2 Ma) volcanic rocks.

The aquifer of the Alto Guadalentín is divided into 2 separate horizons: i) a shallow reservoir located in the Plio-Quaternary rocks, forming the main aquifer and ii) a deep reservoir located in the Nevado-Filábride Complex (from the Permian to Upper Triassic).

Groundwater temperatures are between 21.4 and 45.7°C, with a highly variable electrical conductivity (886-11,290 μS/cm). The *p*H values are between 6.30 and 8.99. The water chemical composition is characterized by 5 hydrochemical facies: $Na(K)-SO_4$ (32%), Na(K)-Cl (26%), $Na(K)-HCO_3$ (16%), $Ca-SO_4$ (16%) and $Ca(Mg)-HCO_3$ (10%). This variability is likely favoured by the depth of the fractures affecting the substratum, which allows the rise of a deep-seated CO_2-rich saline aquifer. Carbon dioxide is the most abundant compound in the dissolved gases, being the concentration of this gas > 80% by vol. in > 75% of collected samples. The $\delta^{13}C-CO_2$ values in the dissolved gases are generally characterized by relatively negative values (< -11.0‰ V-PDB), although most of the samples clusters around -10 to -12‰ V-PDB. A few samples with more positive values, up to -6.9‰, tend to approach a mantle-like end-member (-7 ÷ -3‰). Concluding, the occurrence of a CO_2-rich gas phase in the deep aquifer can possibly be referred to the presence of a magmatic degassing system at depth, likely related to the volcanic activity that has affected the area in the last 13 Ma. The halo of this deep-originated CO_2 is seemingly extending to the whole Mazarrón-Gañuelas basin, as testified by both the water and gas chemistry and $\delta^{13}C-CO_2$ values. Eventually, it is worthwhile to mention that the area has also been suffering a strong agricultural development since 50 years, as testified by the recurrent presence of nitrate at concentrations up to 200 mg/L in some of the studied wells.

GROUNDWATER QUALITY DETERMINATION USING CHEMICAL AND ISOTOPIC EVIDENCES: Mt. VULTURE VOLCANIC AQUIFER (SOUTHERN ITALY)

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Mt. Vulture volcanic aquifer is one of the most important hydrogeological basins of the southern Italy. Groundwater resources are employed for drinking, irrigation and industry uses. Furthermore, the aquifer is characterized by precious mineral waters proving the social and economic interest of the study area.

Contamination and overexploitation of the groundwater are often serious environmental problems affecting particularly drinking water resources. The great increase of anthropogenic activities, in the Mt. Vulture basin, could create a menace from both quality and quantity viewpoint. In the study area, water-rock interaction processes play an important role in controlling groundwater hydrogeochemistry. Understanding these processes is fundamental for sustainable use, management and protection of resources.

The presence of major and trace elements in groundwater is an important issue because it affects possible uses of water. Major constituents, heavy metals and trace elements in subsurface environments come from natural and anthropogenic sources. The weathering of the minerals forming the host-rocks is one of the major natural sources. Moreover, anthropogenic sources include fertilizers, industrial effluent and leakage from service pipes [1].

Particularly, the source of nitrate (NO_3^-) in groundwater of the volcanic aquifer was investigated using chemical and isotopic techniques. Nitrate contamination in surface and groundwater, especially as it relates to land use, is a critical issue. The objective of this investigation was to determine the origin of anomalously high NO_3^- concentrations detected in groundwater from springs and wells in Mt. Vulture area.

Relative to background levels, the NO_3^- concentrations from 34 water points are sometimes anomalously high, suggesting that sources other than naturally occurring soil organic matter have contributed additional NO_3^- to groundwater in the volcanic aquifer. This information, and the dominance of agriculture in the study area, suggest that agrichemical contributions may be significant. To test this hypothesis, water samples were collected and analyzed for dissolved NO_3^-, $\delta^{15}N$ and $\delta^{18}O$ of the NO_3^- ions analysis.

The isotopic data were most definitive and suggested that the sources of NO_3^- in some spring waters, located nearby to the urbanized zones in the southeastern sector of the studied area, are dominated by N-fertilizer and to a much lesser extent, human and/or animal waste. Isotopic values for $\delta^{15}N$ and $\delta^{18}O$ of the NO_3^- ranged from 2.4 to 15.9‰ and from -2.9 to 11.4‰, respectively. The trend of $\delta^{15}N$ and $\delta^{18}O$ data for NO_3^- also indicated that no significant degree of denitrification is occurring in the shallow volcanic hydrologic system within the soil zone, prior to discharging to springs. The isotopic data suggest that the sources of NO_3^- in the spring water are dominantly N-fertilizers. According to the isotopic evidence, there were few springs that showed probable influences of NO_3^- from animal wastes and/or septic effluent.

By measuring the $\delta^{15}N$ and $\delta^{18}O$ of the dissolved NO_3^- in the discharge water in a volcanic and/or sedimentary terrain which drain the studied watershed, it was possible to determine dominant sources of nitrate and whether geochemical processes such as denitrification, which does not occur within the investigated aquifer.

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ENVIRONMENTAL HAZARD RELATED TO ARSENIC IN JUJUY PROVINCE, ARGENTINA (THE NORTHERN ANDES VOLCANIC AREA)

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Numerous areas from NW Argentina present relevant concentration of As in the environment. This element is very toxic for human health and, unfortunately, extremely common both in sediments and in drinking waters from our target region. The metal content in waters ranges from 140 to 220 μg/L [1, 2], and thus represents a serious hazard for human health as demonstrated by the numerous arsenic poisoning related issues lesions, hyperpigmentation, hyperkeratosis and purplish gum affecting native population. These diseases may also sometimes lead to premature death.

This work will discuss As diffusion in the Puna region, situated in Jujuy Province. This area is 100 km^2 wide and it is characterized by many hydrothermal springs and fumarolics activity related to Tuzgle volcano (5486 m). The geological context is represented by Tuzgle Effusive Complex that subdivides the recent volcanic activity in three different facies: pyroclastic, dacitic-riodacitic and andesitic rocks. The study area includes three principal villages, Puesto Sey, Pastos Chicos and Huancar which lines from Tuzgle slopes to the valley. Arsenic migrates along the two main rivers in this region, *i.e.* Rio de Agua Castilla and Rio de Agua Caliente.

In order to map arsenic concentration in the studied area and to understand its origin and mobility, different kinds of samples were collected: rocks, soils, stream sediments and waters.

The mineralogical analyses performed *via* XRD indicate that rocks are mainly constituted by quartz, micas, feldspars and accessory minerals such as pyroxene and amphibole; soils are mainly constituted by quartz, micas, calcite, feldspars and organic matter as confirmed also *via* elemental and thermal analysis; stream sediments contain the same mineralogical main phases.

Some soil samples show peaks which can be attributed to As phases such as unnamed mineral [$Ca(VO)AsO_5$] and rock samples show a new As-Cs-Fe phases still under study.

Chemical analysis on rock, soil, stream sediment and water samples evidenced a very high concentrations of arsenic, ranging from 2 to 4150, from 28 to 890, from 11 to 625 and from 11 to 12880 mg/kg, respectively.

Soils frequently show high concentrations of potentially toxic elements, without however automatically implying a direct threat to human health. A more detailed piece of information on the potential mobility and bioavailability of arsenic in the studied area, was thus pursued by emplacing a standard sequential extraction BCR-SEP procedure.

The greatest arsenic amount (90%) is extracted in the first two steps (1. Exchangeable; 2. Reducible) and only the 4% remain in the residual phase. This demonstrates that arsenic is weakly linked to soil phases, easily migrates and thus is bioavailable.

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CHROMIUM ISOTOPES AND THE CYCLE OF HEXAVALENT CHROMIUM IN GROUNDWATERS FROM THE FRIULI-VENEZIA GIULIA HIGH PLAIN (ITALY)

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Chromium has received increasing attention over the last years, since in the trivalent form it is essential for animal and human nutrition, while in the hexavalent state it is toxic and mediates DNA cleavage becoming a prominent metal carcinogen. Even if intracellular Cr(VI) is metabolically reduced ultimately to Cr(III), and Cr(VI) is reduced by body fluids such as gastric juice, a high or prolonged Cr(VI) ingestion may overwhelm the body's reduction capacity. Chromium is sparingly soluble in its trivalent state in aqueous solution, with a strong tendency to adsorb to surfaces, while Cr(VI) forms highly soluble oxyanions. In natural environment systems, Fe(II), H_2S and organic compounds are important reductants for Cr(VI). Due to the natural tendency of chromium to reduction and adsorption in the trivalent form, it has been often supposed that Cr(VI) groundwater contamination remained confined to restricted areas with respect to the source zone, with limited effects on the environment and humans. However, a number of environmental interactions between Cr(III) and electron acceptor species can generate significant quantities of Cr(VI). These observations suggest that Cr(VI) contamination may extend widely in the subsurface, since in particular conditions polluted soils and sediments continue to leach chromium into ground waters. The reduced partition function ratios calculated from first principles suggest that measurable fractionation of the stable chromium isotopes is expected between Cr(III) and Cr(VI) in equilibrium exchange reactions, in addition to Rayleigh-type kinetic fractionations. In these processes the heavy isotopes preferentially partition into the highly oxidized species. Isotopic investigations focused on the reduction of the toxic Cr(VI) to Cr(III) demonstrated that this process preferentially reduces lighter Cr isotopes resulting in isotopically light Cr(III) and heavy Cr(VI). In addition, recent studies on natural systems as well as laboratory investigations have shown wide variations in the isotopic composition of the developing Cr(VI) during oxidation, and, even if the mechanism of this process has not been totally elucidated yet, isotopes become a powerful tool for investigating the whole Cr redox cycle. The High Friuli Plain underwent an early extensive Cr(VI) contamination from manufacturing, resulting in a plume of Cr(VI)-contaminated groundwaters. Some Cr(VI) was reduced to Cr(III) in the vadose zone of soils and in the sediment which constitute the aquifer by Cr(VI)-Fe(II) reactions. The Cr(III) produced during the natural Cr(VI) reduction remained bound to Fe and Mn oxyhydroxydes and in the carbonate fraction of the aquifer. Even if the industrial activity was made environmentally protective, over the period July-November, 1997 and January-November, 2000, new spikes of hexavalent chromium concentrations were measured in a number of wells and piezometers, reaching concentrations of 3400 μg/L. Since 2008, a renewal of Cr(VI) pollution has been documented, with concentrations in waters reaching 2000 μg/L.

The Cr isotopic data have shown both positive and negative δ^{53}Cr values. The positive delta values are interpreted as the isotopic evidence of Cr(VI) reduction along the flowpaths, since the ^{53}Cr/^{52}Cr of dissolved Cr(VI) increases progressively as the Cr(VI) is partially removed by reduction to Cr(III). The measured negative δ^{53}Cr values are interpreted as evidence of possible Cr(III) oxidation. In particular, these data indicate oxidation of the trivalent chromium originated by the pristine reduction of the anthropogenic Cr(VI), which accumulated onto sediments. Isotopic fractionation follows a Rayleigh distillation law, suggesting an important role of kinetic isotope effects during the oxidative process.

THE HOP WASTE-ROCK DUMP AT THE ROŞIA MONTANĂ GOLD MINE, ROMANIA: A MULTIDISCIPLINARY APPROACH FOR ITS KNOWLEDGE

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The 2.5 ha Hop waste-rock dump from the Roşia Montană gold mine (Romania) are investigated using mineralogical and geochemical analyses.

The Roşia Montană hydrothermal ore deposit is hosted in andesites and dacites of Neogene age piercing the prevolcanic sedimentary basement as breccia pipes. The volcanic and subvolcanic rocks show pervasive adularia alteration with a phyllic overprint, as well as local silicification and argillic alteration. They host polymetallic sulphides and Au-Ag-Te mineralization that are present in epithermal veins, mineralized phreatomagmatic breccias and stockworks. The ore deposit was mined both underground and in open pit for more than 2000 years. Intensive supergenic alteration due to AMD processes is testified by acid sulphate waters and by the precipitation of large amounts of secondary minerals.

The waste dumps show lithological heterogeneities even at the field scale mainly evidenced by differences in colour. Twenty-two samples were collected following a square cell grid. The particle size distribution was obtained by dry sieving. The mineralogy, petrography and geochemistry were studied by means of reflected- and transmitted-light optical microscopy, SEM-EDS, XRPD, XRF and ICP-AES analyses.

Samples were poorly sorted and could be classified as sandy gravel sediments. *p*H values show a wide variability (3-8) strictly related to sulphur and carbonate contents. Lithology, determined on the 250 to 125 mm grain-size, is heterogeneous, comprising the following rock types: variably metasomatized porphyritic dacites, andesites, sedimentary flyschoid rocks and polygenic breccias. These lithotypes contain: 1) AMD-producing sulphides (mainly pyrite with minor to trace sphalerite, chalcopyrite and marcasite) varying from << 1% up to 5%; 2) AMD-neutral silicates; 3) AMD-reducing carbonates (mainly calcite and dolomite with minor siderite and rodochrosite) that are generally trace to minor constituents, with the exception of few samples where they represent about 5% of the total.

Secondary mineral formed as consequence of AMD processes vary from 5 to 15%; they are mainly represented by Fe-oxyhydroxides and -oxides and occur as pseudomorphic replacement after primary sulphides, or as voids and fracture fillings. They are also present as oxidation halos within the groundmass and as tiny coatings that rim sulphide and silicate grains. Ephemeral sulphates recognized on field were not preserved in the samples. Metallic paragenesis is rich, comprising both heavy metals derived from the mineralisation (Cu, Zn, Ag, Pb) and metals from host rock (Rb, Sr, Zr).

Geochemical analyses performed on the different materials of the dump showed a general low content of metals (average of Ag 2 ppm, Cu 18 ppm, Pb 20 ppm, Zn 35 ppm, As 10 ppm).

Static test results, made in order to highlight AMD potential, allow to classify earth materials in two different types of which only one shows ANC/MPA ratio > 1. Kinetic test confirmed both the spatial heterogeneity of waste rocks and the scarce metal release in surficial waters.

BIO-GEOCHEMICAL FEATURES OF WILD FLORA GROWING ON WASTE DUMPS NEAR GROMO AND GANDELLINO ANCIENT MINE AREA (VALSERIANA, NORTHERN ITALY)

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Near Gromo and Gandellino villages, on both sides of the Valseriana in the Central Orobic Alps (Bergamo), several signs of historical mining activities are present. Since 11th Century the mines, exploited specifically for Fe and Ag, played an important role for the economic development of the valley. The deposits, whose ore mineralogy is dominated by sulphide, sulphosalts and carbonates were intensely exploited in the Middle age and abandoned in the early decades of 20th Century. The ore mineralization, represented by a complex and polyphase association of sulphides and sulphosalts containing Cu, Fe, Zn, Pb, Co, Ni, Ag, Sb, As with dominant chalcopyrite and tetrahedrite, is hosted in quartz breccia bodies that crop out along contacts between South Alpine basement and Permo-Triassic cover rocks.

Mining activities generated several waste rocks dumps that are source of dispersion of heavy metals in the environment. Some dumps are evident while other are hidden by wood vegetation. The dumps are colonized by metallophyte plant species, that are able to grow and reproduce on substrates characterised by high heavy metal contents.

Three dumps (Coren del Cucì, Pradel and Vedriol) were investigated in details in order to study the bio-geochemical features of wild flora growing on them. Representative quantities of aerial parts and roots of two tolerant plant species, *Calluna vulgaris* (15 samples) and *Dryopteris filix-mas* (20 samples), were collected on the dumps together with the corresponding rizosphera. Earth samples were collected from 15 to 40 cm depth and the fraction < 2 cm were separated for geochemical analyses. Trace elements concentrations (Pb, Zn, Co, Ni, Ag, Cu, Cd and As) in both earth and plant samples were determined by ICP-AES. Bioaccumulation Factor (BF) and Traslocation Factor (TF) were also calculated for plants data set.

In Earth materials all elements reach high level concentrations: if only averages are considered, Zn and Pb exceed 3500 and 3000 mg kg^{-1} respectively, while As reaches 860 mg kg^{-1}. The three sites show different element associations. High metal concentration values were founded also in soils far from dumps, upholding the presence of an anomalous area that must be carefully controlled and observed for its potential geochemical risk.

Calluna vulgaris shows several BF values > 1 displaying an evident tendency to accumulate metals, especially in roots. In aerial parts BF value for Cd reaches 2.90. Range of TF values uphold the behaviour of this species as a metal bio-accumulator, when present around mine sites [1]. In *Dryopteris filix-mas* metals concentrations are like to baseline values and slightly exceed toxic levels [2] only for As and Pb. BF values are low and < 1 for all elements. Evaluation of trace-element concentrations shows that these two species are not hyperaccumulators; however they are interesting for soil stabilization and could be use to re-establish a vegetative cover at sites where natural vegetation is scarce due to high metal concentrations, such as contaminated habitats. *Calluna vulgaris*, able to grow on acid, ore-characterized and nutrients-poor substrates by employing a metal exclusion-strategy, could be used to contaminated land phytostabilization.

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FLUORINE DISTRIBUTION IN LITHOLOGIES FROM THE ETHIOPIAN RIFT: INSIGHTS ON WATER-ROCK INTERACTION PROCESSES

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Recent papers on the geochemistry of natural water from the Main Ethiopian Rift (MER) suggest that their harmful enrichment in fluorine is mainly related to water rock interaction processes [1, 2]. This implies that natural waters flowing from the surrounding highlands progressively leach this toxic element from the MER volcanic rocks and fluvio-lacustrine sediments. This contribution presents bulk-rock and *in situ* chemical analyses of representative MER lithologies.

Fluorine is rarely analyzed in rocks and soils due to analytical problems. XRF determination is usually hampered for light elements, whereas ICP-MS techniques are precluded by difficulties in the ionization process and by spectral interferences.

Therefore fluorine is generally carried out by ion-chromatography or with potentiometric methods using Ion Selective Electrodes (ISE). However, both techniques analyze fluorine in solution and therefore rocks have to be properly dissolved. Obviously dissolution cannot be carried out by conventional acid attack using hydrofluoric acid, and has to be performed through alkali fusion. Accordingly, samples have been combined with proper fluxes (Na_2CO_3 + KNO_3) and heated at temperature of *ca.* 1000°C in order to be converted in an easily dissolvable glassy matrix. The sample solutions have been analyzed with an ISE NexSens WQ-FL together with calibrated standard solutions. Analyses were also repeated in the standard addition mode. The analyses have been subsequently corrected for the procedural blank, and then cross-checked with the analysis of a certified standard material (the soil GXR4) provided by the United States Geological Survey.

Investigation has been integrated with *in situ* analyses at the School of Geography, Geology and the Environment of Kingston University with a Zeiss EVO 50 scanning electron microscope in conjunction with an Oxford Instruments INCA microanalysis suite. Unfortunately, fluorine tends to migrate away from the heat of the electron beam during the analysis. This is a problem particularly for non-crystalline glassy materials. To minimize the problems, the analysis of fluorine was performed on WDS mode, after modification of the routine analytical conditions, *i.e.* defocusing the beam over a larger area, lowering the beam current, and by moving the beam over the sample.

This approach of study reveals that the local lithologies contain up to 0.3% of fluorine.

Results were integrated with leaching-tests on representative lithotypes simulating the water-rock interaction; powdered samples were mixed with water at a ratio of 1:5 (10 g/50ml), checking the composition of the leaching solutions after 15, 30, 90 days. Two distinct set of leaching experiments were carried out extracting solutes with a) deionized water; b) bicarbonate-calcic water analogous to the recharge water from the Ethiopian highlands. These experiments confirm the findings of Rango *et al.* [1, 2, 3] highlighting that the release of fluorine is more effective for some lacustrine sediments and often coupled with the mobilization of other potentially toxic elements (such as arsenic, molybdenum, uranium).

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DISTINGUISHING SOURCES AND TRACE ELEMENT TEMPORAL PATTERNS IN THE ECOSYSTEM DYNAMICS OF AN IRRIGATED CROP WITHIN THE RAVENNA COASTAL PLAIN

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The understanding of the sources and mechanisms of release and deposition of trace metals in the soil-water system is of the utmost importance in the development of quantitative models for contaminant transport and bio-geochemical cycling. In particular, in the case of agricultural land use and artificially-modified systems such as in irrigated crops, the balance between fertilizers additions, weathering reactions, secondary mineral formation, sorbing and leaching processes to the aqueous solutions may be strongly controlled by the artificial water recharge through canals and ditches. In this context, in addition to trace element analysis, isotopic investigations represent a key to the monitoring of elemental multiple sources and fluxes, including the rainfall rate, and provide valuable indications on the ecosystem dynamics.

The field site selected for this study encompasses the Ravenna coastal plain, and is limited by the Lamone and Montone rivers to the North-West and to the South, respectively, and the Adriatic Sea coast to the East. In the area, a network of artificial canals and ditches serves the water demand for plain irrigation, also representing an important input for the nearshore wetlands (Pialassa Baiona), a reaction zone between ground waters and sea water.

During summer, the water mass balance in the canal network is mostly controlled by the deliberate ingression of freshwaters from the Canale Emiliano Romagnolo (CER), where a pumping station takes water directly from the Po River.

In the present study, trace element and O-H-B-Sr isotopic analyses were performed on the land irrigation waters during two different surveys, in order to evaluate the possible impact on the ecosystem of waters differing in salinity.

The $\delta^{18}O$ and δD values indicate that, during winter, precipitations from the Apennine catchments represent the primary source of water recharge for the canal network, where water undergoes evaporation at different extents. A positive correlation is observed between *p*H and dissolved oxygen, which may be accounted for by variable CO_2 consumption during photosynthesis, probably controlled by a diurnal cycle. This process favours the *in situ* generation of colloidal particles due to the oxidative precipitation of ferric iron oxyhydroxides and probably small carbonate particles, which are able to adsorb trace metals on the surface and contribute to the ecosystem dynamics. The positive correlation between the iron content and dissolved oxygen indicates that not all particles flocculate, possibly facilitating the transport of metals and affecting their bio-availability and cycling. The Sr and O isotopic compositions positively correlate with the chloride content, probably originated from rainfall recharge. This is interpreted as the possible evidence of combined evaporation and selective increase of Cl^- concentration in residual water during infiltration through the soil, coupled with Sr isotopic exchanges with clay minerals increasing depth. During summer, the input of freshwater from the CER canal lowers the concentration of most ions and superimposes to the evaporation-precipitation-exchange cycle, possibly dispersing the mobile colloidal particles which could act as pollutant carriers and enhancing flocculation and precipitation, scavenging trace metals into the sediments. Evidence of mineral weathering and leaching processes are also inferred from boron isotopes.

SESSION 2.3

Geomaterials and their synthetic analogues

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NEAR ATOMIC IMAGES OF TWIN BOUNDARIES AND STACKING FAULTS IN A 15*R* SiC SAMPLE: TWIN LAW AND GROWTH MECHANISM

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In recent years, the study of the main polytypes of Silicon Carbide and their synthetic homologous have received renewed interest in the material science field due to the physical and electrical properties that enable SiC to be employed in high temperature, high power and high frequency electronic devices. The main focus of numerous previous studies has been the characterization of the grown-in structural defects that can damage device performance [1]. However, from a crystallographic point of view, several questions such as polytype stability, stacking fault and twinning formation, foreign polytype inclusions and interface between polytypes in syntactic coalescence, need still to be resolved taking into account the low stacking fault energy that characterizes the most important SiC polytypes. Hence, in this work an original contribute has been offered in analysing by means of HRTEM the local stacking microstructure of twinning, macrosteps on the twin boundaries and stacking faults found in a *15R* twin-related lamellae. HR images revealed that the perfect structure of 15*R* polytype (point group *R3m*), $(23)_3$ was locally interrupted by numerous adjoining stacking faults parallel to (0001) with stacking of the coupled (22) and (33) bilayers superimposed on the twin boundaries. Instead, the twin boundaries showed a zig-zag pattern (32) which passed to (23) through an isolated (33), 6*H* like, sequence. The electron diffraction patterns taken exactly above both the twin interfaces indicate classifying of the twin found in this study as a "friedelian" reticular merohedric twinning. However, two indistinguishable twin operations matched the observed features: a reflection through rational plane (0001) that generates the $\bar{6}$'*m*2' twin point group, and 180°-rotation around [0001] with composite symmetry *6*'*mm'*. Since individual Si and C atoms and even the SiC bilayer polarity could not be established from these HR images, the real twin law was deduced by taking into account that the coherent structural match at the interface. From a geometrical point of view, the stacking sequence will match that which was experimentally observed if a 180° rotation around [0001] is visualized in terms of only some bilayers rather than considering the rotation of the whole sequence of the 15*R* polytype. This type of operation produces the insertion of (33), a one cell thick 6*H* like sequence, while preserving the nearest-neighbour geometric relationship between adjacent SiC bilayers and their polarity. Similarly, the stacking faults can be explained by imaging a 180°-rotation around [0001] of a single bilayer along a slip plane. Hence, it follows that the formation of both, stacking faults and twins, should rely on similar processes. Actually, the growth mechanism was achieved by adding material to the self-perpetuating steps formed at the sites of a single or multiple cooperating screw dislocation and a lateral step flow [1]. The local increase of nitrogen dopant content in the growth surface modified the velocity of the steps, determining step bunching and the formation of macrosteps by the coalescence of multiple SiC growth steps. When the steps were too high, the danger of step bunching increased, macro-steps formed and local super-saturation changes occurred resulting in stacking fault and twinning formation.

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REMOVAL OF HYDROCARBONS FROM WATER BY ZEOLITE MORDENITE

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The pollution of ground water caused by organic contaminants as hydrocarbons and halogenated compounds represents an open problem due to its environmental impact.

The technology up to now available for the water treatment involves the use of active carbons, polymeric resins and granular iron porous barriers. Several studies have been performed on the use of zeolites in the adsorption of gaseous organic compounds. Only recently zeolites are employed in the treatment of contaminated water for the removal of hydrocarbons in low concentrations.

This work is a part of a wider project whose purpose is to study the interaction and mobility of ground water pollutants adsorbed in the zeolites pores. In this communication the adsorption of Methyl Tertiary Butyl Ether (MTBE) and toluene by zeolite mordenite is studied.

Organophylic mordenite (Si/Al ratio 200), was used in its H^+-form. Adsorption isotherm determination was obtained by using both batch and column (chromatography) experiments. Elution chromatography was performed both as pulse injection and in frontal analysis (FA) operational mode. TG and DTG analyses of the as-synthesized sample after adsorption of the contaminants were carried out under a constant flux of air. X-Ray Powder patterns were measured at room temperature on a Bruker D8 Advance diffractometer equipped with Sol-X detector. The presence of the organic inside the linear 12-member channels was revealed by unit cell parameter variations and structural deformations obtained by X-ray structure analyses carried out by Rietveld method on exhausted zeolite. The most evident deformation effects is the lowering of *Cmcm* real symmetry of the parent zeolite to $Cmc2_1$ after adsorption of toluene. Structural refinements and thermogravimetric analyses reveal that mordenite hosts in its bi-dimensional system about 4 molecules per unit cell of both toluene and MTBE. The fast, not-reversible and high adsorption of these hydrocarbons into organophylic mordenite zeolite makes this cheap and environmental friendly material a suitable candidate for the removal of these pollutants from water.

HIGH PRESSURE-INDUCED OVER-HYDRATION OF BOGGSITE

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The high pressure (HP) behavior of zeolites has been up to now studied using either "pore penetrating" (usually water-alcohol mixtures) [1] or non-penetrating P-transmitting media (usually silicon oil or glycerol) [2]. The former media are involved in the so-called pressure-induced hydration (PIH) phenomenon [3], which is characterized by the penetration of additional water molecules into the zeolite channels. On the basis of these experiments, it resulted that zeolites can undergo the following different effects: i) HP-induced structural modifications, without over-hydration; ii) PIH based on increasing occupancy of already existing water sites; iii) PIH accompanied by the onset of new water sites [1]. This over-hydration, and the consequent structural modifications, can in principle significantly modify the zeolite properties, opening possible new scenarios for their industrial applications.

The elastic behavior of the natural zeolite boggsite (Antarctica) [4, 5] is investigated by *in situ* HP synchrotron X-ray powder diffraction, using both silicon oil (s.o.) (P_{amb} - 9.3 GPa) and (16:3:1) methanol:ethanol:water mixture (m.e.w.), as non penetrating and penetrating P-transmitting medium, respectively. Neither X-ray amorphization nor phase transitions are observed in the investigated P-range (P_{amb} - 7.6 GPa), and the original unit cell parameters are recovered upon decompression. The lattice volume decreases in m.e.w. and s.o. are 11.5 and 13%, respectively. The Rietveld structural refinements of the powder patterns collected in m.e.w. reveal a significant over-hydration between 0.3 and 2.9 GPa, corresponding to the penetration of 13 additional water molecules and occurring without any cell volume expansion. In this P-range, the compressibility in m.e.w. is lower than in s.o., due to the entering of additional water molecules in the numerous partially occupied extra-framework sites, located in the large channels of boggsite. At higher P, the compressibility becomes similar for the two media. The reversibility of the HP-induced phenomena in boggiste compressed in m.e.w. is complete as far as the unit cell parameters are concerned. Also the original water content is restored upon pressure release. On the contrary, the structural deformations undergone by the framework are not completely reversible. Boggsite is highly compressible (K_0 = 31 and 37 GPa in s.o. and m.e.w., respectively), when compared with the other zeolites studied under HP. On the contrary, its structure is extremely rigid during dehydration, being the volume contraction less than 1.4% [6]. This behaviour was observed also for zeolite A [7] and bikitaite [8].

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MCALPINEITE FROM THE GAMBATESA MINE: A RE-INVESTIGATION OF CRYSTAL STRUCTURE AND CHEMICAL COMPOSITION

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A Te-bearing mineral association has been found in cherts from the Gambatesa manganese mine (Val Graveglia, Eastern Liguria, Italy) where manganese ore occurs near the bottom of chert sequences ("Diaspri di Monte Alpe Formation") overlaying Jurassic ophiolites. Tectono-metamorphic re-equilibration under prehnite-pumpellyite facies conditions affected ophiolites and their sedimentary covers producing complex veining processes. Te-bearing minerals have been found in a single occurrence in a quartz vein mainly as yellowish green earthy crusts mixed with emerald green aggregates (up to 50 μm), coatings on quartz crystals and black fragments of paratellurite (TeO_2). X-ray powder diffraction evidenced the presence of mcalpineite ($Cu_3TeO_6{\cdot}H_2O$), a rare mineral found at the McAlpine mine (type-locality; California, USA) and at the Centennial Eureka mine (Utah, USA., co-type locality). According to [1], this mineral crystallizes in the cubic system with a *P*-lattice (unknown space group) and its ideal formula may be referred to as $Cu_3TeO_6{\cdot}H_2O$. The presence of water in the holotype was mainly suggested by IR absorption spectra. In addition, X-ray analyses evidenced that the diffraction pattern of mcalpineite is identical to that of the synthetic Cu_3TeO_6 compound ($Ia\overline{3}$ space group), except for the presence of four medium to weak diffraction non indexable lines. As a result, they concluded that the crystal structure hosts single H_2O molecules inside structural voids causing a reduction of symmetry from an *I*- to a *P*-lattice. In this work, samples from Gambatesa mines have been investigated by means of a multi-analytical approach, including X-ray powder diffraction (XRPD), electron microprobe (SEM-EDS), micro-Raman and transmission electron microscope (TEM) in order to clarify the crystallochemical features of this rare mineral. The X-ray powder diffraction was performed on yellowish green earthy crusts hand picked from quartz coatings and on some hand picked emerald green aggregates of Gambatesa mine samples. XRPD results evidenced the presence of the four additional peaks reported by Roberts *et al.* [1]; however, a careful observation by TEM always evidenced a submicrometric intergrowth between two different Cu-Te compounds. The first (emerald green aggregates) represent a natural analogue of the synthetic Cu_3TeO_6, showing an identical single crystal electron diffraction; the other (yellowish green earthy crusts) is characterized by a similar Cu:Te ratio and exhibits poor quality SAED patterns in which is clearly detectable only the strongest of the four non indexable reflections ($d \approx 4.26$ Å) observed in the XRPD patterns. In addition, HRTEM images of both samples show that only the first sample evidenced a higher degree of crystallinity. Micro-Raman spectra of both the natural samples were compared to that of synthetic Cu_3TeO_6 and show no evidence for structural OH group: no signal is observed in the Raman shift range 3000-4000 cm^{-1}, where bands originated by structural OH groups, if present, should be located. Structural data obtained by refinement of the XRPD data are in quite good agreement with those of Cu_3TeO_6; moreover, bond valence sum (BVS) calculations indicate a small discrepancy between the expected and the calculated valences. A careful analysis of the crystal structure reveals that H_2O molecules could be hosted at 8*a* site and a corresponding XRPD pattern can be simulated. As a result no new diffraction line is detected, but only a re-arrangement of peak intensities is observed, thus ruling out the hypothesis that the unindexed peaks in the XRPD pattern of mcalpineite could be originated by H_2O molecules hosted in structural voids of the Cu_3TeO_6 structure.

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SOME EFFECTS ON SANITARY-WARE INDUCED BY VARYING FIRING TEMPERATURE AND TIME, AND QUARTZ GRAIN SIZE

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Sintering temperature, firing time and quartz grain size, coupled with the starting mineralogical and chemical composition, play an important role on the development of a ceramic body. In the present work the mineralogical composition of the green body is fixed and consists in 50% clay, 25% quartz and 25% feldspar. The other controlling parameters have been varied: two different series of quartz grain size (d_{50} = 50 μm and 17 μm) have been fired at three temperatures (1200, 1240, 1280°C) for five time intervals (0, 20, 40, 60, 80 minutes). Different analytical techniques have been performed in order to characterize the sanitary-ware body.

X-Ray Powder Diffraction has been adopted to determine the qualitative and quantitative phase composition using the Rietveld method [1, 2]. All samples contain quartz, mullite and an embedding glassy matrix, and their relative contents are affected by the parameters mentioned above. The increase of firing temperature and time causes the decrease of quartz content and, on the contrary, promotes the glass formation. Mullite is a structuring phase and has been observed to be modestly dependent on the process parameters [3, 4, 5, 6].

Scanning Electron Microscopy analyses have been performed in order to underline the influence of the varied parameters on the micro-structural evolution of the ceramic body. Two different kind of mullite (primary and secondary) have been observed and their distribution is influenced by the process parameters.

Furthermore, water absorption has been affected by the glassy matrix content and firing time: the higher the glass content, the lower the water absorption value. Only the samples with the finest quartz grain size and fired at 1280°C for at least 40 minutes fulfill the industrial required value of water absorbtion.

Finally thermal expansion data have been collected between 30-900°C showing three different field that are related to the quartz content and its α-β transition at 573°C [7]. The quartz content and thermal expansion coefficient (within quartz α stability field) are related to one another *via* a logarithmic correlation ($R > 0.9$). Moreover, the thermal expansion coefficient of the glassy matrix has been calculated on the basis of an optimization method, and is as large as $16.3\ 10^{-6}\ K^{-1}$, showing a relevant dependence on the quartz grain size.

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VOLASCHIOITE (IMA 2010-005) AND ASSOCIATED IRON SULPHATES FROM THE FORNOVOLASCO MINE (APUAN ALPS, TUSCANY, ITALY)

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Small magnetite-pyrite ore bodies had been exploited near Fornovolasco (Apuan Alps, Tuscany, Italy) since Middle Age. These ores are embedded in a metavolcanic-metasedimentary sequence (Scisti di Fornovolasco Fm.) or at the contact between this formation and lenses of dolomitic marbles of uncertain stratigraphic setting, known as "Grezzone metallifero". At Fornovolasco, veins and lenticular bodies of magnetite ± pyrite ± sphalerite ± pyrrhotite ± Fe hydroxides are hosted in these carbonatic lenses [1, 2]. Over 50 different mineralogical species have been described up to now [3, 4].

Well crystallized iron sulphates were identified in masses of altered pyrite in the old tunnels of the Fornovolasco mine. The systematic study of this occurrence allowed the identification of a new mineral species, volaschioite (IMA 2010-005), ideally $Fe^{3+}_4(SO_4)O_2(OH)_6 \cdot 2H_2O$. It occurs as radial aggregates of bladed crystals, elongated on [010], up to 50 μm long and less than 5 μm across. Volaschioite is monoclinic, with a 16.085(2), b 3.054(1), c 10.929(2) Å, β 93.78(1)°, $Z = 2$, space group $C2/m$. It is the natural analogue of the "phase B" synthesized by [5].

Because of its very small size, intensity data were collected at the XRD1 beamline of the Elettra synchrotron facility (Basovizza, Trieste, Italy). The crystal structure was determined and refined up to $R = 7.8\%$ for 219 reflections with $F_o > 4\sigma(F_o)$. The structure of volaschioite can be described as formed by ribbons of edge-sharing Fe-octahedra running along [010], linked together by corner-sharing to form wavy layers. Half occupied [SO_4] tetrahedra are grasped on both sides of the layers, and H_2O molecules statistically occur in two sites between the octahedral layers, forming hydrogen bonds with the oxygen atoms of the layers A regular alternation of [SO_4] groups and H_2O molecules takes likely place along the **b** direction, because it is impossible to locate two [SO_4] groups at distance of only ~ 3 Å. Such ordered sequence should double the b parameter, with the occurrence of additional superstructure reflections. Actually, only continuous and very weak streaks were detected in the diffraction pattern, indicating that a long-range ordering of SO_4 groups and H_2O molecules does not realize.

Volaschioite is an oxy-hydroxy hydrated Fe^{3+}-sulphate. Pyrite alteration takes place with the first appearance of melanterite, $Fe^{2+}[SO_4] \cdot 7H_2O$; in some cases, rare voltaite crystals, $KFe^{2+}_5Fe^{3+}_3Al[SO_4]_{12} \cdot 18H_2O$, are present. In the outer portion of the altered masses, römerite, $Fe^{2+}Fe^{3+}_2[SO_4]_4 \cdot 14H_2O$, and copiapite, $Fe^{2+}Fe^{3+}_4[SO_4]_6(OH)_2 \cdot 20H_2O$, appears. These phases show both oxidation states of Fe and are more hydrated than melanterite. In the periphery of the pyrite altered masses, in contact with air, Fe^{3+}-phases are predominant: goethite and fibroferrite, $Fe^{3+}(SO_4)(OH) \cdot 5H_2O$, are very common. Volaschioite was limited in a very restricted area, under the fibroferrite layer.

This mineralogical sequence is a typical product of pyrite alteration in an oxidant environment, as described by [6]: Fe^{2+} sulphates are the first phases that crystallize, followed by hydrogen-sulphates, sulphates, and finally oxy- and hydroxy-sulphates of Fe^{3+}.

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HT-STUDY OF CARBOBYSTRITE, $Na_8[Al_6Si_6O_{24}](CO_3)\cdot 4H_2O$

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Cancrinite group minerals, $[(Na,K)_6(CO_3,SO_4)][(Na,Ca)_2(H_2O,Cl)_2][Al_6Si_6O_{24}]$, are modular microporous minerals, which are built up by a single module and may present increasing complexity structures depending on the number of layers and on the stacking sequence [1]. Few studies on the thermal behavior of cancrinite and related phases are available. These have been undertaken up to date only on AB... stacking sequences: cancrinite [2, 3, 4], pitiglianoite [1, 5], davyne and microsommite [6], and also very recently cancrisilite [4]. Non linear increase of cell parameters and eventual discontinuities have been described. Some have been related to dehydration [1, 5], structure rearrangement [3], or even displacive phase transitions [6]. It is evident that these microporous materials have a non trivial thermal behaviour and that additional studies may help to seed light.

The next step in structural complexity of cancrinite group minerals is represented by bystrite $[(Na,K)_7Ca][Al_6Si_6O_{24}](S^{2-})_{1.5}\cdot H_2O$ (ABAC..., *P*31*c*) [7]. However, from a comparative point of view the presence of S^{2-} anions characteristic of bystrite makes difficult comparison with AB... sequence minerals. Bystrite has two LOSOD cages, and two □ (cancrinite) cages per unit cell. Recently a new mineral of the cancrinite group has been described: carbobystrite, ideally $Na_8[Al_6Si_6O_{24}](CO_3)\cdot 4H_2O$ [8], which is isostructural with bystrite. Its compositions is closely related to cancrinite - having (CO_3) groups and H_2O groups in the LOSOD cages and H_2O groups in the □ cages - which makes it a perfect candidate for comparative work. Carbobystrite shows also $Na_{-1}K$ substitution in the LOSOD cages.

A single crystal of carboystrite was studied by *in situ* high-T X-ray diffraction up to 525°C. Lattice parameters were collected each 25°C steps and complete intensity data collections were performed at 25, 125, 225, 325, and 425°C and then at room T after cooling down. Upon heating, the cell parameters increased in the range 25-300°C, with the *a* lattice parameter showing a very faint decrease at 75°C. After a couple of hours at 300°C the structure started to collapse of a 5‰ in volume. Upon heating, the collapse progress down to *ca.* 1%. Structure refinements show the starting of a dehydration reaction with loss of half a H_2O group in the channels and migration of K from the LOSOD cages into the □ cages, with concomitant inverse migration of Na (as already observed in pitiglianoite by [5]). The process keeps going slowly and progressively involves also the total release of H_2O from the □ cages. At 525°C the crystal broke in smaller pieces compromising the collection of intensity data. Thus only lattice parameters were collected on cooling. Structure refinement of the larger fragment on a Bruker CCD at room-T reveals that the cracking of the crystal is due to the completion of dehydration (in agreement to what reported by [9] in pitiglianoite) by release of the remaining H_2O groups from the LOSOD cages. No loss of (CO_3) groups at the LOSOD cages is registered. After dehydration, Na and K in LOSOD cages occupy slightly different position at the top and lower windows formed by the 6-membered rings of tetrahedral and perpendicular to [001], showing an off-plane position. Same behaviour is observed in the □ cages.

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NEW DATA ON ILMAJOKITE

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Ilmajokite, ideally $Na_{10-x}(Ce,Ba)_xTi_5Si_{14}O_{22}(OH)_{44}$, is a rare mineral, which occurs as granular deposits, crusts, and brushes of crystals up to 2 mm long on the walls of cavities in the central natrolitic zone of pegmatites in the Lovozero Tundra, Kola Peninsula, near the valley of the Ilmajok River. It has a bright yellow colour but turns turbid and white when drying. It is optically biaxial positive and has oblique cleavage.

It was described by [1, 2] being the solely data available up to now. These authors described the mineral as probably monoclinic with $a \sim 23$, $b \sim 24.4$, $c \sim 37$ Å, while Anthony *et al.* [3] report a = 39.80(4), b = not determined, c = 29.83(5) Å, β = 96°38’, *C*2/*c* or *Cc*. Up to now the structure of ilmajokite is unknown. Although it occurs as apparently crystalline material, it almost does not show any diffraction when powdered [1]. In order to obtain some diffraction information, Bussen *et al.* [1] glued several single crystals but the diffraction at high angles did remain very weak. Ilmajokite has a large quantity of H_2O (24.54 wt.% [1]), which releases on heating losing up to 12.7% at 175°C, although a 6.5% is still retained at 320°C. Water release starts as low as 60°C but it is not complete until 760°C [1]. H speciation was determined by IR finding broad absorptions at 1618 and 3389-2889 cm^{-1} [1].

We collected diffraction data on a single crystal (0.10×0.08×0.04 mm) of ilmajokite provided by E. Semenov in 2004. We performed a data collection at room temperature by means of CCD-Oxford single-crystal diffractometers using both molybdenum and copper radiation. Diffraction experiments yielded very weak data and no diffraction over 3 Å^{-1}. Cell refinement yielded a *C*-centered monoclinic cell with a = 35.774(4), b = 27.407(3), c = 31.131(5) Å, β = 95.66(1)°, V = 30374(7) Å^3. R_{int} was very high (~ 32%) and no model could be obtained from these data. We performed therefore a low-temperature data collection at 125 K using a Bruker-AXS diffractometer with a SMART CCD detector and an OXFORD Cryostream 600 low temperature device. Diffraction was slightly enhanced up to *ca.* 2.8 Å^{-1}. Cell refinement confirmed a *C*-centered monoclinic cell with a = 35.32(16), b = 26.93(12), c = 30.68(14) Å, β = 95.84(2)°, V = 29034(403) Å^3. Internal agreement factor integrating up to 2.8 Å^{-1} was better (~ 17%) but still very high. We observed a volume reduction of up to a 4.5%, being more significant in the shorter lattice value (up to 1.8%), while the monoclinic angle shows a very faint increment.

Structure solution by direct methods and charge flipping methods [4] have not been successful. Thus, the structure solution of this mineral awaits further experiments.

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MINERALS AND RELATED ARTIFICIAL MATERIALS: THE CASE OF DIASPORE

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Diaspore, AlO(OH), is a relatively common mineral in metamorphic bauxite deposits [1]. Aluminium cations are located in octahedrically coordinated interstices between significantly distorted hexagonal oxygen layers. Diaspore possess orthorhombic symmetry with the *Pbmn* space group and lattice parameters $a = 4.40$, $b = 9.43$, $c = 2.84$ Å [2], hardness 6.5-7. Diaspore in nature can be considered as one of the precursors of crystalline alumina usually named corundum (α-Al_2O_3). Its chemical and physical behaviour, in particular thermal treatment leading to corundum was investigated by several authors [3, 4].

The aim of the present study is to revise previous experimental works in order to assess the dependence of the electronic, structural and mechanical properties on the conditions of the heating process. The rough material for the present work is gem-quality diaspore where is geologically found in the Sundikendagı diasporitic metabauxite mine (Milas-Mugla,Turkey) [5], which is the one deposit all over the world [6, 7].

The samples were calcined at different temperature (between 600 and 1000°C) and for different heating times, and treated samples were examined by scanning electron microscope (SEM), X-ray powder diffraction (XRD), low-temperature photoluminescence (PL) spectroscopy and measurement of mechanical properties, among these specific gravity, in order to assess the transition mechanism from diaspore to corundum and the properties of each product. In particular, PL and XRD patterns show that the transformation process into corundum of some treated samples is very advanced. The SEM pictures show a dense network of fractures leading to crystalline domains having the size of hundreds of nanometers. The specific gravity of different treated samples is in general markedly lower than that of both monocrystalline corundum (4.0) and diaspore (3.4) [8]. The patterns of gem-quality diaspore minerals from Turkey show slight differences compared to common diaspore minerals found in other countries of the world. On the other hand, the total mass loss percentage was found to be less than 14%, in contrast to those of other common diaspores (up to 17%). This may also be related to mineral inclusions. Further studies are in progress.

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Co-DOPED HARDYSTONITE, $Ca_2(Zn,Co)Si_2O_7$, A NEW BLUE CERAMIC PIGMENT

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Raising cost, limited reserves and toxicity make a pressing need to reduce the consumption of cobalt in the ceramic industry, trying to improve efficiency and sustainability of pigments [1, 2].

A novel blue colorant, based on the melilite structure, has been developed by searching for a ceramic pigment stable in very aggressive media, like the calcium- and zinc-rich glazes used in porous tiles (stoneware and monoporosa). Melilite-like compound crystallizes in the tetragonal system (space group $P\bar{4}2_1m$), with general formula $X_2T^1T^2{}_2A_7$, where X is a typically a large monovalent to trivalent cation (*e.g.* Na^+, Ca^{2+}, Y^{3+}), T^1 and T^2 are small divalent to tetravalent cations (*e.g.* Zn^{2+}, Mg^{2+}, Al^{3+} in T^1; Si^{4+}, Al^{3+} in T^2); and A is O^{2-}, but also F^-, S^{2-} or N^{3-}. Its structure is characterized by layers of linked tetrahedra ($T^2{}_2O_7$ dimers and four-fold coordinated T^1 cations) connected by X cations in a distorted eight-coordinated antiprismatic site. Tetrahedral site T^1 represents a quasi-regular environment with 4 identical metal-oxygen lengths, but one pair of O-M-O angles different from the other two [3].

Hardystonite, $Ca_2ZnSi_2O_7$, was selected as a typical melilite-like compound which has just one four-fold crystallographic site where Co^{2+} ions can be accommodated, thus ensuring its unrivalled blue color.

Five samples ($Ca_2Zn_{1-x}Co_xSi_2O_7$ with $x = 0.05$, 0.1, 0.2, 0.3 and 0.4) were prepared by solid state synthesis in industrial-like conditions (~ 95% yield) and characterized by XRD, DRS, SEM-EDS and technological testing. Increasing cobalt doping gives rise to a gradual expansion of the hardystonite unit cell, unexpected on the basis of Zn^{2+} and Co^{2+} ionic radii, attributed to a change of the covalent character of M-O bonding. Optical spectra are dominated by the strong absorption bands of Co^{2+} in tetrahedral coordination (crystal field strength Dq = 421 cm^{-1}, Racah B parameter = 793 cm^{-1}).

The best compromise between cobalt concentration and optical response was found to be around $x = 0.3$. The hardystonite pigment bestows a deep blue colour on glazes and glassy coatings, withstanding to aggressive media rich in CaO and ZnO better than industrial blue pigments (cobalt aluminate, spinel) with similar colour efficiency than industrial blue dyes (cobalt silicate, olivine) but with the advantage to avoid specking defects of highly staining colorants.

Furthermore, exploring the wide range of isomorphic substitutions allowed in the melilite structure, a comparison through a set of compounds with a fixed cobalt fraction (Co^{2+} = 0.3 apfu) in the T^1 site ($Ca_2MgSi_2O_7$, $Sr_2MgSi_2O_7$, $Ba_2MgSi_2O_7$, and $Sr_2ZnSi_2O_7$) was attempted.

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INTRODUCTIVE STUDY ON THE INTERACTIONS OF HYDROHCLORIDE TETRACYCLINE WITH EXPANDABLE CLAY MINERALS

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Most of the antibiotics are poorly absorbed by human and animals after intake, with about 25-75% of added compounds leaving the organisms unaltered *via* feces or urine [1]. Because of the dispersion of manure and sewage sludge in fields as fertilizers, antibiotics have the potential to reach soil and aquatic environments. Compared to other well-known xenobiotics such as pesticides, PAHs (Polycyclic Aromatic Hydrocarbons), and PCBs (Polychlorinated biphenyls), there is very little information available on the fate and transformation of antibiotics in soil/water environments. Currently, the primary concern over the use of antibiotics in concentrated animal feeding operations and land application of manure is the development and dissemination of antibiotic-resistant pathogens in the environment [2].

Tetracyclines (TCs) are a group of broad-spectrum antibiotics that have been used for more than 50 years for the treatment of bacterial infections in both humans and animals. The main applications of tetracyclines in animal husbandry are for preventative treatment of bacterial infections and to increase growth rates. TCs are poorly absorbed in the digestive tract with 50-80% excreted unmetabolized. The high polarity (*e.g.*, log K_{ow}) -1.97 to -0.47 for tetracycline, *p*H dependent and aqueous solubility (0.52-117 mM) for tetracycline, can enhance their environmental mobility. Tetracyclines have been detected in soils, surface waters, groundwater samples collected near waste and wastewater lagoons [3].

Sorption studies for TCs are limited and have focused primarily on isolated clays [4, 5], organo-clays, or humic materials. From these studies, cation exchange comes forth as the primary sorption mechanism responsible for sorption of TCs especially under acidic conditions. The aim of this preliminary study is investigate what kind of interactions are possible establish between Hydrohcloride Chlortetracycline (CTC) and K^+ and Ca^{2+} exchanged Wyoming smectite (Swy-2) after the adsorption in aqueous solution as well as to understand the fate of CTC in the soil. X-ray diffraction reveals that CTC specie can intercalate into the interlayer space of smectites as deduced from the change in the basal spacing value, from 11.98 to 17.13 Å into K-Swy-2 and from 14.93 to 16.27 Å into Ca-Swy-2. The FTIR spectroscopy shows that the spectra of the K and Ca-Swy-2 change upon the adsorption of CTC, suggesting important smectite-CTC interaction in the adsorbed state. Batch experiment carry out with Freundlich modeling reveal that there is a stronger adsorption and affinity of CTC on the Ca-Swy-2 than K-SWy-2.

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RECYCLING OF THE PRODUCT OF THERMAL INERTIZATION OF CEMENT-ASBESTOS FOR THE PRODUCTION OF CONCRETE

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Recycling of secondary raw materials is becoming a priority of wastes handling in the countries of the European community. Secondary raw materials can be used to develop interesting new classes of materials of industrial importance and geomaterials. A potentially important secondary raw material is the product of the thermal transformation of cement-asbestos, produced by prolonged annealing at 1200-1300°C. The product is chemically comparable to a Mg-rich clinker. Previous works have demonstrated the efficiency of the transformation process [1, 2]. The challenge is now to find useful applications of the transformation product as secondary raw material. This contribution presents the successful recycling of application of the product of the thermal transformation of cement-asbestos (labeled KRY·AS) for the production of commercial concretes. KRY·AS was added in high percentages (0-20 wt.%) to commercial mixtures for the production of concretes without compromising the technological properties of the final product. Fig. 1 shows for example the compressive strength which is nearly identical for the standard and the 20 wt.% KRY·AS-diluted mixture at 90 days.

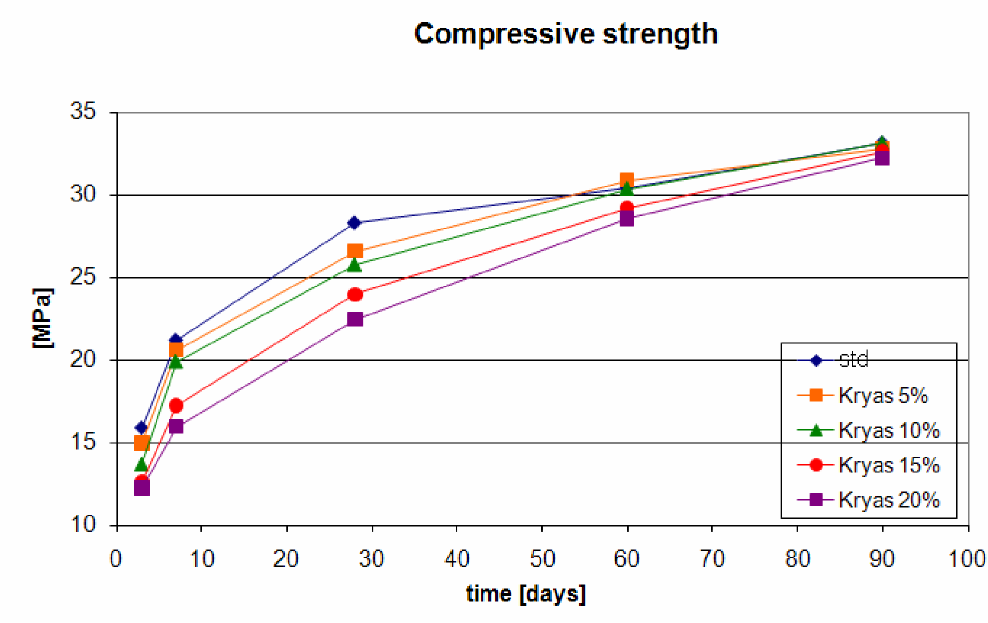

Fig. 1. The compressive strength of the concrete mixtures obtained with KRY·AS.

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SELF-PROPAGATING HIGH TEMPERATURE SYNTHESIS IN ASBESTOS INERTIZATION: A FAST AND EFFECTIVE APPROACH

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In 1992, mining, importation, exportation, production and marketing of asbestos-bearing materials was forbidden in Italy by Decree N° 25 - 27/03/1992, but environmental and health problems related with asbestos waste are still in evidence.

Several methods have been proposed for the inertization of asbestos bearing materials, some of which represent a temporary solution. In other cases, inertization by chemical treatments results dangerous for human health because of the use of toxic substances. Furthermore D.M. 29/07/2004 N° 248 established that treatments should lead to a total crystal - chemical transformation of asbestos in order to allow their recycle as raw materials or make them fit to be disposed.

The Italian patent n. GE2010A000032 (*Processo di inertizzazione di fibre di amianto con modalità di sintesi combustiva "SHS"*) covers a method to obtain chrysotile breakdown by using self-propagating high temperature synthesis (SHS). This technique has been already assessed to synthesize several materials as ceramic, metallic and composite phases by highly exothermic reactions [1].

In the inertization of chrysotile, we used a natural clinochrysotile from a serpentinite vein from the Petronio Valley (Eastern Liguria, Sestri Levante - Genova), preventively characterized by optical microscopy, powder XRD analysis and by electron scanning microscope and *in situ* microanalysis. Chrysotile was mixed with reactants in stoichiometric amounts, according to the following reactions: $Mg_3Si_2O_5(OH)_4 + Fe_2O_3 + 3\ Mg \rightarrow 2\ Mg_2SiO_4 + 2MgO + 2Fe + 2H_2O$ (ΔH_r = -846.43 kJ/mol). Other compositions were studied to investigate the reaction feasibility to proceed also in non-stoichiometric conditions. The maximum chrysotile amount in the mixture to allow the reaction with SHS modality was therefore experimented.

The reaction between ferric oxide and Mg is highly exothermic and provides the necessary T and heat capacity to induce chrysotile breakdown in few seconds. A weight loss of about 10-12% is observed after the treatment due to the water loss by chrysotile dehydroxilation according to the reaction stoichiometry. The escape of volatiles is evidenced also by vortex-texture in the final products. The crystalline phases detected in the products are fosterite, periclase and metallic Fe. Olivine compositions range between Fo_{99-90}. The total disappearance of fibrous phases was evidenced under high magnification.

The maximum temperature reached during reactions is 1718 K, with 45% chrysotile amount, for a corresponding average rate of propagation of 1.9 mm/sec. The average temperature and rate with stoichiometric amount of reactants are 1476 K and 1.4 mm/sec respectively.

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THERMAL BEHAVIOUR OF BORON-ZSM-5

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The isomorphous substitution of Al and/or Si by other tri- and tetravalent metal ions is generally considered a tool for tailoring the catalytic properties of zeolites. A large number of elements have been incorporated into the framework, but only a few (B, Ga, Fe, V and Ti) have been tested, leading to the formation of microporous materials with catalytic properties that are different from those of the parent aluminosilicates. In particular, boron substituted zeolites (borosilicates) display lower acidic strength, which is useful when mild conditions are required (*e.g.* toluene alkylation with ethanol, propylene oligomerization and the conversion of methanol [1, 2, 3]).

In this work the influence of boron on the thermal behaviour of ZSM-5 was studied by *in situ* time-resolved powder diffraction (GILDA, ESRF Grenoble).

A B-ZSM-5 (B-MFI) sample ($Na_2[Si_{82}B_{14}O_{192}]\cdot 6EN\cdot nH_2O$, s.g. *Pnma*) synthesized by ENI S.p.A. in the presence of ethylenediamine (EN) was selected for this study.

The evolution of the B-ZSM-5 structural features was followed through full profile Rietveld refinements in the temperature range 25-900°C.

TG and DTG analyses of the as-synthesized samples (heating rate of 5°C/min) were carried out from 25 to 900°C under a constant flux of air using a STA 409 PC LUXX® - Netzch.

XRD diffraction patterns indicated that B-MFI collapses at about 770°C and at 800°C is converted into β-cristobalite [4]. All the unit-cell parameters increase with increasing temperatures up to the breakdown temperature. This increase is more evident in the 300-500°C temperature range where the expulsion of the template occurs. This result completely disagrees with the case of silicalites heated after calcination, where after a slight increase in volume, up to 100-150°C, negative thermal expansion is evident [5]. This fact is also present when a Si-fraction is substituted by Zr or Fe [5, 6]. In the case of as-synthesized silicalites, the removal of the organic template leads to an overall contraction of the orthorhombic lattice [7].

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THE *C*2/*c*-*P*2_1/*c* PHASE TRANSITION ALONG THE JOIN DIOPSIDE-ENSTATITE: A RAMAN INVESTIGATION

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Raman spectroscopy provides a useful tool to investigate in a non destructive manner the mineral phases. Analysis of the spectra can provide compositional information that complete those from microprobe analysis, and probes changes with composition at a local scale. Among mineral phases pyroxenes are of interest in planetary and cultural heritage studies [1, 2], but the changes due to the *C*2/*c*-*P*2_1/*c* phase transition from Ca-rich and Ca-poor quadrilateral pyroxenes are yet not investigated. A Raman analysis on several synthetic samples along the join diopside-enstatite (Di-En, $CaMgSi_2O_6$-$Mg_2Si_2O_6$), previously investigated by X-ray diffraction and transmission electron microscopy [3, 4], was therefore undertaken.

Peak splitting was observed between $Di_{40}En_{60}$ and $Di_{55}En_{45}$ in some, but not all modes, and was interpreted as evidence for the transition from the *C*2/*c* to the *P*2_1/*c* structure. Preliminary analysis according to Landau theory of the splitting on the peak at 670 cm^{-1} shows a first order behaviour with transition composition $Di_{52}En_{48}$.

Structural changes through the transition and within each phase of the join can be related to the observed Raman peaks with reference to recent quantum-mechanical simulations on diopside [5]. As an example the peak at 1011 cm^{-1}, ascribed to Si-O tetrahedral stretching [5], splits in two peaks at the transition, one of them can be related to the SiA-O bonding, with lower average bond length and higher Raman frequencies, and the other to SiB-O tetrahedral bonds.

Positional disorder within the M2 site was revealed by the amplitude of the peak at 330 cm^{-1}, that does not split at the transition and is related to M2-O motion. The amplitude of the peak increases along the join, doubling between diopside and intermediate compositions, with a steady increase also in homogeneous *C*2/*c* pyroxenes as Ca decreases; from intermediate compositions to that of the iron free pigeonite $Di_{15}En_{85}$ the peak amplitude decreases instead. The behaviour is ascribed to Ca-Mg positional splitting, as demonstrated by the lower peak amplitude as composition approaches the end members.

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THE POTENTIAL REACTIVITY IN TERMS OF ASR OF SOME ITALIAN AGGREGATES

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The Alkali-Silica Reaction (ASR) severely impairs the performance of concrete structures [1], affecting material durability and strength and hence structural service life.

ASR can be described as a chemical reaction between alkalis Na and/or K supplied by the cement paste with quartz (SiO_2) in certain susceptible aggregate lithologies [2], producing an amorphous, hygroscopic and hydraulic silica gel. This gel expands after reaction with water, inducing cracks and fractures in the surrounding concrete [3]. ASR damage leads to material decay and is difficult to repair as it presents an intrinsic quality of concrete made with alkali-reactive aggregate material. As a result, a structure's designed service life is significantly reduced, occasionally damaged structures may potentially threaten public safety and security, and the common tax payer is saddled up with a substantial surcharge.

To prevent ASR deterioration, global and local legislation defines limits for the alkali content in the cement, as well as recommends test procedures to evaluate the potential alkali-expansivity of the aggregates in concrete structures. Different approaches are used to evaluate the potential alkali-aggregate reactivity in concrete long term damage. For instance, petrographical guideline (*i.e.* RILEM AAR-1) [4] and expansion testing (*i.e.* RILEM AAR-2) [5] are commonly employed. The ASR potential of aggregate largely depends on the nature and polymorphism of the silica present, with reactivity gradually decreasing from opal, chalcedony and chert to quartz. Apparently, SiO_2 species containing structural imperfections (*e.g.* atomic substitutions, grain boundaries, dislocations, twin boundaries, planar faults, point defects) seem more prone to undesired dissolution and silica-gel formation in concrete.

This paper presents data on some reactive aggregates from Italy, generally considered as important source for Italian building and construction. Their potential alkali reactivity in terms of ASR have been investigated by means of expansion testing according to RILEM AAR-2 as well as of XRD analysis, including crystallinity indices determined conform the method of Murata & Norman [6] and microstructural analysis using full diffraction profiles.

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THE INVESTIGATION OF MORTARS AFFECTED BY ALKALI-SILICA REACTION BY MEANS OF SYNCHROTRON X-RAY MICROTOMOGRAPHY AND MICRO XRD-XRF

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Recently, the investigations of concretes affected by Alkali-Silica Reaction (ASR), as a weathering phenomena in building materials, has attracted much attention. The ASR consists of chemical reactions between silica aggregate affected by different degrees of structural disorder (*i.e.* opal, chalcedony, chert, *etc*.) and the alkali and hydroxide ions in the pore water of concrete [1, 2, 3]. The ASR results in the precipitation of a gelatinous product (CKSH), micrometric in size, rich in silica, calcium-, sodium-, potassium-oxides and water [4] that surrounds the aggregate. The expansion of ASR gels, because of the osmotic pressure due to the imbibition of pore solution, promotes cracks and fractures through concretes [1].

The ASR mechanism is described by different models [5, 6] but its chemistry remains poorly understood. There has been debate as to which mechanism is dominant in the gel growth at the cement-aggregate interface. Hence, several authors assume that ASR products are gel whereas others report a "crystallised gel" [7], but this is still an open debate.

Up to now, no studies have been performed to investigate what happens at the boundaries between aggregate and cement paste and there has also been debate on whether ASR weathering products have an amorphous or crystalline structure.

In the present study concretes affected by ASR and sampled from a Brazilian dam have been investigated by non conventional analytical techniques. The aim of the present research was double-fold: on one side we have investigated the mechanisms involved in the Alkali-Silica Reaction, supplying thus a major step in the understanding of the ASR product formation. In particular, synchrotron microfocus X-ray diffraction experiments were performed at beamline ID13 of the European Synchrotron Radiation Facilities to gather information on the ASR rim and its surrounds. Furthermore, X-ray microfluorescence analyses allowed to obtain the chemical composition of the ASR gel. On the other hand, we have clarified the mechanism involved in the ASR growth by means of synchrotron X-ray microtomography at SYRMEP beamline of Elettra; the experiments allow to obtain the volume distribution of the microstructural features such as micrometric cracks, aggregate dissolution, *etc.* in ASR-weathered concretes.

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KINETIC STUDY OF MULLITE GROWTH IN SANITARY-WARE PRODUCTION BY *IN SITU* HT-XRPD. THE INFLUENCE OF THE FILLER/FLUX RATIO

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The understanding of the mechanisms controlling the kinetic of the mullite formation has important implications both for industrial processes, since mullite is a major constituent in a variety of ceramic materials, and for the classification and evolution of high-grade temperature rocks in metamorphic petrogenetic reactions [1]. In the former case, a full knowledge of the mullitisation reaction is a key to design or improve industrial processes for them to yield high mechanical performances final products. The microstructure of a fired body, *i.e.* the spatial distribution of its constituent phases and the interconnections between them, are strictly related to its macroscopic properties, such as total porosity, shrinkage and bending strength [2]. In particular, mullite seems to be material to strength enhancement, according to the "mullite hypothesis" that relies upon the interlocking of the fine needle-like crystals characteristic of this phase's habit. Many studies have been carried out with the aim of providing models for the mullite growth mechanism, often paying attention to the role of the precursor raw materials, and to the differences observed in terms of crystallization temperature, chemical composition and crystal structure of the resulting mullite. Gualtieri *et al.* [3] report a study on mullite crystallisation from two kaolinites, thus exploring the influence of the crystallinity degree of the starting phases on the activation energy of the reaction.

The aim of the present work is to investigate by *in situ* high temperature X-ray powder diffraction (HT-XRPD) the phase transformations and mullite formation kinetics as a function of the filler/flux ratio, starting from multi-phase precursor systems constituted by kaolinite (clay component), quartz (filler) and feldspar (flux), so as to mimic compositions consistent with those of the industrial practice for sanitary-ware. In such a view, we have explored three filler/flux ratios to shed light on how they affect the mullite's kinetic parameters. In order to simplify the complexity of the system on study, we have chosen to restrict our attention to pure kaolinite instead of a kaolinite-clay blend, commonly used in the industrial practise. To our knowledge, only one kinetic study on the mullite growth in porcelain stoneware has hitherto been performed, by means of thermal analysis [4]. The results show that the content of feldspar boosts the formation of mullite as proven by the apparent activation energy values determined, ranging from 394 to 1111 kJ/mol, and giving a $dE_a/dx_{\mathrm{feldspar}} \sim -23$ kJ/mol/wt (x_{feldspar}= feldspar weight fraction). The mullitisation temperature has also been observed to depend on the Na-feldspar content, inasmuch as the sample bearing the smallest amount of feldspar flux exhibits a mullite growth onset between 1100 and 1150°C, that is at a temperature about 50 degrees higher than the one observed in the richer blends. The mullitisation kinetic process is described as a one-mechanism transformation, satisfactorily formalised by a nucleation according to the Avrami-Erofeyev equation.

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EXPERIMENTAL STUDIES ON *EX SITU* CARBONATION OF SERPENTINITES

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In order to investigate possible paths of *ex situ* carbonation of serpentinitic rocks and to establish optimal working conditions, several experimental runs were carried out at different P-T conditions in the framework of the 2010-2011 Project "Zero-Emission Biogas Use", ZEBU, funded by the Tuscany Region.

A preliminary geological-petrographical work allowed to select two serpentinite samples, named VB-1, mainly consisting of lizardite with subordinate orthopyroxene, magnetite, and chromite, and VB-2, composed by amphibole (tremolite and possibly pargasite), clinochlore, and subordinate lizardite. Both samples were grinded and sieved. The 63-125, 125-250 and 250-500 (only for VB-1) μm fractions were characterised through N_2 sorption and desorption at 77 K, after degassing at 350°C for at least 24 hours, using an automated analyzer ASAP 2010 Micromeritics. Observed hysteresis suggests that the pores of VB-1 and VB-2 have a bottle-neck behaviour and a slit-like shape, respectively. Computed BET specific surfaces are between 26.0 and 36.6 m^2/g (VB-1) and 29.9 and 34.0 m^2/g (VB-2). This parameter decreases as the particle size increases. The external surface area, calculated by t-plot analysis, varies from 8.1 to 16.9 m^2/g for sample VB-1, and decreases with increasing particle size, whereas it is close to 16 m^2/g for sample VB-2. Preliminary experiments of CO_2 sorption at 100°C were performed on all the sample fractions using the same instrumentation. The data suggest that CO_2 sorption onto these solid surfaces is due to intermolecular physical interactions.

High-P and high-T experiments were conducted with the 63-125 μm granulometric fraction of sample VB-1. The reaction runs were carried out at 300 bar total pressure, at both 250 and 300°C, with an excess of oxalic acid and a small amount of aqueous solution (either pure water or NaCl 100 or 250 g/L), and adopting a water/rock weight ratio ~ 1/10. To this purpose, sealed gold capsules containing these materials were introduced into an externally-heated autoclave for 24 h. Although oxalic acid was expected to decompose to CO_2 and H_2O upon heating, gas analysis revealed the presence of CO_2 and significant amounts of CO and H_2. The experimental runs with a NaCl aqueous phase indicated, *via* XRD analysis, that at 300°C a rare Mg-oxalate (glushinskite) and magnesite formed, in spite of the very low theoretical *p*H (3.6-3.8) values. Conversely, at 250°C the only secondary Mg-bearing phase consisted of glushinskite. Dissolution of serpentinite and consequent precipitation of secondary Mg-bearing minerals are clearly favoured by the presence of NaCl and the high computed CO_2 fugacity, *i.e.*, 114-122 and 74-84 bar at NaCl 100 and 250 g/L, respectively. Further runs with Ag-oxalate are presently in progress to inhibit the production of CO and H_2.

Furthermore, the serpentinite sample VB-1 was dissolved in 2M H_2SO_4 at 70°C. After separation of amorphous silica and cooling to ambient temperature, the $MgSO_4$ solution was treated with NH_4OH, to increase its *p*H, and CO_2 was added to the system. Preliminary results confirm that the *p*H control is fundamental to precipitate Mg-carbonates. In fact, when *p*H attains values ≥ 10, brucite is formed, instead of barringtonite or other hydrous Mg-carbonates.

STRUCTURAL RELATIONSHIPS BETWEEN SARDIGNAITE AND GELOSAITE, TWO NEW BISMUTH AND MOLYBDENUM OXIDES

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Two new minerals, closely related between each other, have been recently approved by the IMA CNMNC: sardignaite (IMA # 2008-040), ideal formula $BiMo_2O_7(OH)\cdot 2H_2O$, space group $P2_1/m$, a 5.7797(7), b 11.567(1), c 6.3344(8) Å, β 113.360(9)°, and gelosaite (IMA # 2009-022), ideal formula $BiMo^{6+}_{(2-5x)}Mo^{5+}_{6x}O_7(OH)\cdot H_2O$ (with $0 \leq x \leq 0.4$), space group $P2_1/n$, a 5.8505(4), b 9.0421(6), c 13.9173(10) Å, β 100.42(1)°. The type locality of sardignaite and gelosaite is Su Senargiu, near Sarroch (CA), Sardinia, Italy, where the new minerals occur in quartz veins within a granitic rock. Crystals of sardignaite are transparent with a pale yellow colour, whereas crystals of gelosaite vary in colour between pale yellow and pale blue.

Electron probe microanalyses showed the presence of Bi and Mo only as the major cations (besides very minor Pb). Hence the two crystal-chemical formulae, which include 7 oxygens, 1 hydroxyl, and 2 (in sardignaite) or 1 (in gelosaite) water molecules, were assessed by means of single-crystal X-ray diffraction structural analyses. The two structures were solved and refined to R indices of 0.056 for 1651 reflections (sardignaite) and 0.023 for 1826 reflections (gelosaite).

The crystal structure of sardignaite is characterized by edge-sharing dimers of Mo-centered octahedra, which are linked to each other through corner-sharing and give rise to corrugated columns running along *b*. The crystal structure of gelosaite display a different arrangement of the same units: in fact in this latter case the Mo-centered octahedra are linked to each other by edge-sharing throughout, and the resulting columns are a bit more kinked (Fig. 1). The ligands of molybdenum are the same in the two structures, and result in $[MoO_5(H_2O)]$ octahedra. Some differences occur also in the bismuth coordination. In fact in sardignaite Bi is linked to 7 oxygens + 1 (OH), which define augmented pentagonal bipyramids, whereas in gelosaite Bi is linked to 6 oxygens + 2 (OH), which define bicapped trigonal prisms. In gelosaite, moreover, Bi-centered polyhedra are arranged in dimers through sharing of the OH-OH edge.

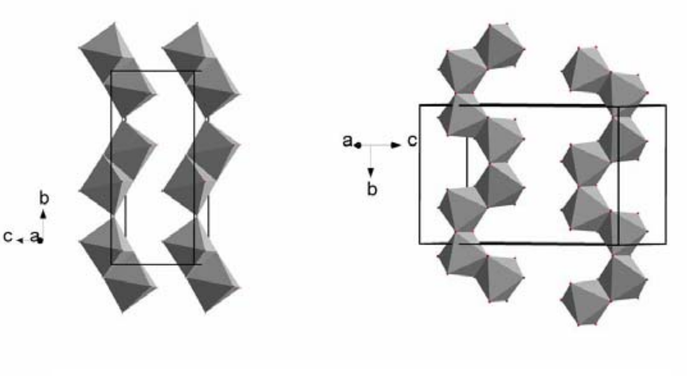

Fig. 1. Octahedral columns in the crystal structures of sardignaite (left) and gelosaite (right).

Besides Mo^{6+}, gelosaite may contain a variable amount of Mo^{5+}, which in the structure finds place at interstitial, partially occupied, sites, with the same coordination as the main Mo sites. Apparently, there is a relationship between the amount of Mo^{5+} and the colour of the crystals, which varies from yellow to blue as the x value in the chemical formula goes from 0 to 0.4.

Sardignaite and gelosaite are the first examples of bismuth and molybdenum oxides within the mineral kingdom, however the synthetic analogue of sardignaite, $BiMo_2O_7(OH)\cdot 2H_2O$, was already known, and it turned out to be structurally identical to the natural compound [1]. Instead of, as far as we are aware the synthetic counterpart of the non-stoichiometric mineral gelosaite, $BiMo^{6+}_{(2-5x)}Mo^{5+}_{6x}O_7(OH)\cdot H_2O$, has not been reported yet.

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RETENTION OF CARBAMAZEPINE ON ORGANOPHYLIC ZEOLITES

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In studies carried out in many countries, more than 80 pharmaceuticals and their metabolites have been detected in aquatic environments at concentrations in the microgram for litres range or lower [1]. Because pharmaceuticals are designed to be biologically active, they have the potential to affect a large variety of non target organisms for a wide range of physiological consequences.

Some pharmaceuticals such as carbamazepine are highly persistent and have been shown to be inert to the biological treatment process. In fact, carbamazepine has even been suggested as a possible anthropogenic marker in the aquatic environment [2].

Adsorption is an important technology for water reuse. Complete or near complete removal of a wide range of contaminants in secondary effluents can be achieved by adsorption. However, retention of trace organics on adsorbents highly depends on both the physicochemical properties of the compound and the adsorbent. Delineation of the fundamental mechanisms governing organic contaminants removal by adsorption on hydrophobic zeolites can be helpful for the potential use of zeolites in wastewater and groundwater remediation.

This study investigates the retention mechanisms of carbamazepine on organophilic zeolites (ZSM-5, mordenite and Y). Laboratory scale experiments were carried out with three well characterized zeolites with the goal of relating pharmaceutical retention behaviour to zeolite characteristics. To accomplish this task the adsorption property were investigated by adsorption isotherm determination, TG and DTA together with structural analysis studied by X-ray powder diffraction.

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ELASTIC BEHAVIOUR OF MFI-TYPE ZEOLITES: HP-INDUCED PHASE TRANSITION AND OVER-HYDRATION

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The response to compression of different natural and synthetic zeolites with MFI topology and different framework and extraframework chemical composition (mutinaite, Na-ZSM-5, H-ZSM5, silicalite), was explored by *in situ* synchrotron X-ray powder diffraction (XRPD), using both silicon oil (s.o.) and (16:3:1) methanol:ethanol:water mixture (m.e.w.) as non-penetrating and penetrating pressure transmitting medium, respectively [1, 2]. Two silicalite samples [space group $P2_1/n$] with different Si/Al ratios (1240 for silicalite 1 and 1850 for silicalite 2) and water content (8.9 and 2.3 molecules for silicalite 1 and 2, respectively) were studied. Their Si/Al ratios are much higher and their water content much lower than those of Na-ZSM-5 (Si/Al = 20.4, 28 H_2O), H-ZSM5 (Si/Al = 11.4, 36 H_2O), and mutinaite (Si/Al = 7.6, 60 H_2O).

The main result of the investigation performed in s.o. is the evidence of a P-induced phase transition in silicalite, from the monoclinic $P2_1/n$ (P_{amb}) to the orthorhombic *Pnma* (HP) (Fig. 1). In particular, silicalite 1 becomes orthorhombic between P_{amb} and 0.3 GPa, while silicalite 2 undergoes the same transition between 0.4 and 0.9 GPa. Mutinaite, Na-ZSM-5 and H-ZSM5 are orthorhombic in all the studied P-range. Both the original space groups and the unit cell parameters are substantially recovered upon decompression for all the studied phases. The normalized cell volume values determined for the different phases in the P_{amb} - 6 GPa range are reported in Fig. 2 as a function of pressure.

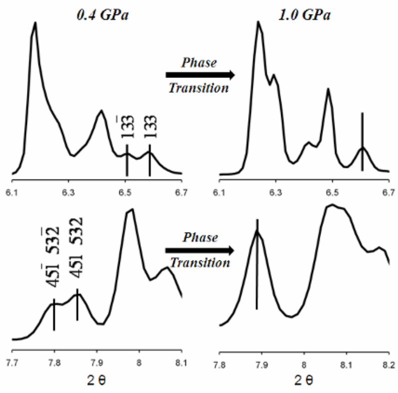

Fig. 1. Selected parts of the XRPD pattern of silicalite 2 at P_{amb} and 1 GPa, showing the effects of the phase transition.

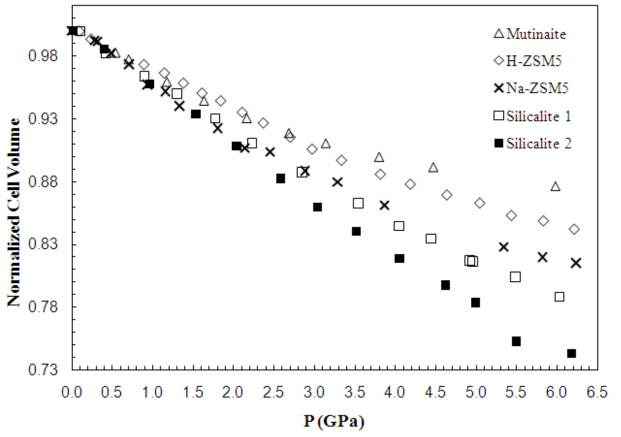

Fig. 2. Normalized unit cell volume *vs.* pressure behaviors for the studied phases.

Another important result of this study is the strong P-induced over-hydration (PIH) observed in Na-ZSM-5 and H-ZSM-5 compressed in m.e.w., with the penetration of 11 and 16 additional water molecules, respectively, up to about 2 GPa. It is worth noting that this PIH, although extremely high in both materials, occurs without any cell volume expansion. Finally, Na-ZSM-5 PIH is only partially reversible (2 extra-water molecules remain in the pores), and hence a material with a different extraframework composition is obtained at the end of the process.

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SYNTHETIC IRON OXIDES NANOPARTICLES FOR BIOTECHNOLOGICAL APPLICATIONS: A MULTIMETHOD CHARACTERIZATION

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With the rapid development of nanotechnology, magnetic nanoparticles are currently being widely studied. It has long been known that the physico-chemical properties of magnetic nanoparticles can be vastly different from those of the corresponding bulk material. We present the development of iron oxide nanoparticles, synthesized by a novel and original procedure in nanometer size range. The nanoparticles are now currently produced in a very simple way, by developing a modification of the reverse micelles method, but avoiding the need of surfactants or polyols, being the synthetic procedure under patent submission. Nanoparticles were chemically coated with silica by the Stöber process in order to generate surface functionalities.

The aim of the project is to define material characteristics in order to develop nanoparticles with proper dimensions, highest magnetic moment and most useful surface functionalities for biotechnological applications.

The complete characterization of this new material and various intermediates was performed by X-Ray powder diffraction (XRPD) at both ambient and high temperature conditions, Mössbauer (MS) and Fourier Transform Infrared (FTIR) spectroscopies and Transmission Electron Microscopy (TEM). XRPD data were collected in the air on a computer-controlled Philips X'Pert Pro diffractometer on which a X'celerator (RTMS) counter and a Antoon Paar HTK 16 High Temperature Camera were mounted. High temperature measurements were performed up to 700°C with a heating rate of 60°C/min and 2 min rest at each measurement temperature.

XRPD at room temperature and MS data indicate that both untreated and heat treated at 400°C samples are composed of maghemite, while those heat treated at a 600°C are composed essentially of hematite, even though some peaks assigned to maghemite are evident. The FTIR spectra confirm the presence of iron- and silicon-oxygen bonds together with a weak band attributed to OH groups.

In situ high temperature experiments show that the maghemite → hematite phase transformation occurs between 500 and 550°C. Following [1], the study of the phase transformation is now in progress.

TEM images showed a highly mono-disperse nanoparticle population with a mean size around 10 nm.

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A STUDY ON THE PHASE TRANSFORMATION OF CALCIUM HYDROXYAPATITE USING *IN SITU* HIGH TEMPERATURE X-RAY DIFFRACTION

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This work describes the results obtained by X-ray powder diffraction (XRPD) measurements at high temperatures on calcium hydroxyapatites ($Ca_{10}(PO_4)_6(OH)_2$) prepared with different synthetic methods, to obtain information on their thermal stability. A previous work [1] evaluated the role of Ca and P precursors and different preparation procedures (hydrothermal and ceramic methods) in the syntheses of calcium hydroxyapatite (HA). In the present work, the consequences of heat treatments are analyzed. *In situ* high temperature XRPD patterns were measured on samples prepared by hydrothermal and ceramic methods. Sample obtained by hydrothermal method was prepared by adding appropriate amounts of CaO, H_3PO_4 to a water solution of citric acid (*p*H = 10 by ammonia addition); the obtained colloidal suspension was heated at 240°C for 96 hours in an autoclave. The suspension was then cooled at room temperature and filtered. The obtained white solid was washed with water and dried at 90°C for 2 hours. Samples obtained by the ceramic method were prepared by thoroughly mixing $CaCO_3$ and $(NH_4)H_2PO_4$ in a molar ratio Ca:P = 1.67:1 in an agate mortar and pelletizing the powder so obtained. The pellets were heat treated (950°C for 2 h for CaP1B and 800°C for 2 h for CaHapB·5n) and then ground and pelletized again to perform a second heat treatment (1100°C for 48 h and 800°C for 2 h, for CaP1B e CaHapB·5n, respectively). XRPD data were collected using a computer-controlled Philips X'Pert Pro diffractometer equipped with an Antoon Paar HTK 16 high temperature Camera and a X'celerator (RTMS) counter. Measurements were performed up to 1200°C with a heating rate of 60°C/min and a 2 min soak at each measurement temperature. The experiments show that for all the samples, at a temperature of 800°C the phase transformations start, producing stable phases that are still present at room temperature. Moreover for samples prepared by ceramic method the first reaction appearing between 600 and 700°C is the decomposition of the carbonate fraction with the consequent formation of CaO that is fundamental for the following formation of the phosphatic phases. The obtained results are not easy to rationalize by both comparing the results or in connection with literature data. Most surprising is the increase of the hydroxyapatite at the expenses of $Ca_3(PO_4)_2$ in samples prepared by ceramic technique. For a deeper understanding of the decomposition processes, we followed two different paths: 1) XRPD measurements under vacuum as a function of heating; 2) accurate determination of the presence of amorphous apatite in the untreated samples that could eventually crystallize during the heating process.

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RECYCLING CONSTRUCTION AND DEMOLITION RESIDUES IN CLAY BRICKS

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Building activity is currently demanding noticeable amounts of natural aggregates, such as gravel and sand provided by sediments, whose extraction could modify river profiles and their equilibrium as well as quarrying activities induce environmental problems. The use of recycled aggregates is promoted by the EU, which has provided guidelines for common strategies for a correct re-use of construction and demolition residues [1, 2]. As for the Italian situation, currently the legislation is encouraging the re-use of construction and demolition residues, but their re-utilisation is hampered by the scarcity of suitable processing plants. As a consequence, this resource is exploited as a poor quality material for low grade applications (*i.e.* road sub-base).

This work is aimed at assessing the effect of construction and demolition residues on the technological behaviour and technical performance of clay bricks [3]. The brickmaking process was simulated at a laboratory scale and both unfired and fired products were compared with reference bodies.

In details, different fine-grained fractions, obtained by industrial sorting in a construction and demolition residues processing plant in Rovigo (Italy), were selected and their chemical composition and physical properties were investigated. The results indicate that it is possible to obtain, through proper crushing and sorting operations, grain-size fractions with quite homogenous chemical and mineralogical composition. Such homogeneity is considerably improved when a careful differentiation takes place during the initial stages of construction and demolition residues production.

Nine different mixtures were prepared adding two different grain-size fractions (< 0.125 mm and 0.6 - 0.125 mm) of construction and demolition residues or natural aggregate to three kinds of brick clay from Holocene or Pleistocene alluvial deposits. These clays represent the typical compositions used in brickmaking: carbonate-poor, carbonate-rich and intermediate amount of carbonates. All the bodies underwent a laboratory simulation of the brickmaking process, consisting of disagglomeration, mixing and humidification, extrusion, drying and firing (900 to 1000°C). Both semi-finished and finished products were characterized by assessing plasticity, drying sensitivity, drying and firing shrinkage and mechanical strength, water absorption, bulk density and phase composition.

The use of construction and demolition residues is technologically feasible. The residues affect in some way the compositional properties porosity and water absorption of the clay bricks. Nevertheless, the characterization of the residual-added semi-finished and fired products highlights their good technological and mechanical properties, which allow them to provide performances similar to standard bricks manufactured with raw natural materials.

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SESSION 2.4

Earth Sciences applied to Cultural Heritage

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"MATT-PAINTED" AND "OINOTRIAN-EUBOEAN" STYLE POTTERY FROM TIMPONE DELLA MOTTA OF FRANCAVILLA MARITTIMA (CS) - CALABRIA

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The fifty sherds examined in this paper come from excavations carried out by the Groningen Institute of Archaeology (GIA) on the acropolis of Timpone della Motta [1], an archaeological site located in Francavilla Marittima, near the well-known Greek colony of Sybaris (Calabria, southern Italy). This site was first inhabited during Middle Bronze age (*ca.* 1500 BC), in the 8th Century BC the site became one of the most important sanctuaries in southern Italy, first as an indigenous Oenotrians cult place, which later, following the foundation of the Achaean Apoichia of Sybaris in the last quarter of the 8th Century BC, developed to a mixed indigenous and Greek sanctuary. We presents an archaeometrical study of two ceramic classes, datable to the 8th Century BC, frequently found in the sanctuary: "matt-painted" pottery and "Oinotrian-Euboean" style pottery, analyzed for information on the probable raw materials provenance area and the technological features of these ceramic categories.

Matt-painted pottery was widely produced in southern Italy during the early Iron Age [2]. The term matt-painted refers to handmade vessel of typical indigenous shape with applied decoration in a matt dark paint. The matt-painted pottery shows different decorative styles in each region. Two predominant styles were present in the Sibaritide: the "undulating band style" and the "fringe style" based on their many decorative elements. Recent research has, however, documented a notably different group of matt-painted pottery on the Timpone della Motta, which display a especially high level of craftsmanship in being very thin-walled and decorated in a miniaturist style close to the matt-painted pottery productions in the southern Salento region. That naturally raises the question if the vessels from the Timpone della Motta were imported from the Salentine area. In that case the fragments from the Timpone della Motta could constitute the only example of deliberated export of Salento matt-painted pottery.

The Oinotrian-Euboean group [3] is contemporary with the matt-painted pottery and unlike the traditional indigenous matt-painted ceramics, the Oinotrian-Euboean pottery was produced on a fast rotating potter's wheel. Both shapes and decorations are clearly recognisable as Greek. Their production is considered as evidence of the presence of Greek potters who lived and worked within the indigenous settlement near Timpone della Motta from the first half of the 8th Century BC. A multi-analytical approach was used, including petrographic, mineralogical and chemical analysis by means of optical (OM) and scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and X-ray fluorescence spectroscopy (XRF).

The results are compared with those deriving from minero-chemical and granulometric characterisation of some clay sediments sampled from outcrops near the study site, representing the potential source of clay used for ceramic production in this area. Preliminary data [4] indicate that the matt-painted fragments belonging to "undulating band style" and "fringe style" and the fifteen Oinotrian-Euboean sherds were probably locally produced, since their chemical composition markedly resembles that of the clay sediments; while is different the composition of the ten matt-painted potteries with southern Salento region similar features.

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ARCHAEOMETRICAL INVESTIGATIONS ON SAN SEVERO MOSAIC *TESSERAE* (CLASSE, RAVENNA): THE USE OF DIFFERENT RAW MATERIALS FOR THE PRODUCTION OF OPAQUE GLASS IN VI CENTURY AD

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The San Severo basilica, built at the end of the VI Century AD, and brought to light during excavations on Sixties, is now interested by a new archaeological study by the University of Bologna.

In this work, twenty-four glass *tesserae* of different colours and degrees of opacity coming from different stratigraphic units (late VI to IX Century AD) were sampled and analysed. The aims of this work were to identify the raw materials, colourants and opacifiers employed in their production. Chemical analyses of major and minor element were performed by EMPA-WSD and the identification of crystalline phases was performed coupling X-ray diffraction and SEM- EDS analyses.

The chemical analyses of major elements allow to classify all the samples as natron based samples, consistently with their chronology. The samples set appears rather homogenous, even if some grouping of samples of the same colour (*e.g.* red) is possible also on the basis of the main components, suggesting the employ of slightly different recipes/raw materials. The major differences are clearly related to the elements responsible for the colour and for the opacity of the glass, that is transition metals, lead, tin and antimony. The coupling of the chemical data with the SEM-EDS and XRD investigations indicates that all the blue samples, coloured mainly with copper, are lead and tin free and are opacified with calcium antimoniates. On the contrary all the green samples are antimony-free and contain high levels of lead and rather high levels of tin. All the red samples contain rather high level of lead, copper and tin being these latter strictly correlated, even if not in the correct proportion to suggest the employ of bronze as copper bearing raw materials. The presence of nano-particle of metallic copper was detected both by SEM and XRD. Among the colourless samples, only one seems discoloured by adding manganese, while the most of the glass shows levels of antimony compatible with the use of Sb-rich glass cullet.

On the whole San Severo samples fit with the chemical composition of the coeval mosaic *tesserae*. The co-presence of Sb-based opacifiers and of tin bearing samples in the sample set, represent a rather peculiar trait, but it is well known that in Italy the tin based opacifiers have been found from the fifth Century AD onwards, but at the same time, antimony-based opacifiers continued to be used, or reused, until the 13th Century AD.

MULTIDISCIPLINARY APPROCH FOR THE STUDY OF THREE TOMBS IN THE PROTESTANT CEMETERY OF ROME (ITALY)

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In this paper, several diagnostic tests were carried out in order to characterize the stone materials, forms of alteration, and protective products applied in the past to three monumental tombs located in the Protestant Cemetery of Rome (Italy).

The Protestant Cemetery is a very important historic site, and has been included in the list of 100 most endangered sites in the world since 2005. In this work, three of its tombs were studied: those of Karl (or Charles) Brjullov, a Russian painter who lived in the first half of the nineteenth century, Lady Elisa Temple, wife of the artist Sir Grenville Temple, and Jefferson Page, an officer in the American Navy. The tombs are both made of white marble and travertine, and the same forms of alteration and degradation, such as blackish biological patinas, black crusts, and chromatic alterations, were found on both monuments.

Petrographic analysis of the different lithotypes made it possible to determine textural characteristics, evaluate the state of preservation, and formulate some hypotheses about their provenance by means of oxygen and carbon isotopic ratios, evaluation of maximum grain size (MGS) and LA-ICP-MS analyses.

Laboratory culture analysis identified autotrophic species and, in some cases, black patinas caused by fungal species were found.

Lastly, Fourier transform infrared spectroscopy (FT-IR) revealed that some synthetic protective products had been used in previous, undocumented restoration processes on some portions of both graves.

PRELIMINARY MINERALOGICAL CHARACTERIZATION OF CRYSTALS FROM SANT'ANGELO CAVE (CASSANO ALLO IONIO, CALABRIA, ITALY)

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The cave of Sant'Angelo is located in Cassano allo Ionio (North-East, Calabria); it extend for about 1325 m and is one of the most developed cave in the calcareous Trias formations outcropping in the Calabria region [1]. It genesis is related with sulphureous water circulation. The cave is composed of a series of horizontal galleries and rooms filled with collapsed deposits, concretions and mineralizations.

The present study was devoted to characterize the concretions and minerals from Sant'Angelo cave. At this purpose, the mineralogical study of 20 samples cleaned by sonication in water was performed by XRPD. On the same samples a detailed petrographic and morphological study was carried out by optical and scanning electron microscopy (SEM). These investigations, for gypsum samples were implemented with micro-Raman spectroscopy, microthermometry and TG/DSC analysis.

It turns out an unexpected mineralogical richness for an environment that was classified only as a gypsum cave.

The mainly detected minerals in decreasing order of amount are: gypsum, calcite, dolomite, magnesian calcite, pirite, apatite mineral group, Fe-oxides, magnesioferrite, rutile, clay minerals, K-feldspar, plagioclase, olivine, quartz, Fe-oxides.

The thermal characteristics of gypsum produce the following thermal changes: dihydrate gypsum becomes hemihydrate gypsum at 157°C and the hemihydrate becomes anhydrous gypsum at 175°C, in good agreement with data from Chandara *et al.* (2009) [2]. The DSC curve shows also, an exothermic pick at 360°C that records the inversion of γ-anhydrite into β-anhydrite [3].

Preliminary data on speleothem fabrics [4], show some change in the organization of crystals within layers characterized by synchronous crystallization from acicular to columnar shapes. This could reveal physico-chemical parameters changes of the cave during the time. Actually our group has already begun to obtain micro-Raman spectroscopy and microthermometric data to evaluate the salinity of fluids inclusion from which gypsum precipitated. A detailed study of such minerals improves the knowledge on speleogenetic evolution of Sant'Angelo cave and in general on the evolution of cave environments in carbonatic rocks.

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A MULTI-ANALYTICAL APPROACH FOR THE CHARACTERIZATION OF CERAMIC FINDINGS OF AIANO-TORRACCIA DI CHIUSI (SIENA-ITALY) ARCHAEOLOGICAL SITE

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In the archaeological site of Aiano-Torraccia di Chiusi (Siena-Italy) the remains of a Roman *villa*, dated between the beginning of 4th Century and the end of the 5th Century or the beginning of the 6th AD, were discovered. The complex, abandoned in the 6th Century AD, was occupied by a group of barbaric artisans (Lombards or Ostrogoths) in the period between the 6th and the 7th Century AD. Numerous ceramic findings (*simil africane*, *ingobbiate*, *acrome grezze*) dated at 7th Century AD were discovered in the archaeological site. These findings were analyzed using different analytical methodologies (OM, XRD, XRF, SEM- EDS, ATR FTIR and micro-Raman) in order to characterize the paste and the cover of the *ingobbiate*, the paste and the tempera of the *acrome grezze* and to determine the compositional relationship among different kinds of ceramics.

This work compares and evaluates the results obtained using different analytical methodologies performed on the same samples, in order to obtain information at different scales. A multivariate statistical technique was used to compare the data obtained.

In the case of *acrome grezze* interesting information were obtained by OM observation and SEM-EDS results: the analyses performed on some minerals and rocks fragments attest the re-employment of stone *tesserae* pertinent the Roman *villa* (*i.e.* numerous marble fragments). For what concerns the *ingobbiate* and *simil africane,* the analyses performed at different scales (XRD and XRF for the bulk), and SEM- EDS, ATR FTIR and micro Raman (for bulk and covering) reveal a clear chemical, mineralogical and textural difference: in the *simil africane* high SiO_2 and Al_2O_3 values in the bulk and a typical Fe enrichment in the cover were found, while in the *ingobbiate* findings no chemical/ mineralogical difference between the paste and the cover, but only a clear difference in the grain sizes, was registered.

COOKING AND PLAIN WARES FROM THE FORUM AT POMPEII: AN ARCHAEOMETRIC APPROACH

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The contribution will illustrate and discuss results of a recent research project focused on the study and analysis of cooking and plain wares retrieved by archaeological excavations carried out in the forum at Pompeii in 1980-1981 [1]. The analyzed vessels span the period of time comprised between the late IV-early III Century BC and the 79 AD.

An interesting variety of morphological and functional types will be discussed with reference to analytical data and quantified vessels' analysis through time. Particular emphasis will be given to information provided by minero-petrographic analysis carried out on a representative selection of casseroles and cooking pots, storage jars and table wares, including flagons and jugs. Archaeometric data, combined with ceramological analysis, allow us to reconstruct and discuss changes in pottery manufacture, clay provenience, vessels' function and use over several centuries of everyday life at Pompeii and in the Vesuvian area.

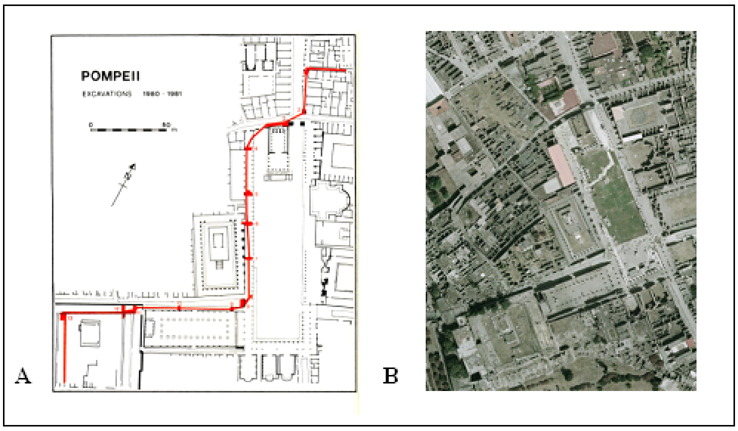

Fig. 1. The investigated areas in the forum at Pompeii [2].

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UNIQUE TUNGSTEN AND TIN GEOCHEMICAL SIGNATURE OF HEMATITE-ORES FROM ELBA ISLAND (ITALY) AND ITS IMPLICATION ON TRACEABILITY OF IRON IN ANCIENT REDUCTION SITES

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In the Mediterranean area, iron oxides, hydroxides and carbonates have been used since 1500 BC for the production of iron artefacts by one-step direct reduction. In spite of the investigations carried out during the last decades, it remains quite difficult to establish the origin of the raw materials (Fe ores, slags, blooms) found in archaeological sites, on the basis of their petrographic and geochemical/isotopic signatures. The opportunity to trace of iron ores through the circum-Mediterranean region would have many important implications for a better understanding of the political and economic development in ancient time. Indeed, it is well known that Fe ores were commonly transported to a great distance from their original ore deposits following commercial routes, local skillfulness, and availability of wood for reduction process. To date, a provenance study of Fe-materials found in ancient reduction sites in Italy (*e.g.* Elba Island, Baratti-Populonia, Ischia, Marzabotto, *etc.*) has not yet been performed. We report here on the first attempt to fully characterize the geochemical signature of the iron ores from the eastern Elba Island, which were used as raw material for iron reduction since at least the Etruscan time. In addition to its rich iron ore deposits, Elba Island had a prominent importance for its crucial position with respect to naval routes in the northern part of the central Mediterranean Sea. The iron ores (hematite, goethite, magnetite) from the main mining sites of eastern Elba have been studied by ICP-MS and SEM-EDX along with a wide selection of iron ores (hematite, goethite, siderite) from other Italian and European mining districts which were already known in ancient times. A series of archaeometallurgical samples (mineral charges, slags and blooms) from Roman and Medieval sites from Elba Island and Populonia have also been analyzed following the same protocol.

Our study indicates that, compared to other Italian and European iron ores, the hematite ores from Elba Island display a constant and distinctive geochemical pattern characterised by strong positive anomalies of W and Sn (up to thousands of μg/g) which are correlated to the occurrence of tiny (1-10 μm) crystals of scheelite, cassiterite, and possibly ferberite, as accessory phases in the hematite ore. First investigation of Fe mineral charge residues, reduction slags and Fe blooms from ancient reduction sites in Tuscany strongly suggest that Fe ores from Elba mines were used, and that their peculiar W-Sn geochemical signature was preserved by slags and blooms during the reduction process, thus providing us a very powerful tool for tracing the Elba iron ores in the iron reduction sites of the ancient world.

PETROGRAPHICAL CHARACTERISATION OF METALLIC SLAGS FROM ARCHAELOGICAL EXCAVATION OF PORTA PAOLA (FERRARA, ITALY)

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The aim of this work is to define the petrographical composition of some metallic slags coming from an archaeological site opened during requalification actions in the Porta Paola area in the city of Ferrara. These slags were found under the street level of via Bologna, where in the Medieval period there was a branch of the Po river used as a commercial way for ships [1]. These data have been helpful in the reconstruction of the technological process which through several smelting steps involves the separation of the silicate phases from the Fe-enriched phases. This process was suitable to obtain pieces composed almost of pure Fe, with a small amount of impurities.

Bulk chemical composition of the slags has been obtained through XRF analysis, carried out in the laboratories of the Earth Sciences Department of Ferrara University. Then on some selected samples EMPA analysis has been performed in order to better define the chemical composition of the silicate phases. Chemical microanalysis by EMPA has evidenced the presence of melilite and kirschsteinite, both of them high temperature silicate phases with a melting temperature close to 1300°C. In order to obtain such a high temperature it was necessary to have well ventilated kilns where oxygen promoted the combustion process. Increasing of oxygen or higher quantity of oxygen during the combustion lead to an environment suitable for the formation of Fe oxides such us wustite, olivine and melilite [2, 3]. The glass analysed in some samples is like the other silicate phases, is Fe-, Al- and Ca-rich. Bulk glass compositions can be described in terms of the components FeO, Al_2O_3, SiO_2 and CaO and can be plotted are depicted in FeO-Al_2O_3-SiO_2 and CaO-FeO-SiO_2 ternary diagrams [3, 4].

High contents of Si and Ca, observed in the XRF analysis of the samples, have suggested that during the combustion processes Quartz and calcium carbonate were added as melting phases in order to decrease the melting temperature of Fe rich minerals.

Although the furnace types for ironmaking in Ferrara are not well known, it can be hypothesized that such an efficient ventilation in the past was obtained using the force of water, that is linking the hydraulic wheel of a mill to the furnace.

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THE WOODEN ALTARPIECE OF CHAPTER HALL OF THE ST. ANTONIO IN POLESINE MONASTERY IN FERRARA

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Wooden altarpieces began quite widespread in the northern Italy between 1400 and 1500, and according to the manufacturing places they are grouped in two main types: the Florentine Types and the Venetian-Lombardy Types [1]. Less known are the Emilian altarpieces and between them the wooden altarpiece of the Chapter House of the St. Antonio in Polesine Monastery in Ferrara represents a unicum due to its complex architecture and its iconographic elements. Its columns, its capitals, its central arch, supported by two pilasters, reproduce the rhythm of the facades of the church. Other architectural elements are contained in an additional outer frame, decorated with a painting program typical of the miniatures and enriched in the lower part by a polychrome decoration on a gold background [2, 3].

The altarpiece studied was created using a carved wooden as support, on the ground layer was applied a strata of plaster and glue, mixed with organic fibres. This layer was then covered by a bolus basis where was placed a golden leaf. Thin layers of clay minerals and aluminium hydroxides (bauxite in the innermost layer and laterite in the outer layers) were used to create a waterproof effect on the surface giving a texture for applying other layers. These layers had the role to preserve the waterproofing plaster and the bauxitic-lateritic layers acted as a barrier, preventing the entry of moisture in the underlying layers of plaster.

A microclimatic survey performed in the Chapter House has shown that temperature and humidity conditions are not suitable for the conservation of the wooden altarpiece due to ascent capillary. Biological analysis of the structure has not highlighted warping and biological attack excepting in the *predella*. In the thicker areas cotton networks, identified by biological analysis were used as support of decorations, the organic material appears in correspondence of the animistic figures that decorate the columns, due to swelling of the plaster. Restoration actions aimed at interrupting the process of progressive swelling and detachment will be required.

SEM analysis of superficial samples of gold have shown presence of deposits of pollutants, presumably due to the fumes of burning candles, and presence of salts, mainly constituted by phosphorus. The high hygroscopicity of these deposits has produced mechanical stress on the golden leaves favouring the biological attack such as *Ascomycetes*.

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RECONSTRUCTING THE HISTORY OF THE PORTAL OF THE *SALA DEL CONSIGLIO GENERALE* OF THE REPUBLIC OF SIENA (ITALY) USING MICROSTRATIGRAPHIC ANALYSIS

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The restoration of the *Teatro dei Rinnovati*, which began in 2003 and was completed recently, involved significant demolition and reconstruction work in the sector between the *Palazzo Pubblico* and the *Palazzo dei Rinnovati*, which is the part of the building that includes the entrance to the theatre. During the demolition work architectural surfaces were brought to light that had been completely covered with plaster or even bricked over in a series of previous construction phases and other interventions carried out over the centuries.

Of the various surfaces brought to light during the abovementioned works, of particular note is the ancient portal that likely served as the entrance to the *Sala del Consiglio Generale* of the city. This Chamber originally constituted the main floor of the *Palazzo dei Rinnovati*, before being used as a theatre. Microstratigraphic examination of the numerous samples obtained allowed us to retrace the history of this portal and, with the invaluable help of architectural history and archival data, to attempt a precise temporal collocation of the main phases in its history, marked by the presence of eight stratigraphic layers.

The history of the portal began in around 1340 when it acquired its original finishes according to contemporary tastes [1, 2] and continued (after a long period in which the portal was exposed on the outside, as testified by the evident phenomena of deterioration), through a series of levels, each of which can be related to historically documented events such as fires and especially building work, that gradually incorporated the portal within the building. According to our reconstruction, the last traces of the ancient portal disappeared in 1869, to reappear today after 140 years of complete oblivion.

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TEXTURAL AND MORPHOMETRICAL ANALYSIS APPLIED TO ARCHAEOLOGICAL POTTERY (TAKARKORI, LYBIAN SAHARA): A POWERFUL TOOL IN DESERT ARCHAEOLOGY

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This work proposes the application of image analysis to textural morphometrical analysis as an extension of routine petrographical, mineralogical and chemical characterization to answer provenance and technological questions about some of quartz-bearing ceramic sherds found in the archaeological site of Takarkori (Lybian Sahara, 6100-5000 BC).

Four digital images for each of the 15 thin sections relative to samples analyzed have been acquired each both in plane polarized and cross polarized light by a digital camera connected to a petrographic microscopy. A freeware image analysis software (ImageJ) has been used to isolate the quartz inclusions in a binary image and to obtain quantitative textural and morphometrical data. In order to obtain reliable results it was followed the same algorithm for the image processing of all the samples, which was defined taking into account the fabric.

In agreement with petrographical results, grain size distributions and morphometric characteristics obtained confirm the distinction of samples in two different groups called Q (which contains only quartz) and QC (which contains quartz and secondarily calcareous aggregates) belonging to a common petrofacies, which is the quartzarenitic ground of the archaeological site. As a matter of fact, quartz inclusions for both Q and QC have similar granulometric characteristics confirming the *in situ* provenance of raw materials and a morphometric variability that strengthen the distinction observed. With reference to site's geological setting, sediment characterizing QC samples may be referred to *wadi-shallow lake* environment while that of Q group samples to *wadi* one. Starting from a common fluviatile sediment, alternation of alluvial, eolian and erosive events has produced a subangular and tabular sediment with a more fine sand distribution characterizing QC and a more round and almost circular with a medium-fine sand distribution relative to Q. In this general trend only one sample (tk43, Q) has a higher quartz inclusions content with a coarse-medium sand distribution allowing then the hypothesis of a provenance from more distant places justifiable by local population nomadism.

Although image analysis provided textural and morphometrical data consistent with those obtained by petrographical analysis, it added much detail in pottery fabric characterization, allowing a sedimentological interpretation. Thus the application of image analysis to pottery sharing a common petrofacies, such as those produced in desert areas, is a powerful tool for provenance determination and may give a valid contribution to technological analysis.

MINERALOGICAL SURVEY ON HISTORIC *HAFT-RANGUI* TILES IN *JAME-I ABBASSI* MOSQUE OF ISFAHAN (CENTRAL IRAN)

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Jame-i Abbassi Mosque, as an important historic monument in the Iranian architecture, shows a vast application of one kind of architectural decoration so-called *Haft-Rangui* tileworking. *Haft-Rangui*, which literally means "Seven Colours", has been the common technique for decorating architectural facades during 17th Century till now. Many mosques, palaces and some churches in Isfahan, famous historic city in central Iran, were decorated with this kind of ornaments in this period. As an illustration, each *Haft-Rangui* tile is made by a terracotta body as a substrate for upper multicoloured glassy layer; as a tradition these colours have been white, black, green, turquoise, brown, cobalt blue and yellow.

Here, in this essay, an attempt is made to shed light on mineralogical and technological aspects of the ornaments. As a matter of fact, some analytical methods of surveying material composition; such as, XRF (X-ray Florescence), ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) SEM-EDS (Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy), XRD (X-ray Diffraction) and PLM (Polarized Light Microscopy) are used to reveal technical points of the *Haft-Rangui* tiles. Compositional, mineralogical and structural-textural characteristic of the bodies has been discussed. Furthermore, elemental composition of bodies and glazes is considered as well. As consequence, the results show that two layers of glazes have been applied on top of the terracotta bodies composed by clay minerals. Moreover, an intermediate white glaze has been used in order to act as a substrate between multicoloured glassy layer and fired clay body. In addition, firing process of multicolour glassy layer (except white glaze) has been occurred in an individual stage; so that, the white glaze had been previously fired in an individual process.

THE USE OF INNOVATIVE TECHNIQUES FOR THE STUDY OF DEGRADATION AND ALTERATION PRODUCTS ON STONE MATERIALS

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The degree and distribution of the main types of observable rock deterioration in an urban environment are related to different kinds of wetting and particularly to the exposure of the stone surface to rain. In a polluted environment, two kinds of crusts are usually developed on calcareous rocks, the so-called white and black crusts.

The aim of this study is to characterise some black crusts and oxalate patina appearing on monuments and sculptures located in different cities.

Traditional techniques, consisting of polarising optical microscopy (OM), scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDS) and Fourier transform infrared spectroscopy (FTIR) analysis, were used in combination with innovative techniques, such as laser ablation inductively coupled mass spectrometry (LA-ICP-MS) and micro-FTIR. LA-ICP-MS micro-analytical technique allows to determine the chemical composition of black crusts in terms of trace elements and to monitor their variability from stones to black crusts thus permitting to evaluate the thickness of contamination. The qualitative distribution map of degradation products can be obtained by means of micro-FTIR operating in ATR mode.

The results obtained by applying traditional techniques find considerable support in the innovative method used here, which could determine the concentrations of a large number of trace elements (including heavy metals) in the black crusts examined, and thus could also be used as a reliable indicator of environmental pollution.

THE MILLING IN THE PROCESS OF MAKING HISTORICAL MORTARS

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Several texts describing traditionally made mortars of historic buildings [1, 2, 3, 4] show that there are many factors involved in preparing a mortar: method of milling, aggregate/binder ratio, type of raw materials, *etc*.

Plinius Secundus Gaius and Marcus Vitruvius Pollio stress the importance of milling when preparing mortars. In general, mortar resistance and duration is attributed to the presence of reactive silica in the pozzolanic material which, in pastes with a calcium hydroxide base, react, forming calcium silicate hydrates, commonly called C-S-H phases. However, experiments that study the effect of these variables are few in the scientific literature. The work has the aim to verify the effect of the milling between lime and clay brick powder before and after the addition of water. Starting and resulting materials were investigated by XRPD, SEM/EDS, DSC/TG, colorimetry, densimetry and porosimetry. The results underline that the milling is a determinant factor in the mineralogical composition of the final product.

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EVOLUTION OF RENAISSANCE AND MANNERISM ARTISTIC FOUNDRY: A PETROGRAPHIC STUDY OF CASTING CORES USED TO CRAFT FLORENTINE BRONZE MASTERPIECES

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The petrographic and geochemical characterization of core materials used to craft bronze artworks represents a recognized tool in archaeometallurgical studies. It can provide relevant contributions to the solution of knowledge problems such as those related with the development of art foundry, as well as provenance, attribution and dating of the object under study (*e.g.* [1], and references therein). Notwithstanding, till today only a few investigations have been carried out on the topic, mainly concerning ancient age artistic productions. Overviews regarding core materials used in Renaissance bronzes have been reported by some Authors [2, 3, 4], but further insights are needed in order to achieve a deeper knowledge on 15th and 16th Centuries art foundry, especially concerning large bronze artworks.

Here we report a petrographic study of casting cores of masterpieces by Lorenzo Ghiberti (*Sacrificio di Isacco*, 1401, and *Porta del Paradiso*, 1425-1452), Donatello (*David* and *Amore-Attis*, 1430-1450), Andrea del Verrocchio (*Incredulità di San Tommaso*, 1466-1483), Giovan Francesco Rustici (*Predica del Battista*, 1506-1511) and Vincenzo Danti (*Decollazione del Battista*, 1570-1571).

Samples were taken from these artworks and studied by means of polarized light microscopy in thin (cross) section, computerized image analysis, XRD, SEM-EDS.

The core materials of these sculptures show remarkable petrographic similarities, thus suggesting a well established tradition in the selection and processing of raw materials, kept during the whole period analysed. The collected data suggest the general use of silty-sandy clays, provided from the origin with a certain content of natural temper components, to which variable contents of *chamotte* fragments and organic fibres have been purposely added. In some artworks, a further addition of sand can be hypothesized. Gypsum additions have been observed in Verrocchio's and Rustici's sculptures. Probable differences in supply localities of raw materials are testified by weak differences in composition of matrix and skeleton grains, being anyway coherent with the Florentine geological background. Colour, mineralogical association and microstructure are quite variable among different artefacts and sometimes within a single artefact, strongly depending on the distance from the metal wall (*i.e.* transient heating produced by metal pouring), on the presence of organic matter and on the exposition (closed or open shapes, or possible pre-cooking before the casting).

General and peculiar features pointed out in the present work provide important data on the evolution of the art foundry during the Renaissance and Mannerism.

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QUANTITATIVE MULTIPHASE-ANALYSIS OF MEDIEVAL LIME MORTARS BY THE RIETVELD METHOD

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In this study we present the results obtained from the quantitative mineralogical analysis of mortar samples through X-ray powder-diffraction using the Rietveld methods. The study was aimed at verifying the significance of Rietveld Quantitative Analyses (RQA) in relation to the results obtained through other techniques and to evaluate the effectiveness of the method in the quantitative mineralogical characterization of mortars with variable composition and complexity.

The investigated materials were selected from the 33 bedding mortars taken from the archaeological site of Sipontum (Foggia, 11th-13th Century AD) and recently investigated by a multi-technique approach, which included optical microscopy (OM), X-ray fluorescence spectrometry (XRF) and Laser Ablation IPC-MS on the lime lumps [1].

X-ray powder diffraction results are in well agreement with previous studies which clearly showed two distinct petrographical groups of mortars (labeled as group A and B, respectively). The former, which is characterized by the occurrence of quartz and calcareous sand, shows X-ray patterns dominated by calcite and quartz reflections. Weight percentages estimated through the Rietveld refinement range from 62 to 85 wt.% for calcite and from 7 to 20 wt.% for quartz. Minor and variable amounts of plagioclases and K-feldspars are also present, with estimated percentages ranging from 5 to 6 wt.% and 3 to 12 wt.%, respectively. Low intensity reflection for $d \sim 10$ Å ($2\theta \sim 8.8°$) indicate the presence of minor and non detectable amounts of phyllosilicates, presumably muscovite/illite, in one sample. Mortars belonging to the second group which are characterized by the occurrence of nummulites (group B), show calcite as the major constituent in addition to subordinate amounts of quartz. The Rietveld weight percentages are: ~ 98 wt.% for calcite and ~ 2 wt.% for quartz.

The consistency of Rietveld results was tested deriving the chemical composition of each sample from the determined crystalline fractions and assuming stoichiometric compositions for all phases. The obtained chemical compositions of the samples match almost well those resulting from XRF, in particular for samples of the group B, which contain more than 90% of calcite. The major discrepancies between XRF and Rietveld results were obtained for samples containing phases with variable compositions. Our findings let to exclude significant discrepancies between XRF and Rietveld data related to the occurrence of amorphous phase in the investigated mortars.

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SESSION 2.5

Scientific Gemology

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TANZANITE AND OTHER ZOISITES FROM MERELANI (NE TANZANIA): NEW GEMMOLOGICAL AND CHEMICAL DATA

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Zoisite is an orthorhombic (space group: *Pnma*) polymorph of clinozoisite and is not considered a member of the epidote-group, which includes only monoclinic minerals [1]. Tanzanite is the gem name for the violetish-blue coloured vanadium-bearing zoisite occurring in the Merelani mining deposit (northeastern Tanzania) located at the centre of the Great Rift Valley region. The more than 5 km long area of the Merelani mineralization is occupied by late Proterozoic metasedimentary rocks and is divided into four government-controlled main blocks. Most gem-quality tanzanites occur in fault zones within outcrops of graphitic gneisses and schists, together with small quantities of transparent zoisite crystals of various colours (brown, yellow, green, pink, colourless). The colour of tanzanite and zoisite on the market today has generally produced by heat-treatment, although the response of the stones changes with the varying amounts of vanadium, chromium, and titanium [2].

In the present work we have investigated five rough samples of zoisite from the Merelani area, consisting of one specimen with the typical violetish-blue colour of tanzanite and four stones ranging in colour from yellow-green to yellow-brown. From this material, we obtained five faceted gems weighting from 0.22 to 0.52 ct (zoisites) up to 2.44 ct (tanzanite). The gems and the rough grains have been characterized by traditional gemmological tests combined with EMPA-WDS and LA-ICP-MS measurements in order to determine their optical, physical and chemical properties. The faceted gems have been also heated at temperature up to 800°C with steps of 50°C. The annealing time for every step varied from 15 to 120 min, with the increase of the temperature. The gemmological tests have been repeated after each step.

Both tanzanite and zoisites examined have a composition close to the idealized formula $Ca_2Al_3[Si_2O_7][SiO_4]O(OH)$, but contain some other minor and trace elements substituting for calcium and aluminium. In particular, the tanzanite sample is enriched in vanadium and chromium (V = 2625 ppm; Cr = 224 ppm) respect to zoisites (V = 1139-1571 ppm; Cr = 81-140 ppm) whereas is depleted mainly in titanium and strontium (tanzanite: Ti = 43 ppm, Sr = 1266 ppm; zoisites: Ti = 95-268 ppm, Sr = 1451-2549 ppm). All the examined samples show comparable rare earth elements (REE) distribution patterns with a marked enrichment of LREE relatively to M-HREE, but the determined concentration is higher in tanzanite (ΣREE = 384 ppm) than in zoisites (ΣREE = 123-364 ppm). Before the heat treatment, all the examined gems were biaxial positive (refractive indices and birefringence ranging over 1.687-1.692 to 1.698-1.702 and 0.008-0.013, respectively) with a strong trichroism; the density varied from 3.20 to 3.46 g/cm^3. When viewed with a gemmological microscope, most gems contain several inclusions such as fluid veils, opaque solid grains (probably graphite) and fractures. The four yellow-green to yellow-brown zoisites responded to heat treatment by turning violet-blue and dichroic at approximately 450/550°C. The violetish-blue tanzanite became dichroic, but showed no change in colour. According to the most recent data reported in literature [3], colour variations are probably due to a change of the oxidation state of vanadium and titanium (Ti^{3+} + V^{4+} converting to Ti^{4+} + V^{3+}) with heating.

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THE MINERALOGICAL-GEMMOLOGICAL CHARACTERIZATION OF ANDRADITE GARNET (DEMANTOID VARIETY)

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Andradite garnet (ideal composition: $Ca_3Fe_2Si_3O_{12}$; space group: $Ia\bar{3}d$) is a rock-forming mineral typically found in metamorphic rocks (*i.e.* serpentinites and skarns). Green andradite, described with the varietal name "demantoid", represents the most appreciate and precious gemstone among the garnet group minerals, due to its rarity and brilliance. Currently, gem-quality specimens present on the marketplace come from the serpentinites rocks occurring in Russia (Nizhniy Tagil, Central Urals), northern Italy (Val Malenco, Sondrio), southeast Iran (Kerman Province) and northern Pakistan (Kaghan Valley), and from calcsilicate skarns of Namibia (Erongo, Damaraland) and northern Madagascar (Antetezambato, Antsiranana).

The aim of the present study is a multi-methodological investigation of demantoid garnets from these notable localities, by means of gemmological standard testing, EMP and LA-ICP-MS chemical analyses, UV-Vis-NIR and mid-IR spectroscopy and single-crystal X-ray diffraction, in order to provide a full mineralogical-gemmological characterization of this gem.

The gemmological properties (colour: green or yellowish green; optic character: monorifrangent with anomalous double refraction; refractive index: > 1.81; density: 3.79-3.88 g/cm^3; UV fluorescence: inert) of all the samples here investigated are typical of andradite variety demantoid [1, 2]. With respect to the internal features viewed with the optical microscope, demantoid hosted in serpentinites has inclusions of minerals typical of this geological environment (*i.e.* chrysotile crystals in "horsetail" arrangement and Cr-bearing magnetite crystals), significantly different from those observed in demantoid occurring in calcsilicate skarns (*i.e.* liquid inclusions, wollastonite, quartz and calcite crystals, growth channels and colour zoning). Chemical analyses show almost pure andradite composition (Adr ≥ 96 mol.%) for all the demantoid here investigated. The only exceptions are a few samples occurring in skarns, which show a grossular-andradite chemical zoning, typically found in garnets from these rocks [3]. The investigated samples have a low abundance of minor and trace elements, except for chromium, which ranges from a few ppm up to the wt.% level. This chromophore element is involved in the colour of demantoid hosted in serpentinites, along with Fe^{3+} [2], which represents instead the only main cause of colour in green garnets from skarns, as confirmed also by UV-Vis-NIR investigation. The Cr-content does not affect the unit-cell constants (a = 12.0518-12.0630 Å) [4, 5] measured on some selected samples, at least within the range here examined (~ 1 wt.% as Cr_2O_3), and the refined electron content at the Fe site (*i.e.* $\Sigma e^- \sim 25.2$-25.7) confirms that Cr^{3+} shares the octahedral site along Fe^{3+} [5]. The mid-IR spectra show the presence of minor amount of hydroxyl groups [6], which are incorporated in the structure, probably by the hydrogarnet substitution [*i.e.* $(SiO_4)^{4-} \leftrightarrow (O_4H_4)^{4-}$]. The rare earth elements (REE) distribution pattern (LREE-enriched and HREE-depleted with a strong europium anomaly [3]) of the andradite garnets here investigated indicates that the substitution of Fe^{3+} (and Cr^{3+}) for Al in the ugrandite-series garnets favours the incorporation of LREE, highlighting that the crystal chemistry plays an important role in the REE distribution.

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CHARACTERIZATION OF SALT- AND FRESHWATER PEARLS BY SEM AND μ-RAMAN SPECTROSCOPY

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The last decade the market has witnessed the decreasing in both production of Akoya pearls due to coastal pollution [1] and value due to increasing spread of Chinese freshwater pearls of various colours except black. Some of the white freshwater pearls could rival the saltwater Akoya pearls and a doubt arises that in the next future they can be confused with saltwater pearls.

Much progress has been made concern the identification of salt- and freshwater pearls and their relationships [2]. The present work represents an attempt to solve this problem. Seven samples, in particular two freshwater cultured pearls (one of them "chocolate"), a natural Red Sea saltwater pearl, an Akoya saltwater cultured pearl, and three additional saltwater cultured pearls (South Sea, Tahitian, and "golden") were investigated with SEM-EDS in low vacuum condition and μ-Raman spectroscopy. These techniques are non-destructive and do not require sample preparation. The nacreous surface of pearls displays structures that are step-like, labyrinthine (*i.e.*, resembling fingerprints) or spiral [3]. These structures seem to depend on the pearl mollusc species, varying growth conditions, or both. EDS analysis reveal Ca, C, O as major elements. As all calcium carbonate polymorphs are reported in pearl mollusc, including the rare vaterite [4], μ-Raman spectroscopy was performed to identify aragonite, calcite and vaterite.

μ-Raman spectra of investigated pearls showed characteristic bands of aragonite. In addition, freshwater and saltwater pearls showed peculiar bands that are distinctive of the origin of the pearls.

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THE BLUE COLOUR OF Co-SPINEL: CATION DISTRIBUTION AND UV-VIS-NIR ABSORPTION SPECTROSCOPY OF $MgAl_2O_4$-$CoAl_2O_4$ FLUX-GROWN SINGLE CRYSTALS

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Blue Co-bearing spinels are rare in nature and actively sought as gemstones, while synthetic Co-spinel powders are largely used as ceramic pigments.

Spinel single crystals belonging to spinel *s.s.* ($MgAl_2O_4$) - cobalt spinel ($CoAl_2O_4$) series were synthesized by flux growth method with $Na_2B_4O_7$ as flux. Low cooling rates (2°C/h) and linear temperature profiles were applied in the thermal interval 1200-800°C. Thermal runs were performed in reducing atmosphere (10^{-8} - 10^{-15} atm) created by a continuous flow of CO_2 / H_2 with a ratio of 100/4 cm^3/min. With increasing Co^{2+} contents, the crystals varied in colour from light blue to intensely dark blue. Selected crystals were investigated by single-crystal X-ray diffraction, electron-microanalysis and UV-VIS-NIR spectroscopy to obtain chemical composition, structural characterization, cation site population and quantitative optical absorption. The crystals were found to be chemically homogeneous, with composition dominated by $Co^{2+} \rightarrow Mg$ substitution and structural parameters *a*, *u* and T-O increasing with Co^{2+}. The T site is mainly populated by Mg and Co^{2+}, with Co^{2+} showing a marked preference for tetrahedral coordination with respect to Mg. The optical absorption spectra, measured between 2000 and 35000 cm^{-1}, show the three spin-allowed electronic *d-d* transitions of tetrahedrally coordinated Co^{2+}. Notably, the absorption bands of Co^{3+} are not observed, in agreement with the highly reducing conditions imposed during crystal growth. Accordingly, the observed transitions due to Co^{2+} in tetrahedral coordination are the cause of the characteristic blue colour of cobalt spinels.

SPECTROSCOPIC AND OPTICAL FEATURES OF SOME PINK AND BROWN DIAMONDS

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Sixty diamonds, both pink and brown, from the Argyle mine (Australia) were investigated. Surface and internal characteristics, gemmological properties, FT-IR, UV-Vis, CL and ESR features were taken into consideration. All specimens, resulting from the cutting of bigger diamonds, were rough, small and irregular in shape. Hexagonal depressions, trigons, fractures and dislocation planes were the most common surface features observed [1]. Anomalous birefringence was detected in all specimens. Signs of plastic deformation were mostly observed in brown diamonds that showed also an evident colour zoning.

Depending on the aggregation state of the nitrogen defects in the IR spectra, both pink and brown diamonds resulted type IaAB (mostly with B > A). Total nitrogen concentration was lower in pink specimens (< 100 ppm), while brown diamonds showed a B-defect concentration of 700 ppm. Only one brown diamond could be considered a "regular diamond" [2]. In all the other specimens a scarcity or absence of platelets was detected, loading to the conclusion that any platelets had undergone a more or less catastrophic degradation. All stones contained IR active hydrogen, but they could not be defined "H-rich diamonds" [3].

A broad absorption band, showing a maximum between 510 and 550 nm, governed the UV-Vis spectra. This band possibly relates to dislocations and it is certainly responsible for the pink or brown colour [4, 5]. Other important UV-Vis features were the 415 nm (N3 centre) peak and the 390 nm band, often superimposed on the N3 centre. The NIR spectra of brown diamonds showed a weak absorption peak at 4168 cm^{-1}, possibly due to the "amber centre", a feature only found in brown diamonds exhibiting "graining" [6], and containing nitrogen in the A form. The centre was confirmed by the ESR signal from the W7 defect, produced by a centre having the structure $N\text{-}C\text{-}C\text{-}N^+$.

Both pink and brown diamonds exhibited CL spectra consisting of two wide components centred at 450 nm and at 512-520 nm, showing superimposed specific emission systems [7]. CL emission confirmed the presence of lattice dislocations.

From structural and spectroscopic data, it was concluded that the examined pink and brown diamonds developed in a strongly N-impoverished eclogitic environment, suffered post-growth plastic deformation and probably annealing at geological temperatures for very long period of time.

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ALUMINUM MINERALS AND RELATED ARTIFICIAL MATERIALS: PREPARATION OF MICROSPHERES BY MEANS OF AN OXYHYDROGEN FLAME

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An oxyhydrogen flame Verneuil apparatus (Fig. 1) was used in a non-conventional way to produce translucent/transparent microspheres/hollow shells with diameters in the range 5-100 microns by melt quenching in water of fused ceramic Al_2O_3 and eutectic Al_2O_3-Y_2O_3 ceramic powders. SEM/EDS micro-analysis, powder X-ray diffraction and Differential Thermal Analysis (DTA) were performed on the microspheres/shells. Al_2O_3 spheres/shells formed are constituted by a series of transition-alumina phases together with a corundum phase. By annealing at 1400°C for 20 hours the transition-alumina phases disappear and only the corundum phase remains. Al_2O_3-Y_2O_3 starting powders were produced by a flame-combustion process to help formation of the amorphous phase during melt-quenching.

Amorphous spheres/shells were indeed obtained for compositions Y_2O_3 22 mol.% (Fig. 2) corresponding to a metastable eutectic point and for 25 mol.% Y_2O_3 compositions. Phase separated spheres containing δ-Al_2O_3 domains in a Y_2O_3-enriched YAG matrix resulted for starting composition of 15 mol.% Y_2O_3 corresponding to a hypo-eutectic composition near the equilibrium eutectic point at 18% Y_2O_3. The glass transition temperature of amorphous spheres was Tg = 880°C. The potential applications of the resulting materials as well as the didactical value of the present preparation approach are underlined relating it with previously published works [1].

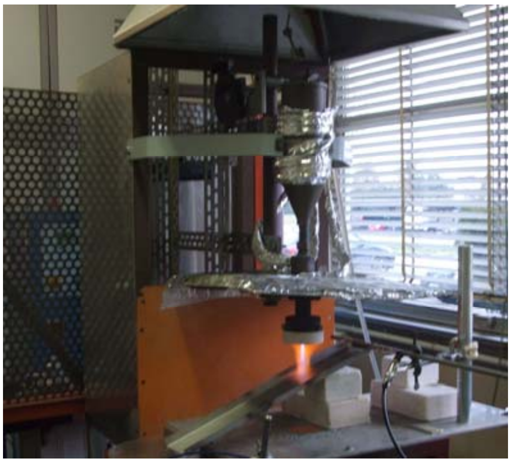

Fig. 1. Photo of the modified Verneuil apparatus used for melt-quenching.

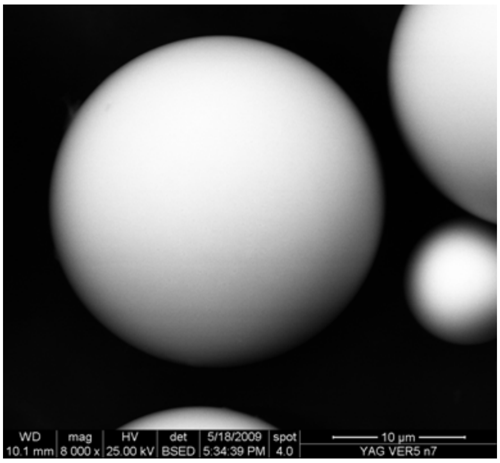

Fig. 2. SEM image of glassy $(Al_2O_3)_{0.78}(Y_2O_3)_{0.22}$ microsphere.

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CRYSTAL CHEMICAL CHARACTERIZATION OF ALEXANDRITE FROM ROYAL MINERALOGICAL MUSEUM OF NAPLES

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Alexandrite gemstones, belonging to $BeAl_2O_4$ chrisoberyl mineral suite, are characterized by *metamerism* property, mainly due to Cr^{3+} replacement within Al(1) and Al(2) sites [1]. The typical colours of this mineral are green grass under daylight, and raspberry red under incandescent light; chromatic changes, in any case, can arise as a function of impurity factors, like large iron amounts, solid and/or fluid inclusions: it is the so-called alexandrite effect [2]. Such particular feature donates to the alexandrite a high value within gemmological field.

The present Royal Mineralogical Museum of Naples gemstone comes from Tokowaya River mines, *ca.* 96 km east from Ekatherinburg, Urali Mountains, historical locality where in 1833 the first alexandrite gemstone was collected [3]. The introduction date within Museum is not known, but it was reported in the catalogue which Eugenio Scacchi compiled starting from 1885.

The specimen is a 6-peak twin made up by three different twins each other compenetrated with size of 3.5×5×2 cm, and a weight of 71 ct; in each twins is possible to notice the cross streaks. In daylight the specimen displays a deep bluish-green colour, while in incandescent light it displays a deep purple violet one; besides, under UV light (365 nm), it usually becomes transparent, while under short UV frequencies (254 nm) it is opaque [4].

The gemstone is also characterized by a strong pleochroism; in particular, under incandescent light it shows a red carmine colour along n_α optical direction, becoming yellow along n_β and green along n_γ ones; under daylight, it shows a purple violet colour along n_α optical direction, becoming pale yellow-green along n_β and bluish-green along n_γ. Besides, within the present alexandrite there are fluid and solid inclusions both primary and secondary with micrometric sizes; last, in a small region of the specimen there are iron oxide impurities.

Single crystal X-ray diffraction data were collected by means of Nonius Kappa CCD diffractometer equipped with a graphite fine-focus sealed tube. Unit cell parameters are: $a = 9.4003(15)$, $b = 5.4705(12)$, $c = 4.4343(7)$ Å. The structure was solved within orthorhombic space group *Pnma*, in good agreement with values from literature [5].

Quantitative chemical analysis of major and minor elements were carried out by means of WDS technique (Cameca SX50): average contents in Fe_2O_3 and Cr_2O_3 are, respectively, 1.326 and 0.299 wt.%; Si, Zn, Co, Ni, and Ca are in traces. Last, Be content was determined by means of an experimental spectroscopic technique, Laser Induced Breakdown Spectroscopy (LIBS) [6]; values are in good agreement with those obtained by difference in WDS analysis.

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SINGLE CRYSTAL X-RAY DIFFRACTION STUDY OF STRUCTURAL MODIFICATIONS INDUCED BY HEATING IN UNCOLOUR, BLUE AND YELLOW ZOISITE FROM MERELANI ARUSHA (TANZANIA)

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It is well known that the practice of heated gemstones in order to improve their colour and to enhance their value is very common. Systematic changes in the structures of minerals, such as changes in bond lengths and bond angles, which determine the degree of distortion of coordination polyhedra, are common during the heating process. Zoisite is a sorosilicate with idealized formula $Ca_2Al_3[Si_2O_7][SiO_4]O(OH)$, which is orthorhombic, space group *Pnma*. The crystal structure was determined by Ito [1] and Fesenko *et al.* [2], and later refined by Dollase [3]. It consists of one type of endless octahedral chains parallel to *b* with two distinct octahedral sites M1,2 and M3. These chains are cross by isolated tetrahedral SiO_4 (T3) and Si_2O_7 groups (T1 and T2) in the *a* and *c* directions. When zoisite is heated between 370-650°C, it becomes an intense sapphire-blue colour (variety tanzanite) [4]; this behaviour was explained in terms of change of the oxidation state of transition metal ions, such as V [5, 6]. The aim of this work is to study the structural modifications induced by heating in uncoloured, yellow and blue varieties of zoisite when heated. Crystals of zoisite from Merelani Hill, in the Arusha Region, were preliminarily characterized by XRF analysis to verify their chemical composition. TG and DTA measurements (heating rate 5°C/min) carried out under a constant flux of air using a STA 409 PC LUXX® - Netzch reveal that in all cases the weight loss is very low (~ 0.3%) and no deprotonation occurs. The UV-VIS spectra, recorded by using a Xenon lamp and an integrating sphere, indicated that the change colour in the yellow zoisite is related to the disappearance of the 22000 cm^{-1} band. Single-crystal X-ray data were collected on a Nonius Kappa CCD diffractometer (Mo*K*α radiation) at room temperature, and after heating at 500°C. Structural refinements of natural and treated crystals show no significant structural variation (Table 1).

Table 1. Unit cell parameters of natural and heated zoisites.

	Natural				Heated			
	a (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)	*a* (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)
Uncolour zoisite	16.2152(3)	5.5575(1)	10.0500(2)	905.67	16.2067(4)	5.5902(1)	10.1130(5)	916.22
Yellow zoisite	16.2068(2)	5.5577(1)	10.0536(2)	905.55	16.2037(2)	5.55330(5)	10.0428(1)	903.69
Blue zoisite	16.2140(3)	5.5546(1)	10.0422(2)	904.42	16.2099(2)	5.5543(1)	10.0380(1)	903.77

Increasing temperature enhances proton movement in the structure of yellow and blue varieties and consequently switching between two adjacent H positions.

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HYDROXYL INFRARED ABSORPTION OF GEM QUALITY RUBIES

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The use of infrared absorption in the region of stretching vibrations of X-OH groups (particularly from 3000 to 3800 cm^{-1}) has drawn more attention during the last two decades in gemmology. In this work a study of the vibrations in this range is presented for unheated natural rubies from different sources.

There are several works published on the hydroxyl absorptions in corundum ([1], and references therein). These absorptions are either due to inclusions inside the corundum or to their structural defects. We found that in natural ruby, patterns due to boehmite, diaspore, calcite, limonite, chlorite, kaolinite and mica inclusions are observed. A series of absorptions at about 3300 cm^{-1} because of hydroxyl defects is also observed.

A systematic study of all these absorptions is done in rubies to check the possible relationship between the absorptions and the geographical origin. Although there are few absorptions which are characteristic of only one geographical origin, some of them have not been observed in rubies of specific geographical origins yet.

Thus, the infrared absorptions with microscopic, spectroscopic and chemical analysis can give valuable clues for the origin determination of rubies.

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THE ORIGIN OF THE OPTICAL ABSORPTION OF MAGMATIC SAPPHIRES

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We present the results of optical absorption and light emission experiments (radio- and photo-luminescence) performed on blue coloured Type 2 sapphires of magmatic origin. These results, together with a detailed elemental analysis, clarify the role of metal species in the spectroscopy of this system. Specifically, we give evidence that in the iron-rich variety of natural sapphire, the 17500 cm^{-1} band (almost exclusively attributed until now to inter-valence charge transfer (IVCT) transitions $Fe^{2+} \rightarrow Ti^{4+}$ in face-sharing octahedra) may receive contributions from crystal field (CF) localized transitions of Cr^{2+}, Ti^{3+}, Cr^{3+}, and V^{3+} ions, while the absorption at around 20000 cm^{-1} arises from excitation to the ^2E state of Ti^{3+} ions, as we recently found in Type 1 light-blue iron-poor sapphires of metamorphic origin. The data also suggest that the absorption at about 14000 cm^{-1}, up to now attributed to IVCT transitions $Fe^{2+} \rightarrow Ti^{4+}$ in edge-sharing octahedra, is consistent with the contribution expected from the $^5T_2$ transition of Cr^{2+} in concentration of the order of 10^1 ppm (as estimated by comparison between the total chromium content from X-ray fluorescence and the Cr^{3+} concentration calculated from electron paramagnetic resonance EPR data). As regards iron sites, the intensity comparison of the weak spin-forbidden Fe^{3+} transitions in blue and yellow magmatic sapphires – the latter containing Fe^{3+} ions only – shows that Fe^{3+} sites are predominant, also when the optical absorption is dominated by the spin-allowed absorption band of Fe^{2+} ions responsible for the intense blue colour. A CF analysis of the whole spectrum is finally proposed, showing an interpretative scheme accounting for luminescence, EPR, elemental data, consistent with data on analogous systems.

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COMPUTERIZED MICRO-TOMOGRAPHY – A NEW TESTING METHOD FOR PEARLS

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Pearls of marine origin come mainly from bivalve molluscs, above all from the genus *Pinctada*. Pearls from other genera (Tridacna, Pinna, Pecten, *etc.*) are rare. Freshwater mussels produce pearls in Europe, North America and Asia. Abalone, Conch and Melo pearls come from marine gastropods.

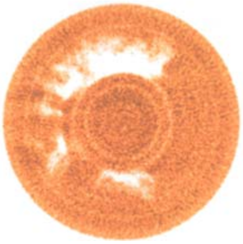
Since the early 20th Century, cultured pearls are produced, both of marine (Akoya cultured pearls, South Sea cultured pearls, Tahitian cultured pearls) and freshwater origin (Japan and above all China).

Natural pearls are built up of calcite prisms and outer layers of aragonite platelets in a concentric arrangement, cemented together by an organic substance (conchioline) that may also produce irregular secretions. Cultured pearls have similar structures unless they have an implanted mother-of-pearl bead.

X-radiography enables to take two-dimensional films or digital images of pearls that reflect the growth structure because calcium carbonate absorbs X-rays while organic substance within a pearl allows X-rays to pass through.

Computer tomography takes radiographs from many different directions when the tomograph turns in a circle around the pearl and irradiates it with X-rays. A special computer programme assembles the radiographs into a tomogram that allows a full three-dimensional view.

A pilot testing project with natural and cultured pearls from different sources was carried out with the equipment of the Computerized Tomography Center of PROMINTRO in Moscow. The examples show tomograms (from left to right) of a North German river pearl, a freshwater cultured pearl with a drilled bead from Japan and a Chinese freshwater cultured pearl without a bead.



From the test series it can be concluded that computer tomography delivers superior results to two-dimensional X-radiography. The method has the disadvantage that it is time-consuming and that the equipment is very expensive.

GROWTH MARKS APPLIED TO THE ORIGIN OF GEMMOLOGICAL MATERIALS: GROWTH DEFECT CHARACTERIZATION OF YELLOW SAPPHIRES BY X-RAY DIFFRACTION TOPOGRAPHY

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The study of structural defects performed on natural crystals such as hydrothermal quartz [1, 2, 3] and pegmatitic beryls [4, 5] showed that extended growth defects can be considered *growth marks* when characterizing minerals grown in the same conditions and differentiating them from others grown under different, although very similar, conditions. The *growth marks* concept has been recently employed also in studying tourmaline crystals from pegmatite pockets of Island of Elba (Italy) that exhibited a Mn-rich core (greenish), grown under pegmatitic condition, and a Mn-free elbaitic overgrowth (colourless), grown under the hydrothermal stage of the pegmatite crystallization [6, 7]. From all the aforementioned studies a common conclusion can be deduced: the crystallization under pegmatitic and hydrothermal conditions produces different growth defects. In particular, accordingly also with other previous studies [8, 9, 10] crystals or limited portions (overgrowth) grown under hydrothermal condition show dislocations. Instead, minerals grown under pegmatitic condition should be dislocation-free.

The concept of growth marks can be successfully extended to gem minerals. Actually, the study of the growth defects characterizing different growth environments can be really useful to determine not only the origin of stones, but also to distinguish between natural and synthetic gems.

In this work, three gems of yellow sapphire, oval brilliant cut, were studied by X-Ray Diffraction Topography (XRDT), using conventional source and Mo$K\alpha_1$ radiation. Although the X-ray absorption due to the increase of thickness in correspondence of pavilion, the obtained topographs show a high crystalline quality with an almost total absence of deformation fields associated to defects. This finding permits to exclude a synthetic growth that, generally, causes a high density of defects [11]. Thus, the results obtained permit to hypothesize that the studied gems have a natural origin. Moreover, the topographs taken until now show that the samples are dislocation free. This result permits to reject a growth mechanism by spirals and suggests some genetic considerations about the possible formation environments of natural corundum.

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SESSION 2.6

Medical Geology, food characterization and provenance

***Convenors*:**

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THE $^{87}Sr/^{86}Sr$ SIGNATURE OF SANGIOVESE WINE FROM THE CHIANTI AREA: CONSTRAINTS FROM A MICRO-VINIFICATION EXPERIMENTAL STUDY

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The use of radiogenic isotopes of heavy elements as Sr represents an innovative method to trace the geographical origin of wines.

Strontium has four naturally occurring isotopes. Three of them (^{84}Sr, ^{86}Sr, and ^{88}Sr) are non-radiogenic. The fourth, ^{87}Sr, comes, in part, from the natural β-decay of ^{87}Rb and its concentration in the minerals depends on the age of the rock and on the Rb/Sr ratio. Thus, every soil/rock system has a particular $^{87}Sr/^{86}Sr$ ratio due to the different bedrock characteristics.

It has been shown by several authors, how elements are taken up by plants with the same isotopic proportions in which they occur in the soils and in precipitations, so that $^{87}Sr/^{86}Sr$ isotope ratio does not change during biological processes and reflects in plants the environment of growth: bedrock, soil, and soil water [1, 2, 3]. Isotope abundance ratios are then excellent provenance indicators or tracers of wine origin, on condition that no fractionation of Sr isotopes occurs during the vinification process [1].

Our work has focused on the isotopic analysis of Sangiovese wines produced by grapes coming from 11 experimental vineyard parcels located in the Torricella area (Brolio, Siena), characterized by different soils and bedrocks. The vinification was performed under a controlled laboratory environment following a procedure that rules out possible adulteration or contamination. For isotopic analysis with thermal ionization mass spectrometry (TIMS) the analytical procedure has be calibrated in order to purify the element of interest from the matrix, prior measurement. Thus, each wine sample (about 5 ml) has been dried and treated with a 30% hydrogen-peroxide solution and suprapure concentrated nitric acid, in order to remove the organic fraction. Then, the element selection has been performed using a special resin, with high Sr-recovery efficient, loaded in high purity chromatographic micro-columns.

Our results demonstrate that the $^{87}Sr/^{86}Sr$ isotopic ratio is well distinct among wines obtained from grapes grown on different soil, but, more important, data show how every wine isotopic signature is preserved among different years. In conclusion, we verify that the method can be applied as a possible good wine tracer, for same wine-making process, in a specific region.

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TRACE AND ULTRATRACE ELEMENTS IN GRAPES: POSSIBLE APPLICATION FOR GEOGRAPHICAL TRACEABILITY

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Wine is among those products in which a scientific system could be used to reveal its origin area, since its qualitative and organoleptic characteristics are unavoidably linked to the territory. The reference of a product to a territory is not only associated to the pedologic characteristics, but refers to the synergistic interaction between soil, climate and winemaking traditions that determine the unique geographic area in which the grape has grown.

At the present time there are many studies on food traceability. For example for the olive oil the research is aimed to find out a link between the territory of origin and the product, analyzing the relationship of stable isotopes of carbon in the numerous fatty acids that constitute the saponificable fraction in the oil [1] and within the sterol [2].

Other studies process the data obtained from ^{1}H NMR spectra using chemometric methods [3, 4] or using the oxygen isotope ratio, which was determinant to detect possible dilutions of the wine, but not sufficient for the traceability [5]. Many of these studies revealed that climatic and biological factors, such as temperature, rainfall, type of irrigation water, age of the vineyard and the vintage days (all parameters change over time) are variables that, in some cases, may lead to errors in determining the area of origin. The georeferencing of grapes, obtained by the isotopic ratios of light elements is therefore not exempt from problems.

The aim of this work is to characterise specific parameters in grapes, based on the assumption that these markers, linked to the territory, must be present in the soil and subsequently inherited by the grapevine.

Euganei Hills (NE of Italy) are an ideal test site because in this zone there is a high quantity of vines farms in soils with a high geochemical heterogeneity. Concentration of major (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and trace elements (Ba, Ce, Co, Cr, La, Nb, Ni, Pb, Rb, Sr, Th, V, Y, Zn, Zr, Cu, Ga, Nd, S, Sc) on 20 samples of soils (collected in a range of 30-40 cm of depth) has been analyzed by XRF. Moreover ICP-MS analysis has been carried out on wine grapes samples, with more attention on rare earth elements. In the investigated areas the grapes have shown typical concentration ratios of some trace and ultratrace elements suitable to identify the production areas.

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UNDERSTANDING THE THERMAL TRANSFORMATION OF SERPENTINE MINERALS

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Serpentine minerals are important components of the oceanic crust and play a chief role in lithosphere dynamics. Their structural and mineralogical modifications under increasing temperature have major implications not only in petrology but also in industry and health. For example, the use of chrysotile in the asbestos industry represents a reason of concern due to the possible development of pulmonary diseases after inhalation. Thermal behaviour of serpentines has been the subject of many studies, with particular attention to chrysotile because of the obvious implications in the asbestos issue [1, 2]. In this work, X-Ray powder diffraction (XRPD) studies were combined with Transmission Electron Microscopy (TEM) observation to describe the process of transformation of the serpentine polymorphs at high temperature in view of a possible recycling of the transformation product, especially chrysotile. The samples investigated in this study are: i) lizardite from dark-green, massive veins outcropping in the Monte Fico quarries (Elba Island); (ii) antigorite which occurs from pale-green, splintery veins in massive serpentinites from Elba Island; iii) chrysotile standard asbestos SRM1866A provided by NIST. It was observed that the thermal transformation of chrysotile into forsterite and enstatite takes place directly, but this does not occur in antigorite and partially in lizardite. As a matter of fact, in the latter it was observed a metastable transition phase with a characteristic peak at about 9 Å. Rietveld refinements (Fig. 1) and TEM observation confirmed the presence of a talc-like phase in antigorite and lizardite at 800°C.

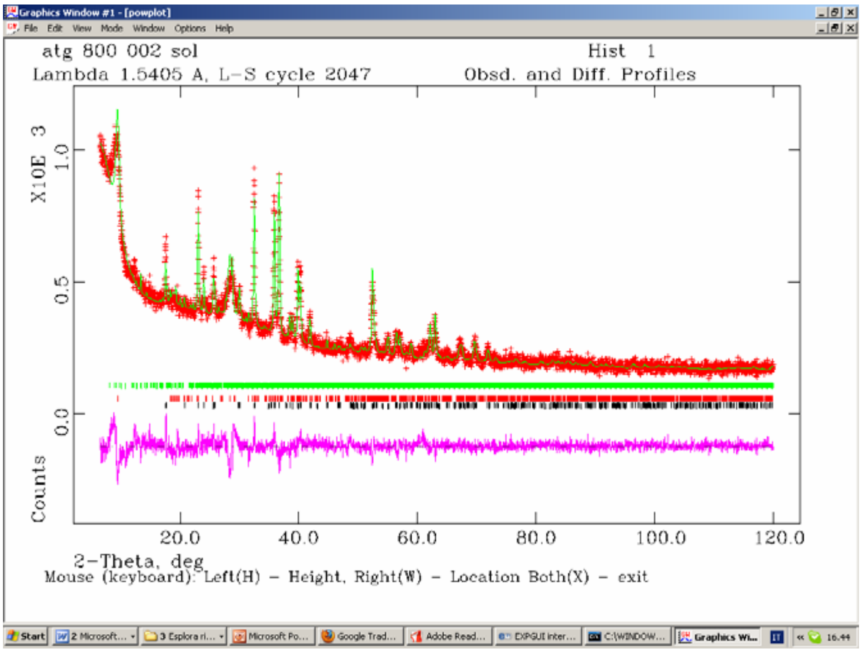

Fig. 1. Rietveld refinement of the antigorite sample heated at 800°C

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X-RAY MICRODIFFRACTION AND URINE: A NEW ANALYSIS METHOD OF CRYSTALLURIA

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Crystalluria refers to crystals being in urine. The qualitative and quantitative analyses of these crystals have clinical significance in the diagnosis and prognosis of urinary calculi formation (urolithiasis). The aim of this work is to provide an accurate methodology to better analyze the crystalluria in patients with urolithiasis to help in a proper evaluation and treatment of the disease.

The procedure involves an urine collection, the separation of the solid residual, and its analysis by X-ray diffraction.

1000 g of urine has to be collected and readily centrifuged for 30 minutes at 4500 rps. After the supernatant has been thrown away, residual has to be washed once by distilled water. After washing, the residual has to be dried at 50°C for 24 h. The residual is then ground and analyzed by X-ray diffraction. The data collection has to be carried by a microdiffractometer in order to analyze very low amounts of residual. The sample holder can contain until 30 mm^3, but a fine analysis can be carried out with less amount too.

In this work a Rigaku D-max Rapid microdiffractometer was used. This instrument is equipped with an image plate detector, a flat graphite monochromator, a CCD camera for the positioning of the sample in the path of the X-ray beam. The analyses were carried out at 6° of omega angle fixed, 180° of rotation range of phi angle, using Cu$K\alpha$ radiation, power 1.20 kW (40 kV and 30 mA), collimator 100 μm of beam diameter, time 2 h. The μXRD data were collected as two-dimensional images. The quantification of the mineral phases occurred in the residual has to be obtained using a standard phase. In particular a collection of corundum NIST 676 standard was carried out at the same instrumental conditions. The 10% of the standard pattern was added to the 90% of the pattern obtained by the residual sample using the Rigaku R-Axis Display software. The spectrum obtained was converted into 2θ-I profiles and quantitatively refined by Rietveld method.

This kind of analysis should be carried out as soon as possible: at room temperature the residual gets to increase both its amorphous and crystalline phases; besides urine cannot be frozen because weddellite crystallizes spontaneously at +4°C, whatever the phases of the initial sample.

Examples of crystalluria containing weddellite, struvite, uric acid are shown.

LIFESTYLE INFLUENCE ON TRACE ELEMENT CONTENTS IN HUMAN SCALP HAIR OF YOUNG RESIDENTS IN DIFFERENT URBAN CONTEXTS. PRELIMINARY RESULTS

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A causal relationship between earth material and human health, although not always proven, is highly plausible because many chemical elements in rocks and soils are directly inhaled by respiration or transmitted, *via* air, water and vegetation, into food chain and then to human body. It is well known that metals and metalloids may result essential to biochemical and physiological functions, but it is also well known that health problems may derive from either dietary deficiencies or excesses. Among the techniques employed to assess the exposure of living organisms to metals and metalloids present in the environment, the human biomonitoring has attracted the attention of investigators over the past decades. More specifically, the human biomonitoring is a method for assessing human exposure to chemicals by measuring the searched chemicals or their metabolites in human tissues or specimens, such as blood, plasma, serum, breast milk, urine, teeth and also hairs. However, some of these specimens may not always be the best indicators of element intake because of the homeostatic system of control in the human body. Human hairs seem to be particularly appropriate as they offer several advantages. Hairs are stable and their composition does not change over short time period. Furthermore, sampling procedure is very easy, requires no specific professional skills, is painless and non-invasive. The present study deals with the trace elements content of hair samples from the scalp of 136 young students, between 11 and 14 years of age, of female and male gender, resident in the metropolitan area of Palermo (80 samples) and in a small rural town, Altavilla (56 samples), 20 km far from Palermo. The concentrations of 18 elements (Al, As, Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Se, Sr, U, V, Zn) in hair were determined by ICP-MS. In order to eliminate external contamination, each hair sample was firstly properly washed. The obtained results were in line with the ranges of values published in other studies. The most abundant elements resulted Zn, Cu, Al, Sr, Ba, Pb in Palermo as well as in Altavilla, although with different abundance orders. All the remaining analyzed elements were below 1 ppm. Zn is known to be an essential element recognized in more than 300 enzymes depending on this element for catalytic, structural, and regulatory functions. Cu is considered an indispensable catalytic cofactor in redox chemistry for proteins. Al and Sr are typical geogenic elements; their different abundances in Palermo and Altavilla samples are related to the different lithological site, carbonate rocks in Palermo and calcarenites-clays at Altavilla. Sr is also strictly related to calcium content in bones. The highest levels of most elements were found in Altavilla samples: this may indicate a possible different exposure due to different lifestyles, as evidenced by Al and Pb. In fact, children living at Altavilla spend more time outdoors than those living in Palermo. The higher Ba concentration in children from Altavilla may be also related to the Ba content of local drinkable water. Significant gender-related differences were found for certain elements. This was the case of Sr and Zn, more abundant in female subjects, and Cr, Li, Pb, Sb and U which were more abundant in males. When the elements are subdivided in essential and not essential, and their ratios with respect to aluminum are compared with those in air particulate matter and road dust, it appears evident that some elements typical of anthropogenic sources (Cd, Pb and Sb) are taken by $PM_{10-2.5}$, $PM_{2.5}$ and the finest fractions of road dust. Data concerning subjects exposed and not exposed to passive smoke are also reported. Further, it has been examined the relationship between exposure to passive smoke and concentration of nicotine (and its metabolite cotinine) in hairs. A first result of this work is that the reported data and concentration ranges can be used as guidelines for to evaluate environmental or occupational exposure to these elements.

CALCIFICATION OF THE HUMAN HEART VALVES: A MINERALOGICAL APPROACH

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Normal physiologic processes result in development of mineralized tissue. Bones and tooth enamel are the main example of biominerals [1, 2]. Pathologic processes lead to calcification of the atherosclerotic plaques, kidney and salivary stones and other pathologic deposits. Most of these seem to be constituted from a mixture of calcium phosphate phases [3] but their formation mechanisms are not completely known. In cardiac pathology, calcification of heart valves can be advanced by a congenital malformation or an infectious process or related to the senile degeneration.

Pathological mineral deposits occurring in human cardiac valves were studied using Polarizing Microscopy, Scanning Electron Microscopy (SEM-EDS), Electron Microprobe (EMPA), X-Ray Powders Diffraction (XRPD), Infrared Spectroscopy (FTIR). Samples were obtained as surgical waste from thirty patients undergoing valvular replacement in case of severe aortic and mitral stenoses.

The experimental results showed that the mineral phase grown in human cardiac valves is a calcium phosphate with poor crystallinity. It develops as nodules in the organic matrix (Fig. 1a). The FT-IR spectra may be used to infer the presence of $(OH)^-$ and CO_3^{2-} groups (Fig. 1c). The ν_3 region of the CO_3^{2-} group in the infrared spectra has a saw-tooth profile similar to sample PC18, a synthetic type A-B CAp [4], but in samples of aortic valves *a*-parameter is smaller and the *c*-parameter is greater than those of PC18 [*i.e.* TV12 a = 9.4165(8), c = 6.8951(7) Å; PC18 a = 9.4803(3), c = 6.8853(3) Å] probably due to substitutional carbonate groups in phosphate positions which cause a shrinkage in the *a*-parameter.

Pathological phase investigated can be considered a bioapatite as the inorganic component of bone and tooth enamel, even if it possesses unusual morphologies (Fig. 1b) for a calcium phosphate and a Ca/P ratio unlike that of normal mineralized tissue.

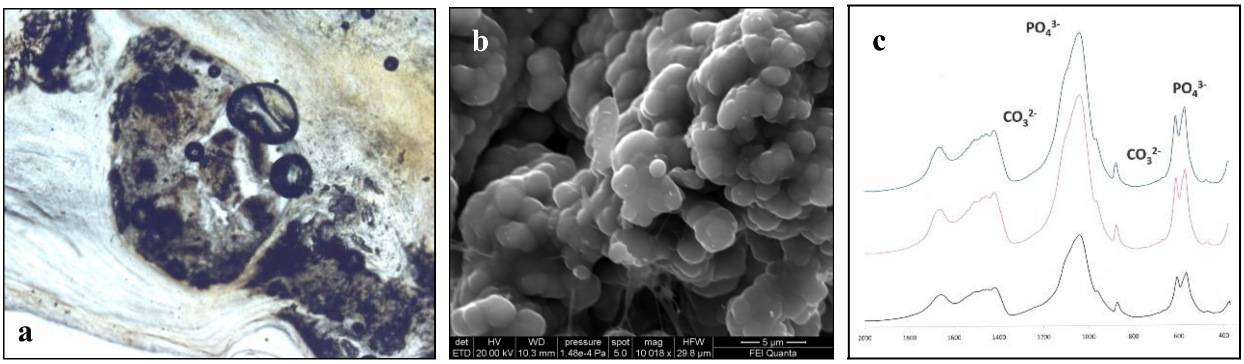

Fig. 1. (a) Thin section of mineralized aortic valve observed using polarizing microscope in transmitted light. (b) SEM image of biomineralization. (c) FTIR- spectra of three samples.

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SOLID-LIQUID INTERACTIONS IN HUMAN LUNG SYSTEM ENHANCED BY YTTRIUM AND REE DISTRIBUTIONS IN BRONCHO-ALVEOLAR LAVAGES

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The eruption that took place during the 2001 on Mount Etna was characterised by a violent explosive activity and by the largest production of pyroclasts over the last 300 years. The fall out affected the densely populated urban area of Catania.

In order to assess the effects of solid-liquid interactions between lung fluids and atmospheric particulate matter, distribution of yttrium and rare earth elements (YREE) were investigated in lung fluids collected with the broncho-alveolar lavage (BAL) procedure on a selection of exposed individuals.

Results pointed out that Shale-normalised YREE patterns in BAL have a “V shape” characterised by depletion in intermediate REE (from Nd to Tb) compared to the weak enrichment of heavy REE and a strong enrichment in Y and light REE (La, Ce). Comparing the flat YREE distribution in the soluble and glass fraction of ejected volcanic ash, we propose that complex interactions between volcanic particles and lung fluids took place; for instance, inhalation of volcanic particles might affect co-precipitation of YREE-phosphates in lungs.

This research highlights that the combination of YREE fractionation in bronchial fluids can represent a potential tracer of exposure time to atmospheric fallout and may reveal as a diagnostic tool in monitoring the environmental stress.

IDENTIFICATION OF HIGH RADON AREAS AND GEOLOGICAL ASSESSMENTS IN SOME ITALIAN REGIONS

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The indoor radon exposition is internationally known as a health hazard; so in many countries specific laws and regulations and so-called radon - risk maps have been introduced. In Italy the radon exposure legislation regards only general workplaces (D. Lgs. n. 241/00 [1]) and only one national survey in the 90's has been conducted in dwellings on large scale by APAT, ISS and ARPA regional agencies [2]. In absence of guidelines, few Italian Regions have started surveys for the identification of "radon prone areas", with independent standards and protocols and this involves a bigger uncertainty on the definition of a national risk map failing guidelines.

In the present work a standardized methodology for indoor radon measurements has been set up in collaboration with U-Series Srl (Bologna) and a passive measurement technique (solid state nuclear track detectors) has been developed. This technique has been validated through an inter-laboratory comparison conducted by the German Federal Office for Radiation Protection (BfS) in 2008.

An indoor radon monitoring survey has been conducted in all Italian Regions with the developed methodology and 5425 measurements have been elaborated to obtain the annual average radon concentration in regional scale. For the survey, the detectors were installed in underground rooms in workplaces and the measurements were performed over one solar year. The data also permitted to verify the relapse of seasonal fluctuations on radon concentrations.

Indoor radon concentrations resulted generally higher (annual mean radon concentration of 110 Bq/m^3) than the concentrations obtained in the National Survey (annual mean radon concentration of 70 Bq/m^3), mainly as a consequence of measurements only in underground rooms.

Only for the Italian Regions with the largest number of sampling (Lombardia, with the case studies of Milano Province and Milano city, Emilia Romagna, Toscana, Puglia) the data have been georeferenced and elaborated, using geo-statistical technique, to produce a map of annual average radon concentration. Then the maps have been integrated with geological knowledge of highest concentration macro-areas identified in order to better determine them, pointing out not negligible radon concentrations also in traditionally no–risk zone. In particular, the correlation between radon concentrations and some geological features has been proved in the traditionally no-risk zone of Milan Province with the city of Milan; some hypotheses have been formulated to understand the geological origin of the radon source.

The application of the developed methodology will be useful to give advices to fill legislation gaps or to draft urban development plans.

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PRESENCE OF OLIVINE IN ASBESTOS-CONTAINING MATERIALS WIDELY USED IN THE PETROCHEMICAL INDUSTRY

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Asbestos, used in Italy up to 1992 both for civilian and industrial purposes, had been widely used also in the petrochemical industry and shipyards in the area of Priolo and Augusta, Syracuse province (Sicily, Italy).

Once the asbestos sheeting had been identified as a commonly used material, as insulating material in hot-fluid lines, as anti-spark protection in soldering processes and as wrapping in thermal treatments, then the operation temperatures were reproduced under laboratory conditions in order to assess the variations in mineral phase composition, fabric and mechanical properties by means of various analytic methods. Thermal treatments were carried out by progressive heating the sheets to 110, 250, 550 and 750°C.

Simple observations by light microscopy showed the occurrence of significant changes both in texture and sheet consistence even at low temperatures (*i.e.* 110-250°C) with increasing textural modification as a function of the treatment temperature.

The mineralogical investigation carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods confirmed that not only physical, but also mineralogical modifications occurred. The chrysotile fibres, making the fabric of asbestos sheets, controlled the morphology of the newly formed phases (talc and forsterite) which appeared as the result of metamorphic transformations due to the increasing thermal treatment temperature (> 550°C). SEM analysis showed that a fibrous aspect was retained for the olivine aggregates instead of the typical prismatic habitus. This can be explained by a topotactic mechanism (*i.e.* ionic diffusion of Mg and Si, leaving the oxygen lattice unchanged) acting during the transformation from the chrysotile to olivine.

XRD confirmed that the chrysotile-to-olivine transformation was completed at 750°C. The SEM images from the same samples showed that a relatively undisturbed fibrous structure was still observable in agreement with the high degree of pseudomorphosis by which the olivine (sub-micrometer sized) crystals were oriented to maintain the microscopically-fibrous aspect of the parental phase. All these features are consistent with the rapid conversion of chrysotile to olivine through the topotactic mechanism.

Very little is known about the chemical, physical and mechanical properties of olivine fibres obtained from chrysotile. It is likely that, if inhaled, their bio-durability would be different compared to that of chrysotile rising questions to their potential health hazard for human beings.

Therefore, doubts remain as to whether working operations carried out in conditions which have involved exposure to olivine fibres may have led to pathological consequences similar to those caused by exposure to asbestos.

SESSION 2.7

Innovative instrumental methodologies for Earth Sciences (communications by supporter Societies)

INNOVATIVE GRADIENT CAPILLARY ION CHROMATOGRAPHY

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The ultimate innovation in IC is the capillary scale. Until now the HPIC was used to be performed on standard analytical 4 mm or narrow bore 2 mm column because the hardware (pump, detectors cells) and related fluidics was not able to deliver flow rate below 0.2-0.1 µl/min. Nevertheless commercial capillary diameter columns were not available. The described approach for capillary HPIC is based on another important recent innovation in IC hardware, the Electrochemical Eluent generation [1]. Such technology allow to generate the necessary ion strength for the isocratic and gradient ions elution inside of an ultrapure water stream, in a narrow void volume (microliter scale) applying a potential, so the current value controls the eluent concentration. The dimension of Electrochemical Eluent Generation fluidic is suitable to deliver flow rates as low as 10 µl/min particularly in gradient elution because the low gradient delay volume. Low eluent consumption make it possible to leave the system always on consuming only 5 liter of water/year; sensitivity and extended eluent concentration to 200 mM seems to be other advantages of a capillary/eluent generation system as well as the little sample volume used (400 nl). Packed 0.4×250 mm and 0.25×250 mm. Monolithic commercially available columns was used in the work to perform common application at Capillary scale.

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RAMAN SPECTROSCOPY: A POWERFUL TOOL FOR THE IDENTIFICATION OF MINERALS IN NON-PREPARED SAMPLES AND IN THIN SECTIONS

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The Raman effect has been discovered in 1928 by the Indian Physicist C.V. Raman, which observed that when a radiation with specific wavelength is directed onto a material, a small part of the radiation diffused by the sample lies at wavelengths slightly different from that of the incident beam. In particular the diffused radiation is constituted by: a) Rayleigh diffusion, very intense, at the wavelength of the incident beam; b) Stokes lines with wavelength lower with respect to that of the incident beam; c) anti-Stokes lines with wavelength higher with respect to that of the incident beam. Stokes lines are more intense than anti-Stokes lines, therefore they are used to describe the Raman spectrum of a sample. The shift between the wavelength of the excitation source- laser beam- and of the Raman bands is independent from the excitation wavelength, but it is directly dependent on the vibrations of the chemical bonds constituting the analyzed sample: the Raman spectrum is therefore characteristic for each material and it constitutes a "molecular fingerprint" for the identification. Moreover using micro-Raman spectroscopy, with an optical microscope coupled to the spectroscope, it is possible to select the area where the laser beam is addressed and, on heterogeneous samples, to register the spectrum of the different constituting phases.

Recent works carried out using an HORIBA Jobin Yvon LabRam HR 800 μ-spectrometer, equipped with an Olympus BX41 microscope, two interchangeable lasers working at 632.8 and 784.3 nm and a CCD air-cooled detector, demonstrated that:

1. Raman spectroscopy allows to identify the mineral phase also when the chemical and crystallographic aspects are very close, as the minerals belonging to the family of the amphibole asbestos [1] or amphibole phases not yet regulated [2, 3];
2. it appears the only technique allowing the certain and quick identification of the serpentine phases – antigorite, lizardite, chrysotile – in massive samples and/or in thin sections [4, 5]. This is very important because only the chrysotile, among the serpentine phases, is considered by the law an "asbestos" and requires remediation;
3. it is a quick method to identify different phases constituting a sample, a rock, and hand-made materials [5, 6, 7, 8], allowing to know also the morphology of the different constituting phases;
4. it is easily applicable also to study inclusions in minerals allowing recording the spectrum from solid, liquid and vapour phases co-existing in the inclusion [9];
5. it allows the identification of mineral phases in histological sections from patients affected by important respiratory diseases [10].

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