GEOITALIA 2011
Ottavo Forum Italiano di Scienze della Terra
Torino, 19 - 23 settembre 2011

Nelle pagine seguenti vengono riportati alcuni degli abstract presentati al congresso biennale della FIST “GEOITALIA 2011 - Ottavo Forum Italiano di Scienze della Terra”; il forum FIST, come avviene da sempre, ingloba l’annuale congresso della SIMP.

A seguito di un accordo con la presidenza della FIST, si è ritenuto utile includere in questo volume di Plinius tutti gli abstract delle sessioni di maggior interesse per i Soci SIMP. Sono state selezionate quelle sessioni tematiche in cui il convener principale (indicato da un asterisco nelle pagine seguenti) afferisce ad uno dei settori scientifico-disciplinari di ambito SIMP (GEO/06, GEO/07, GEO/08, GEO/09), e quelle in cui almeno uno dei conveners è socio della SIMP, più naturalmente le sessioni disciplinari dei settori sopra elencati.

Si sottolinea che questo non rappresenta in alcun modo – nemmeno parzialmente – il volume ufficiale degli abstract del congresso: quest’ultimo viene pubblicato a cura della FIST (Epitome, vol. 4). Qui si è ritenuto solo di rendere un servizio utile per i Soci raccogliendo un sottoinsieme (anche se piuttosto ampio) degli abstract presentati a “Geoitalia 2011”. Gli abstract vengono pubblicati così come sono stati ricevuti, ad eccezione di piccole correzioni e modifiche editoriali.

Si ringraziano i Conveners che hanno inviato gli abstract delle loro sessioni e Grazia Martelli per la collaborazione.
Sessione tematica D3:
Metalli pesanti nell’ambiente: sorgenti, rilascio, trasporto, immobilizzazione, trasferimento alla biosfera

Conveners:
Enrico Dinelli (Università di Bologna) *
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UPTAKE OF As(V) FROM AQUEOUS SOLUTIONS BY Zn-Al SULPHATE LDHs: FIELD EVIDENCES AND LABORATORY STUDIES

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Layered double hydroxides (LDHs), a group of compounds with general formula $\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2(\text{An})_{\text{ch}} \cdot y\text{H}_2\text{O}$, have a high anionic exchange capacity (AEC), which can widely vary as a function of their composition. The potential use of LDHs for As removal from contaminated mine water is based on the fact that the aqueous speciation of As under natural oxidizing conditions is dominated by oxyanions such as $\text{H}_2\text{AsO}_4^-$ and $\text{HAsO}_4^{2-}$. In this study we investigated the efficacy of natural and synthetic Zn-Al sulphate LDHs in removing As(V) from water solution in batch experiments. This choice ensued from field investigations, which pointed out the capacity of natural Zn-Al sulphate LDHs in attenuation of dissolved As content in NAMD (Net Alkaline Mine Drainage) of the old Baccu Locci mine (southeastern Sardinia, Italy).

Preliminary results showed that Zn-Al sulphate LDHs are effective removers of As(V) from water solutions through anionic exchange with sulphate in the interlayer, while minor amounts of As(V) are likely removed by surface adsorption. The efficiency of As(V) removal increases with Zn/Al ratios in LDH, because of the reduced ionic charge of the metal-hydroxide layers that facilitates the release of sulphate to solution and the entrance of arsenate in the interlayer.

In the laboratory experiments with synthetic LDHs, we used As concentrations of several orders of magnitude higher than found in the field at Baccu Locci. However, experiments with natural LDHs showed a similar capacity in removing As(V) from water solution, indicating that their potential exchange capacity is only partially exploited in the natural system.

The AEC shown by Zn-Al sulphate LDHs encourages further investigation of more complex aqueous systems and different inorganic pollutants.
UNUSUALLY HIGH CONCENTRATIONS OF BERYLLIUM BACKGROUND VALUES IN VOLCANIC ROCKS OF LAZIO:
GEOCHEMISTRY AND MINERALOGY

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Beryllium is widely distributed in soils at low levels (crustal abundance 2-6 mg/kg), but it can also occur naturally in higher concentrations in a variety of materials exploited for many industrial applications. Unfortunately, beryllium is also one of the most toxic natural elements and is known to be a human carcinogen.

We report and analyze a diffuse, unusually high (up to 80 mg/kg, average approximately 18 mg/kg), natural occurrence of beryllium in pyroclastic layers related to the Pleistocene activity of the Vico volcano (northern Latium).

The naturally occurring beryllium content in most of the studied samples is extremely high and even greater than that found in sites contaminated by the accidental release of beryllium into the environment by industrial activities. Only 8 out of the 120 analyzed samples gave values below the Italian limit for potentially unacceptable risk for industrial soil-use (10 mg/kg); in no case values below the limit for residential soil-use (2 mg/kg) were observed.

Additionally, experiments to define Be leachability have been carried out for selected samples, providing evidence of significant mobility in contrast with data presented in the literature that indicate beryllium as an element with low mobility in oxidising surface environmental conditions. This is a crucial point to consider, because a relatively high mobility under certain pH and redox conditions involve a significant risk factor.

The geochemical behavior of the element explains the anomalous Be concentration values because its incompatibility in common rock-forming silicate minerals is concentrated via fractionation during magma crystallization. An additional contribution may be related to the volcanic late-stage fluids permeating through the emplaced rocks.

Combined mineralogical (optical microscopy, SEM-EDAX, EMPA and X-ray diffraction) and geochemical analyses suggests that the higher beryllium concentration in pyroclastics and associated soils are related to the presence of finely dispersed Be-containing minerals, such as gadolinite (Cámara et al., 2008), or hellandite-group minerals (Oberti et al., 2001). However, the possible presence of Be in volcanic glasses is also presently under investigation.

Finally the occurrence of such natural high background concentrations of potentially harmful elements, as it is the case for beryllium studied here, highlights the need for systematic geochemical studies and mapping to produce multi-purpose reference databases for risk assessment and land management.

NEW METHODOLOGIES FOR THE DEFINITION OF SOME HEAVY METALS ORIGIN IN SEDIMENTS: A CASE HISTORY COMING FROM AN APPLICATION IN PONTINA PLAIN

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Metal elements like Cr, V, Pb, Tl, U, As are often present with high concentration in soils and one of the most frequent problem coming out in environmental applied geology is to set up if this concentration is referred to the background of the soils, or it is due to anthropogenic activity, as in many cases it is requested to dig and move the soil in the aim of build a new work. In this framework a correct geochemical characterization of soil outcropping in the work area, is needed to better understand the actual nature of this elements concentration. The natural chemical composition of soils depends on the mineralogical structure of rocks they come from and on the weathering processes these rocks have been subjected in the geological time. As a matter of fact to establish the real health state of a soil and its potential contamination state it’s very important to set up the background values of some heavy metal elements present in it. These background values can be reached by different methodologies, most of them are based on statistical elaboration of data referred to chemical composition of the soil under study. In the last years it has been outlined, on the other hand, the importance of the application of geochemical parameters to understand the actual origin of these elements in the soils.

In the case history under study, referred to a site placed in Pontina Plain, in the South Latium Region, were sedimentary deposit coming from the weathering of volcanic rocks, it has been set up the geological and hydrogeological framework of the area, in the aim of investigating the origin of the natural presence of some elements. Than, it has been made the granulometric analysis to set up their geometric distribution and separate the fraction minor than 2 mm, which has been used in the chemical analysis as it is asked by the italian law. Chemical analyses have been carried on for the determination of the concentration of Cr, V, Pb, Tl, U, As and the other major elements which are the most important constituents of sediments, outcropping in this area. Geochemical analyses results have been, than, elaborated by statistical methods following the italian guidelines, released by ISPRA, referring to the definition of groundwater and soil background values definition. The background values output by the statistical elaboration, have been compared by the results come out by the application of geochemical methods for the definition of the heath state of the soil. These methods employ two different parameters the Igeo, (Müller, 1979; Förstner & Müller, 1981) which an accumulation index of metals in the soil and the EF, Enrichment Factor (Müller, 1969; Forstner & Müller, 1973). These two parameter, to be calculated, need the values metal concentration of in samples coming from the top-soil (20-30 cm under the topographic level) and from the sub-soil (at least 90-100 cm under the topographic level). The two different depth of sampling the soil are needed in the aim of analyzing also soils which are certainly not affected by anthropogenic activity. The comparison of results, reached by different methods to set up the background values of some metals in the soil, is discussed in this paper, to highlight as the application of geochemical methods can give more effective indications on the actual health state of the soil, and on the possible anthropogenic impact, as they can better represent the real history of the sediments, and the geological, geochemical and pedological processes involved in their composition.
A research agreement was approved in 2009 among the Tuscany Region, the Institute of Geosciences and Earth Resources of CNR based in Pisa and the Tuscan Universities of Florence, Pisa, and Siena, for the implementation of a research and innovation project in the field of environmental geochemistry, named “Geobasi Toscana”. The aims of this two-year project are the determination of the natural geochemical baselines for several substances, some of which are potentially harmful, as well as the reorganization and elaboration of all available geochemical data for natural waters (including surface-, ground-, and transition-waters) and active stream sediments. The “Geobasi Toscana” project continues along the path opened in 2004-2006 by the “Geobasi” project, which was funded by the ministry of the University and Scientific Research of Italy and involved several Italian universities to tackle the complex meaning of elemental compositions in different geo-environmental matrices by means of an integrated multidisciplinary approach. In turn, the roots of the “Geobasi” project are found in the guidelines outlined through a previous APAT-CNR research agreement, whose main outcome is the National Geochemical Archive of Italy (Ottonello, 2008). In this reference framework, it was possible to test innovative approaches in geochemical mapping during the development of the “Geobasi Toscana” project. These methods were then applied to study the behavior of Cd, Hg, Ni, Pb, As, and Cr in the active stream sediments of the Siena area as well as the distribution of other parameters, including U, Cl, SO₄, and Hardness in the fluvial waters of the whole region. Analytical data used to study stream sediments refer to 417 samples collected in the Siena province over a total surface area of 2000 km² approximately, with a density of 1 sample each 5 km². Analytical data of 949 fluvial water samples come from CNEN geochemical surveys carried out in the sixties. They were processed using both deterministic and geo-statistical approaches. In particular, methods of spatial analysis developed for studying compositional data were applied. In this type of data (percentages, parts per million, molar fractions, etc.), each variable represents a given proportion of a total, which is fixed a priori. From the geometric point of view, compositional data does not occupy the real space, whose dimensions are equal to the number of variables, but are situated in a restricted space, known as simplex (Aitchison, 1986), which is part of the real space. This constrained, non-Euclidean geometry causes several problems if data analysis is approached using the methods of classic statistics. In this research works, new graphical and numerical methods were therefore proposed, respecting the geometric peculiarities of the sample space. Results were discussed in the light of the geochemical behavior of the considered elements and taking into account the geo-lithological characteristics of the investigated areas.

ANOMALOUS ARSENIC CONCENTRATIONS IN SOILS FROM THE VITERBO AREA

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The presence of anomalous concentrations of As in the groundwater of the volcanic complex of Monti Cimini (Viterbo, Italy) has been documented in literature by a number of papers (Cremisini et al., 1979; Vivona et al., 2007; Angelone et al., 2009). Specifically, Angelone et al. (2009) ascribed the As enrichment of the aquifer to deep thermal waters belonging to the hydrothermal system active in this area.

Thermal waters in the Viterbo area are known to precipitate calcite, as a consequence of CO₂ degassing, when hydrothermal fluids emerge to the surface. The continuous precipitation of calcite led to the formation of a number of travertine plateaux having variable extensions: one of the largest is located a few kilometres westward of Viterbo, in the so called Bullicame area. At Bullicame, travertine rocks crop out in close proximity to the present day thermal spring (the Bullicame spring), whereas in the remaining area of the plateau travertines are relatively scarce, and are strongly pedogenised. Very little attention has been devoted up to now to the presence and availability of arsenic in soils and in the underlying travertines in the Bullicame plateau. The aim of this work is to give a first assessment of the environmental impact of arsenic in this area. A relatively small area, with respect to the entire plateau, has been studied (approximately two hectares centered around the Bullicame main spring); four soil and ten travertine samples were collected. For all samples, major and trace elements were determined by XRF, while As was determined by hydride generation flame atomic absorption spectrometry. Furthermore, all soil samples and four travertine samples underwent a sequential extraction procedure (SEP), modified after Wenzel et al. (2000) by introducing a carbonatic extraction step, in order to take into account the mineralogical nature of the Bullicame samples. Almost all the samples showed As concentrations far above the maximum permissible limit set by Italian law (20 mg/kg for residential areas, and 50 mg/kg for commercial and industrial sites, as stated by D.Lgs. 152/2006), both in soils (As range 81 to 651 mg/kg, with a mean value of 347 mg/kg) and in travertines (from 39 to 279 mg/kg, mean value 136 mg/kg). SEP results for calcites in travertine showed that arsenic is almost exclusively bound to carbonates (the acetic buffer extracts over 95% of total As) only when Fe concentration is very low (<< 1 wt.%): when Fe exceeded 1 wt.% arsenic yields from the acetic buffer step dropped down to 36% of the total. In soil samples As is instead primarily associated with the Fe(Al)-oxyhydroxide fraction (about 80% of the total). Collected data suggest a widespread presence of As in both soils and travertines of the Bullicame area. Arsenic is mainly associated in the Fe(Al) fractions in soils whereas in the travertine calcite and Fe-oxyhydroxides may behave as traps for the metalloid.

The distribution of aqueous components, including toxic and harmful elements, in different aqueous fractions can be investigated via their determination in non-filtered and filtered water samples. Concentrations determined in non-filtered samples can be roughly regarded as total amounts. Filtration through 0.45 µm pore-size filters is conventionally used to remove the matter in suspension, thus concentrations determined in the water fraction < 0.45 µm might be regarded as ‘dissolved amounts’. However, in this fraction the aqueous components may occur either as ‘truly dissolved’ species or hosted in fine particles of < 0.45 µm size, such as clay and colloidal materials.

Results of hydrogeochemical surveys carried out in Sardinia (Italy) showed significant differences in concentrations of specific components when water was sampled under different seasonal conditions, and analyses were carried out in different aqueous fractions (non-filtered samples, aliquots filtered through 0.45 µm and 0.015 µm pore-size filters).

Concentrations of nitrate in surface water and groundwater did not significantly change when determined in different aqueous fractions (unfiltered and filtered aliquots), indicating that nitrate occurs as truly dissolved species. However, nitrate concentration in river and stream waters sampled under high flow condition was higher than that in water collected under low flow condition.

Variations in the dissolved amount of trace elements appeared to depend on the composition of rocks drained, and the occurrence of mineral deposits. Concentrations in river and stream waters were also dependent on hydrological conditions, such as runoff, flow and turbulence. Specific trace elements showed distinguished trends.

The elements B, Li, Rb, Sr, Ba, As, Sb, Mo, and U in the studied waters showed small differences in concentrations determined either in non-filtered or filtered water samples. Their concentrations were often positively correlated with total dissolved solids (TDS) and/or major ions. Dissolved concentrations in surface waters were higher in summer, when the contribution of rainwater to the rivers was minimum. These elements occurred as truly dissolved species (either as free ions or aqueous complexes), which concentrations appeared related to the intensity of water-rock interaction processes.

The elements Al, Fe, Pb, Zn, Cd, Co, Ni, Cs, Y, REE and Th were not related to TDS and/or major ions; they showed higher concentrations under high flow conditions; marked differences occurred between total and dissolved amounts; concentrations in the water filtered through 0.015 µm were much lower than in the water filtered through 0.4 µm, especially when sampling was carried out after storm events that enhanced the load of solid matter in the water. These observations indicate an aqueous transport of these elements mainly via sorption processes on very fine particles.

Considering that seasonal variability in concentrations of harmful components may affect the water quality, results from this study can be useful to understand the human health and aquatic life risk exposure to potential contaminants.
THE GEOGENIC NATURE OF SOME HARMFUL ELEMENT ANOMALIES IN THE CENTRAL SECTOR OF THE PELORITANI MOUNTAINS (SICILY, ITALY)

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In the Southern Sector of the Calabria-Peloritani Arc, the Peloritani Mountains extend in the NE Sicily. They consists of a stack of nine continental crust tectonic units, involving Pan-African and Variscan crystalline basements, and remnants of Meso-Cenozoic sedimentary covers. Basements and covers are locally affected by an Alpine overprint. Geometrically to the bottom and geographically to the south, the Units are: Aspromonte, Mela, Piraino, Mandanici, Ali, Fondachelli, San Marco d’Alunzio, Longi-Taormina, Capo Sant’Andrea. The Pan-African basement (Aspromonte Unit) derives from a Proterozoic plutonic and metamorphic low crust, the Variscan basements (other units) from Paleozoic sedimentary-volcanic sequences. Sulphide and sulphosalt mineralizations are very widespread in the study area. Topsoil samples (n = 122) have been collected over an area of 300 sqkm in the Central Peloritani Mts., from the Ali to the Bafia Villages, and the concentrations of 53 elements, including potentially harmful metals, have been determined by means of ICP-MS after an aqua regia acidification. Concentration data have been georeferenced and geochemical maps have been produced by means of a GIS aided spatial interpolation process.

In accordance with a regional study carried out by De Vivo et al. (1999), on 1198 stream sediments, collected across the Peloritani Mts. area, results obtained by the present study show that higher values of Pb, As, Zn, Cu and Sb are mostly concentrated in a spatially limited area between the Fiumedinisi and Ali Villages. As a matter of the fact, Pb shows anomalous concentration values in correspondence with both C. Postlioni (Mandanici (> 1600 mg/kg) and Fiumara di Ali (> 400 mg/kg), As presents values of concentrations higher than 700 mg/kg between Fiumedinisi area and Ali and Cd is 8 mg/kg in correspondence with the Fiumara of Fiumedinisi. Concentrations of Pb, As and Cd often exceed the trigger and action limits established by the Italian environmental law (D. Lgs. 152/06) for both a residential and an industrial/commercial land use. To discriminate between an anthropic and a geological origin of harmful elements (mostly metals), in the soils of the central sector of Peloritani Mts. the ratios of \( \frac{206\text{Pb}}{207\text{Pb}} \) versus \( \frac{208\text{Pb}}{207\text{Pb}} \) isotopes both in local galena and soil samples have been determined. The isotopic ratios of Pb have been obtained at USGS (United States Geological Survey) in Reston (VA, USA) by means of mass spectrometry after a step-leaching procedure producing a leachate and a residue fraction of each soil sample.

Results show that the leached fraction of soil samples with more 1600 mg/kg of Pb (C. Postlioni, Mandanici) has ratio \( \frac{206\text{Pb}}{207\text{Pb}} = 1.169539 \) and \( \frac{208\text{Pb}}{207\text{Pb}} = 2.460557 \) which indicates that contamination of soils collected in the area between the Mandanici area and Ali Village are geogenic and mostly related to the presence of sulphide and sulphosalt minerals.

A factor score analysis was also ran on the dataset and results obtained show that the Ag, As, Sb, Pb, Cd, Zn, Hg, Ni can be associated in a unique factor since they clearly marks the areas where old mines were present: San Carlo, Vacco, Magliuso, inside the Fiumedinisi territory, and Tripi, inside the Ali territory.
ZINC BIOMINERALIZATION PROCESSES AT INGURTOSU MINE (SW SARDINIA)

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The Ingurtosu Pb-Zn mine (S-W Sardinia) was exploited for about a century until 1968. Huge amounts of tailings were abandoned, resulting in long-term heavy metal dispersion processes in both stream sediments and waters. Zn and Pb concentration in tailings and stream sediments attains values up to thousands of mg per kilogram. The maximum Zn concentration in water attains several hundreds of mg per liter, whereas Cd and Pb concentrations are in the order of thousands of µg per liter. Heavy metal concentration in waters of Rio Naracauli, the main stream of the area, is abated by seasonal biominalization processes. Precipitation of hydrozincite \([\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6]\) and of a Zn-rich amorphous phase results in a decrease of Zn concentration down to a few mg per liter. Other metals such as Pb, Cd, Cu, and Ni are coprecipitated with the Zn phases. TEM analysis of hydrozincite has shown that nanocrystals that are approximately 3 nm long aggregate by an imperfectly oriented aggregation mechanism (De Giudici et al., 2009). This results in the formation of mesocrystals. These are hydrozincite platelets flattened onto the (100) crystal face that were observed by SEM. Hydrozincite globules are made by a further aggregation of these micrometric platelets. SEM images of hydrozincite show that both shape and size of globules are apparently influenced by environmental conditions (namely sunlight, rainfall, runoff, stationary hydraulic conditions; Medas et al., 2011). The cell parameters of Naracauli hydrozincite are all similar, and slightly different with respect to the published structures, possibly suggesting a different stacking order along \(a_c\). The nature of binding of Cd and Pb to hydrozincite was investigated by X-ray absorption spectroscopy (XAS). For Cd, the results of extended X-ray absorption fine structure (EXAFS) analysis, backed by anomalous X-ray diffraction, suggest a disordered mode of occurrence, presumably as an amorphous surface precipitate (Lattanzi et al., 2010b), while for Pb a more complex model is suggested (Lattanzi et al., 2010a): this metal is supposed to occur partly as an amorphous surface carbonate, partly either as a substituting ion in the tetrahedral Zn site of the hydrozincite structure, or as an inner-sphere surface complex. Microscopic and spectroscopic investigation on the Naracauli zinc silicate are undergoing.

Acknowledgements. This paper was funded by EU grant 226870 UMBRELLA (coordinator Erika Kothe, University of Jena).

ENVIRONMENTAL GEOCHEMISTRY OF AN ACTIVE MINING AREA: 
THE HUANUNI BASIN (BOLIVIA)

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Mining activities, concentrated on cassiterite exploitation, developed in the Huanuni basin are operating 
without any responsibility for the environment and the population living in the catchment. The area, with a 
population over 50,000 inhabitants approx. is located in the Oruro department, Bolivia. Active mining operations 
discharge liquid and solid wastes without any threatment directly into various rivers. A detailed study on the 
geochernistry of water, bedload sediment and suspended material has been carried out in the area to evaluate the 
degree of pollution in the area, better constrained by the application of a sequential extraction analysis on 
selected bedload and suspended sediments.

Samples were collected around three active mines in the Huanuni basin following the occurrence of Acid 
Mine Drainage in the are. Electrical Conductivity, temprature, pH, were measured directly in the field, filtered 
and acidified and unacified water samples were collected for the analysis of major and trace elements and the 
anionic composition. The fraction < 63 µm of the bedload sediment, directly sieved in the field, and in selected 
sites the suspended sediment were collected and analysed for total metal content by XRF. Their bulk 
mineralogical composition has been determined by XRD. To selected samples, a 3-step plus aqua regia 
sequential extraction procedure has been applied in order to constrain metal distribution within the sediment.

Surface water show strong acidic conditions (pH 2.9-4.5) in several sites, with high SO42- concentrations 
(up to 2400 mg/l), and high metal contents (580 mg/l Fe, 141 mg/l Zn 82 mg/l Al, 6000 µg/l Cd, 5650 µg/l Cu, 
2600 µg/l Pb, 1440 µg/l Co, 540 µg/l U, 24 µg/l Tl), generally decreasing downstream from the active mine 
areas. Their distribution is however different between the mines impacting the catchment and can be used as 
traces of the source area.

The bedload sediment chemical composition is characterized by high concentrations of Cu, Zn, Pb, but 
also Sn, As reach high values. Concentrations of Cd, Co, Cu, Cr and Zn are higher in suspended sediments. In 
general a decrease in sediment concentrations is observed downstream from the active mines, and also for bedload 
sediments differences can be outlined among the different mines. The results of the sequential extraction point 
out differences in metal distribution: in the most polluted sites Cd, Co, Cu and Zn are associated preferentially to 
an oxidizable fraction and it is important to note that in the suspended sediments the proportion associated to the 
exchangeable fraction is higher. A completely different distribution is displayed for example by Arsenic or Pb, 
which are almost completely associated to the residual fraction.

The study shows the hazard of the suspended sediment release in the river system and the possibility to 
reduce the contamination removing the disposal of the liquid waste. Sequential extraction data suggest that care 
must be taken for the different geochemical behaviour of critical elements.
PRELIMINARY REPORT ON HEAVY METALS CONTENTS IN SOILS OF CORNIA, BRUNA AND ALMA COASTAL PLAINS (SOUTHERN TUSCANY)

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Southern Tuscany hosts a number of ore deposits which have been actively exploited since the Etruscan period until very recent time. Natural processes of rocks weathering led to the dispersion in the environment of toxic elements. The Department of Earth Sciences of University of Florence has conducted over the past ten years, numerous studies about the distribution of arsenic and heavy metals in mineralized areas of Tuscany, particularly in the Pecora basin.

The Pecora river drainage-basin is located in the SW part of Colline Metallifere. The area hosts several polymetallic ore bodies and a pyrite ore deposit. The studies have identified several geochemical anomalies (As, Cu, Pb, Zn) both in the areas which host the ore bodies and in the coastal plain (Scarlino Plain). The studies suggest that in Scarlino Plain the primary geogenic geochemical anomalies have been overprinted by an anthropogenic input. To increase the knowledge concerning the distribution of As and heavy metals in other Tuscan coastal plains, research is under way in the alluvial plains of the Bruna, Cornia and Alma rivers. The Bruna Valley is the catchment area adjacent to the Pecora Valley, bordered on the S-SE with the latter through a watershed that divides them. The two areas, based on paleo-reconstructions hydrographic studies, show a relatively recent common history. The Cornia Valley is the catchment area bordered on the N-NO by the Pecora basin. This basin hosts several polymetallic ore bodies and high-enthalpy geothermal fields, located around the area of Sasso Pisano. Finally, the Alma basin is bordered on the north by the Pecora basin and on the south by the Bruna basin. This small size basin has lithologies common with neighboring basins, but not directly affected by mineralizations. The “Pian d’Alma” coastal plain may represent the geochemical baseline of the Southern Tuscany.

The preliminary analysis have focused on soils and stream sediments, to better understand the correlations between the downstream transport of rivers and the soils. The soil represents together with water (even from a legal point of view) the matrix of most interest to the risk of human exposure to contamination by heavy metals and toxic elements. We have made physico-chemical analysis, particle size analysis, mineralogical analysis for X-ray powder diffraction, chemical analysis for the determination of major element (X-ray Fluorescence) and for the determination of 35 minor elements and traces (AAS and ICP). The preliminary results show high concentrations of As (21-57 mg/kg) in the coastal plain of Piombino (Cornia basin). These values exceed the law limit of 20 mg/kg for Private and Public Land Use and several samples are also over the law limit of 50 mg/kg for Commercial and Industrial Land Use (D. Lgs. 152/06). The samples which present high concentration of As, also have contents in Co over the law limit of 20 mg/kg. The values in soils sampled indicate that also in the coastal plain of Castiglione della Pescaia (Bruna basin), there are several samples which have concentrations of As (7-29 mg/kg), Zn (31-163 mg/kg) and of Co (8-36 mg/kg) that are over the law limits (20 mg/kg, 150 mg/kg and 20 mg/kg respectively – Private and Public Land Use. Instead, the soils sampled in Pian d’Alma present concentrations below the law limits, with the exception of a sample which shows an anomalous concentration of Pb (612 mg/kg), over the law limit (100 mg/kg – Private and Public Land Use, D.Lgs. 152/06). Soils and stream sediments of the all three basins of interest are still under investigation.
Short-term changes in water chemistry, and especially in dissolved trace element concentrations, associated with diel cycles during base-flow conditions at a specific sampling station in the Baccu Locci stream draining the homonymous old mine area in Sardinia (Italy) were investigated. Diel fluctuations in pH and alkalinity were correlated with the temperature-dependent CO₂ solubility and the biological-induced CO₂ production, both of which were higher during the night.

Adsorption/desorption to/from streambed material, in particular ferrihydrite, is believed to be the main in-stream mechanism causing the observed diel variations in dissolved concentrations of As and Zn. Arsenic was mainly affected by the dual action of temperature and competing carbonate ions, whereas pH seemed less important.

Temperature acted in accordance with the exothermic feature of anion sorption onto hydrous metal oxide surfaces; aqueous carbonate species exerted their competitive effect in relation to alkalinity variation. Zinc was primarily affected by temperature, in accordance with the endothermic feature of metal cation sorption onto hydrous metal oxide surfaces, and secondly by pH.

Co-precipitation of As and Zn with calcite is another possible mechanism that, to be better investigated, would require a further finalized examination of inorganic and biological materials coating the streambed. All these processes potentially controlling the diel cycles of trace elements should be carefully considered to assess the effectiveness of remediation actions currently in progress at Baccu Locci.
Oxidation of metal sulfides, in particular pyrite, by oxygen or Fe(III) is considered the main process generating AMD (Acid Mine Drainage). However, secondary minerals from sulfide oxidation can significantly contribute to AMD generation.

Secondary metal sulfates are common phases in sulfide ore mines and their formation-dissolution cycle is often influenced by climatic conditions. Melanterite, the heptahydrated ferrous sulfate, is one of the most diffuse oxidation products of pyrite. Moreover, its presence has been recently hypothesized in the evaporites on the surface of Mars.

Field observations in mine sites show that melanterite is associated with acidic waters and laboratory experiments confirm this finding. However, simple dissolution of melanterite, without oxidation of Fe(II) to Fe(III), cannot generate AMD because the hydrolysis of Fe(II) is not able to significantly lower the water pH. Both commercial and natural melanterites always contain small amounts of Fe(III), probably as a ferric sulfate of some sort.

Modeling of laboratory batch experiments with PHREEQC has shown that Fe(III) concentrations in melanterite in the range of 0.16-0.20 wt.% are sufficient to significantly lower the pH of very dilute interacting waters as a consequence of Fe(III) hydrolysis. Since melanterite is very soluble, its rapid acid-generating dissolution can occur without invoking oxidation of Fe(II) to Fe(III) that is slow under acidic conditions, as well as without involving the acidity-generating precipitation of a Fe(III) phase.

In the field, the rapid dissolution of Fe(III)-bearing melanterite by rain water may thus generate AMD and also provide a supply of Fe(III) for subsequent sulfide oxidation. These results should be taken into account when evaluating the origin of AMD in mine sites in order to prevent its impact on the environment and plan its treatment.
MINERALOGY, GEOCHEMISTRY AND FLUID INCLUSIONS ON QUATERNARY SEDIMENTS OF THE PECORA AND BRUNA VALLEYS (SOUTHERN TUSCANY, ITALY)

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Recent studies showed that Quaternary deposits of Pecora Valley (southern Tuscany, Italy) display anomalous As concentrations (up to more than 1000 ppm) (Costagliola et al., 2010 and references therein). Based on these results, the origin of As can be imputed to the dismantling of sulfide mineralization hosted by the pelitic-arenaceous member of Palombini Shales, widely cropping out in the Mt. Arseni and Accesa Lake areas. The Bruna river catchment borders to S-SE the Pecora river catchment, through a watershed that divides them. The two areas, based on paleo-hydrographic reconstructions reported in literature, show a common paleo-hydrological history. This leads to the hypothesis that the As anomaly affecting the Pecora Valley (PV) can also influence the Bruna Valley (BV).

To highlight the geo-environmental evolution of this part of southern Tuscany, the mineralogical and geochemical characteristics of the BV sediments were determined and a study of fluid inclusions found in quartz hosted in BV and PV Quaternary sediments was carried out.

The study included: 1) sampling of sediments, quartz veins and crystals, both in PV and BV Quaternary deposits; 2) study of the minero-lithological features of the sediments; 3) determination of the As content of the sediments; 4) microthermometry of fluid inclusions.

The BV Quaternary deposits show minero-lithological features and concentrations of As comparable to the Quaternary deposits of the PV, emphasizing the presence of a common source of the metalloid for both areas. They differ only for a different content in trace elements (Zn and Pb), stressing a higher affinity of the BV deposits to base metals mineralization.

Quartz from all the examined areas trapped two-phase (liquid + vapor) aqueous liquid-rich inclusions. Homogenization temperatures of these inclusions are mostly in the 200-275°C range, whereas the computed salinity values are from 0.1 to 13.8 wt.% NaCl equiv.. In some cases, such inclusions coexist with vapor-rich inclusions, suggesting boiling processes. The estimated minimum trapping depth for two-phase inclusions is between 200-600 m, under hydrostatic conditions. Such features indicate an epithermal style of fluid circulation, a quite common occurrence in southern Tuscany. In particular, microthermometric data of two-phase inclusions are similar to those of fluid inclusions hosted in minerals from some pyrite and/or base metals mineralization located close to the examined areas. In one sample (collected near the Accesa Lake) three-phase fluid inclusions (liquid H2O + liquid CO2 + vapor CO2) were also observed, in addition to two-phase inclusions. The computed salinity of three-phase inclusions is between 0.8 to 12.8 wt.% NaCl equiv., and homogenization temperatures fall in the 265-275°C range. Such inclusions probably testify the production of CO2-rich fluid from decarbonation processes during thermo-metamorphism related to the emplacement of Pliocene-Quaternary intrusions. The estimated trapping depth for such inclusions is at least at 1900 m depth under lithostatic pressure. These data suggest the presence of a complex hydrothermal system located at different depths, that could potentially mineralize several hundred meters of crust. The subsequent dismantling of the mineralized rocks would result in an As anomaly of regional importance, affecting most Quaternary deposits cropping out in southern Tuscany (PV, BV, probably Cornia Valley and the marine sediments off the coast of Piombino up to Elba Island). Thus, the data obtained in this work suggest that PV is only a portion of a larger area affected by As anomaly.

MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF OCHREOUS PRECIPITATES FROM THE ROŞIA MONTANĂ GOLD MINE (ROMANIA)

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The Roşia Montană gold mine (Apuseni Mountains, Romania) is characterized by active and intense Acid Mine Drainage (AMD) processes that cause the widespread circulation of strongly Acid Sulphate Waters (ASW; pH ≤ 3) containing very high levels of ecotoxic elements deriving not only by the sulphide mineralizations but also from host-rock and gangue minerals (such as Cd, As, Cu, Pb, and Zn; Bird et al., 2005; Florea et al., 2005).

The Roşia Montană hydrothermal ore deposit is hosted in andesites and dacites of Neogene age piercing the prevolcanic sedimentary basement as breccia pipes (Rosu et al., 2004). 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 mineralizations that are mainly present in epithermal veins, mineralized phreatomagmatic breccias, and stockworks (Wallier et al., 2006). The ore deposit was mined both in underground and in open pit for more than 2000 years.

In the mining area, contaminated waters mainly flow in the watershed of the Roşia and Abrud Rivers, which are indirect tributaries of the Danube River. In order to monitor the mineralogical variations and to evaluate the toxic elements partitioning between contaminated waters and authigenic minerals, twelve samples of ochreous precipitates and the associated mine waters were sampled in July 2010.

The mineralogy of the precipitates was made by XRPD, whereas their bulk chemistry by ICP-MS. T, pH, Eh, and electrical conductivity (EC) were measured in situ with portable instruments. The chemical analyses on mine waters were made by ICP-MS, AAS, and chromatography.

Two groups of waters were distinguished on the basis of pH, Eh, SO₄, EC, and dissolved metal contents. The first group corresponds to the ASW, characterized by the lowest pH (2.70-3.08) and the highest Eh (460-484 mV), SO₄ (688-4800 mg/kg), EC (1073-5780 µS/cm), and metal contents (Fe, Zn, Mn, and Co). The second group includes either unpolluted and mixed waters, characterized by a general reduction of metal load as well as by significant variations of pH (3.77-6.50), Eh (237-363 mV), SO₄ (326-436 mg/kg), and EC (249-619 µS/cm).

The XRPD analyses evidence that the precipitates are characterized by K-jarosite [K+Fe³⁺(SO₄)₂(OH)₆] and schwertmannite [Fe₁₆O₁₆(OH)₁₂(SO₄)₂] in different proportions. As expected, after the mixing of the ASW with the Rosia and Abrud Rivers, the presence of minerals of detrital origin significantly increases.

The bulk chemistry of the precipitates evidenced significant enrichment in Fe (up to 41.27 wt.%) and S (up to 5.01 wt.%) and high concentrations of trace metals and As (up to 2930 ppm). Moreover, a positive correlation between Fe and S with As, V, and P have been observed, whereas most of the other elements shows the opposite trend (e.g. Al, Ti, Cu, and Ni). These data suggest a strong control of schwertmannite and jarosite on specific trace elements of environmental concern (particularly As).

Crystallochemical investigations by TEM and spectroscopic techniques will be performed to better understand the interactions of authigenic Fe-oxyhydroxysulphates with metals in the contaminated waters from the Roşia Montană Mine area.

LOCAL TECTONIC CONTROL ON HYDROLOGICAL PATTERNS:
A KEY TO UNDERSTAND THE As-Sb CONTAMINATION
IN THE ABANDONED TAFONE MINE AREA

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Southern Tuscany “Colline Metallifere” are one of the principal epithermal district of Italy: carbonate rocks hosting mineralizations occur at the edges of major epithermal fields as Larderello, Mt. Amiata and Latera district. Mineralizations are typically localized at the contact between carbonate rocks (mainly “Calcare Cavernoso” Fm) and the overlying flyschoids units (“Ligurides and Sub-Ligurides” AUCTT.) or “Macigno” sandstones. Stibnite (Sb carrier) and pyrite (As carrier) are the most common sulfide epithermal minerals: here mining activity is historically dated back at least to Etruscan times (Cipriani & Tanelli, 1983).

The “Colline Metallifere” epithermal district is co-genetic to Neogene magmatism (Tuscan and Roman provinces) emplaced during the last phase (late Miocene till now) of the Appennine extensional regime: genesis of NW-SE trending grabens filled by late Miocene-Pliocene sediments lastly faulted by Plio-Pleistocene NW-SE direct and NE-SW strike-slip systems (Brogi, 2011). Tafone mine represents an important area (a NW-SE graben less than 7 km length and up to 2 km large) to evaluate the impact of As and Sb contaminations.

The stibnite and pyrite mine is located on the southwestern flank (Monte Maggiore) of the Tafone Graben (TG), near the “Fosso del Tafone” (FdT). The mineralization system outcrops at the intersection of the southern NW-SE extensional system of TG, with one NE-SW trending strike-slip segment. Mineralizations are hosted in Triassic dolostone and in Calcare Cavernoso Fm. overlying the paleozoic metamorphic phyllades and partially overthrusted by dark shales and calcarenites (Ligurian units). FdT flows, from NW to SE, on the southwestern flank of the TG along the extensional lineament. Tributaries are, instead, distributed perpendicularly to the FdT, and evolved over NE-SW strike-slip minor tectonic discontinuities.

Our focus is the presentation of a comprehensive data set of As-Sb contaminations in the area along FdT, and their spatial correlation with local tectonic settings \textit{i.e.} tributaries distribution. It has been observed a strong variability of As-Sb contents in waters (As: 1-20 µg/l; Sb: 0.9-119 µg/l), in stream sediments (As: 23-3060 mg/kg; Sb: 16-1360 mg/kg) and in soils (As: 61-1360 mg/kg; Sb: 23-5140 mg/kg) with maximum concentration of As in stream sediments and Sb in soils (Petrini, 2007).

The peculiarity of the study area is represented by a discontinue distribution of As-Sb along FdT: for example in the mining zone \textit{(i.e.} the expected most contaminated area), it is possible to observe an anomalous strong downfall of the As-Sb contamination due to the confluence with northern side tributary “Fosso del Molinaccio”. We focus on dilution, by a local tectonic controlled hydrographic pattern, of the As-Sb concentrations along the FdT. Accumulation of toxic elements as As and Sb represents a serious hazard for both environment and human health.

Considering the wide extension of Tuscan epithermal district and the large population living in the area, the understanding of the geological factors controlling the spreading of toxic elements in the environmental system is highly relevant.

IMMOBILIZATION OF HEAVY METALS IN WATER AND SOIL
BY PHOSPHATE TREATMENT

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Heavy metals such as Pb, Cd, Cu, Zn, Hg, Cr, and Ni are the main contaminants of surface water, groundwater, and soils. The heavy metals are of great concern because of their extreme toxicity even at low concentration and the tendency to accumulate in the food chain.

Conventional methods for heavy metal removal from water and soil include chemical precipitation, filtration, solvent extraction, electrochemical technique, ion exchange, and adsorption. In particular, chemical immobilization is one of the most used for reducing the bioavailability of heavy metals. The aim is to immobilize the ions trapping them in minerals with low solubility and stable in the environment in a wide range of conditions. Synthetic or natural apatite and phosphate rock have been proved to immobilize divalent heavy metal ions such as Pb, Zn, Cd, Cu, Co, Cr, Ni, and Sb in contaminated waters and soils. The mechanisms of metal removal include ion exchange, surface complexation and dissolution/precipitation.

In this study the removal of Cd, Pb, Zn, and Cu from aqueous solutions by both synthetic hydroxyapatite (HA) and natural phosphate rock (FAP) was investigated in batch conditions at 25 ± 2°C. The metals were applied both as single- or multi-metal (Cd + Pb + Zn + Cu) systems with initial concentrations from 0 to 8 mmol L⁻¹. The removal capacity of phosphate amendments generally ranges between 50 and 99%. In the multi-metal systems competitive internal metal sorption reduced the removal capacity by 13-83% compared to the single-metal systems. The sorption of heavy metals by phosphate amendments follows the Langmuir model. Heavy metal immobilization occurs through a two-step mechanism: rapid surface complexation on the ≡POH sites followed by partial dissolution of phosphates and ion exchange with Ca resulting in the formation of heavy metal-containing phosphates.

The sorption of Cu on HA was further investigated by means of the results of a combined structural simulation and EXAFS analysis. The EXAFS results suggest that the heavy metal is present in the Cu⁺² form. The structural experimental and theoretical analysis shows that Cu is bond to about four O atoms at a distance of about 1.95Å. In all the studied cases the immobilization site of Cu is the same. The fixation of Cu occurs in the surface sites of hydroxyapatite whereas the sorption in the Ca sites in the inner part of the structure is unlikely.

The effectiveness of phosphate treatment for Cd, Pb, Zn, and Cu immobilization in mine waste soils from sulfide mine areas (tailing dumps, ore stocking areas, streams, etc.) in Tuscany and Sardinia (Italy) was examined in batch conditions. Application of HA and FAP effectively reduced the heavy metals water solubility generally by about 84 to 99%. Between the two amendments evaluated, HA was slightly more effective with respect to FAP in immobilizing heavy metals. Although the lower effectiveness of phosphate rock, its application to reduce metal solubility in contaminated soils may minimize soil acidification and potential risk of eutrophication associated with the application of highly soluble phosphate sources.
ANTIMONY CONTAMINATION FROM MINING AND METALLURGICAL WASTE DEPOSITS IN THE VILLASALTO OLD MINE AREA (SE SARDINIA, ITALY)

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The historical mine and smelter of Villasalto-Su Suergiu (SE Sardinia) operated from 1882 to 1981, being the largest industrial complex in Italy for antimony ore extraction and metallurgy. The site is characterized by the presence of several mining and metallurgical waste deposits. Environmental surveys and studies performed from 2006 by IGEA S.p.A and DIGITA evidenced, over an area > 6 km² downstream of the old mine, that soils, stream sediments and waters are affected by serious Sb and As contamination and by the presence of high levels of toxic metals (Zn, Pb, Cu, W). Sb contamination, in particular, attains several orders of magnitude beyond the limits of Italian and EU regulations. The Su Suergiu mine exploited quartz-calcite-sulfide-scheelite veins and lenses, hosted by cataclastic Silurian-Devonian carbonaceous black shales and limestones. The ore included stibnite (main economic mineral), scheelite, arsenopyrite and Zn-Pb-Cu sulfides. The smelter produced metallic Sb and various Sb oxides and sulfides. Mining and metallurgical waste dumps are the most relevant centers of pollution in the area. Three kinds of wastes have been identified: a) mining wastes - 13 heaps of waste rocks (about 130,000 m³ in total); b) metallurgical wastes - 1 large heap of various pyrometallurgical residues (about 50,000 m³); c) mixed wastes - 2 heaps of mixed mining and metallurgical residues (about 70,000 m³). The solid transport downstream has been considerable over the years; about 20,000 m³ of waste residuals have been assessed along two watercourses that cross the area. In Su Suergiu area, seepage waters show Sb and As contents up to 32 mg/l and 3.8 mg/l respectively; mine drainage waters show up to 2.6 mg/l Sb and 0.1 mg/l As. The influence of Su Suergiu polluting centers extends well away from the mine; up to 8.8 mg/l Sb have been determined in stream waters at the confluence with the Flumendosa river, 4.5 km far from Su Suergiu. The metallurgical residues show the most relevant contaminating potential. They include 7 different types of slags, casting residuals, metallurgical dusts that have been characterized by ICP-OES, ICP-MS, AAS, XRPD, SEM-EDS; contamination potential has been determined by leaching tests (D. Lgs. 152/06). Vacular coarse-grained slags are the most abundant metallurgical residues. They are constituted of gangue and ore minerals remnants in a glassy matrix rich in Ca-Al-silicates, with Fe (Zn, Cu) sulfides and oxides, metallic Sb, Sb oxides. Sb contents are up to 2.7 wt.%. Eluates from standard leaching tests evidenced up to 107 mg/l Sb. Metallurgical dusts are prevailing fine-grained materials consisting of quartz, Na-Al hydrated silicates, Na-Sb hydroxides (mopungite, NaSb(OH)6), Sb oxides (sernamontite, cervantite), Fe hydroxides. XRPD analyses evidenced the presence of amorphous matter. Although not abundant (< 10000 m³), dusts have high metalloids and toxic metals contents (6-8 wt.% Sb; 0.8-1.3 wt.% Zn), associated to soluble Sb phases, like mopungite. Eluates from dust leaching tests show very high Sb contents (120-150 mg/l Sb), and are distinctly alkaline (pH 10.4-10.8). The contaminating potential of metallurgical wastes is therefore related to high Sb availability and is controlled by an alkaline environment that enhance Sb mobility. A new research program on these issues, funded by Sardinia Regional Administration (L.R. 7/07), is currently under way, carried on by a DIGITA and IGAG-CNR work group with the collaboration of IGEA S.p.A. The program includes a further sampling of waste deposits, particle size analyses in order to define the distribution of the contaminants in the different size classes, leaching tests, studies on Sb speciation. Moreover a laboratory investigation will be carried out on mining and metallurgical residues, and on mine and seepage waters, aimed at eliminating or stabilizing the toxic elements in order to reduce their migration to the surrounding areas, applying different techniques.
Arsenic, a toxic element with metalloid properties, is almost often present in environmental samples, especially in volcanic area. Its accumulation in environment has been found to be hazardous to both the ecosystem and human health. Unfortunately arsenic is extremely common in numerous areas from NW Argentina and in particular in volcanic areas of Puna (Jujuy Province). Concha et al. (2006) pointed to the As content in Puna waters ranging from 140 to 220 μg/L. In particular, in shallow and drinking waters the As concentration ranges from 40-1010 and 10-790 μg/L, respectively, reaching values up to 12800 μg/L at thermal springs. Clearly thus represents a serious hazard for the population, demonstrated by numerous signs of poisoning as: dermal lesions, peripheral vascular disorder and other internal injuries, that could lead to premature death. The focus of this study is to highlight, in a natural laboratory such as an active volcanic field, the links between As contamination and the geological setting.

Cerro Tuzgle (5486 m.a.s.l.) represents an HK-calcalkaline stratovolcano surrounded by small shoshonitic centers, dated back to late Miocene to present as confirmed by numerous active thermal springs. These eruptives are distributed along the eastern edge of Puna Plateau, following a N-S trend similar to regional thrusts (Coira & Kay, 1993). The Tuzgle volcano and minor centres emplaced at intersection of N-S elements with left-lateral segments of transtensive “El Toro” system, thus remarking that volcanism derived from magma uprising, facilitated by the brittle failure of the Puna back-arc crust (Coira & Kay, 1993). N-S distribution of basement superunits (Ordovician sediments and Faja Eruptiva; Tertiary-Quaternary clastics and evaporites) outlines the importance of inherited tectonic lineaments in the area. Tuzgle volcanic field produced an alternation of effusive flows (andesitic and shoshonitic, to dacitic-rhyodacitic) and explosive pyroclastites (rhyolites), as recognized by field and fabric analyses (Coira & Kay, 1993). Hot hydrothermal springs and fumarolics are distributed along local tectonic discontinuities; furthermore also hydrographic pattern seems to be strongly related to the local faults distribution: the two major N-S rivers are Rio de Agua Castilla and Rio de Agua Caliente and along them are settled the three major villages of the area: Puesto Sey, Pastos Chicos and Huancar. In order to map arsenic concentration and understand its relationship with geological framework, different kinds of samples were collected: rocks, soils, stream sediments and waters.

Thin sections and XRD analyses indicate that all samples are mainly constituted by the same mineral assemblage: quartz, micas (Bt+Ms), feldspars (Sa+Pl) and accessories (Di-Aug+Kat-Hbl±Fo±Sp) pointing to genetic link between recent volcanics and soil-sediment system. Thermal analyses show presence of organic matter in lasts. Contamination has been finally measured on volcanic rock, soil, stream sediment and water samples evidencing a very high concentrations of As, in the ranges 2-4150, 28-890, 11-625 mg/kg and 11-12880 μg/L, respectively pointing to maximum values reached in rocks (source?) and water (carrier?). Informations on potential As mobility, have been obtained applying standard sequential extraction BCR procedure on soil and sediment samples. Results demonstrate that As is weakly bounded to matrix host and can easily mobilized becoming environmental-bioavailable. Mineralogical analyses highlight the common origin of sediments and soils from the recent volcanics, and point to water as main carrier of As. If the volcanic system could represent the As-reservoir, the tectonic of the area seem to be the controlling factor on As distribution, since thermal springs and rivers follow the brittle failure pattern of the area.

FINDING OF A Cs-RICH PHARMACOSIDERITE-LIKE MINERAL:
PRELIMINARY DATA

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During a survey of the As environmental distribution in NW Argentina, we observed a Cs-rich arseniate phase. The mineral occurs in a rhyolitic rock, collected near one hydrothermal spring on the slope of Tuzgle volcano (Puna region, Jujuy Province), as a thin crusts consisting of very small tetrahedral crystals (average < 2 μm), covering the walls of the rock cavities.

Preliminary SEM/EDS and microdiffraction X-ray analyses in thin section, suggested the mineral to be very close to pharmacosiderite KFe₄(AsO₄)₃(OH)₄·6-7H₂O, but with anomalously high Cs contents. Complete WDS-EMP analyses gave a composition compatible with the formula (Cs₀.₄₇K₀.₄₂)₀.₈₉Fe₄.₂₅(As₀.₉₆P₀.₀₄O₄)₃(OH)₄·6.₄₃H₂O, thus confirming the similarity of the Cs-bearing phase with pharmacosiderite. The structure of pharmacosiderite (Buerger et al., 1967) consists of FeO₆ octahedra and AsO₄ tetrahedra connected to each other to form a three-dimensional network of channels. The pore has 8-membered ring openings, with alternating arsenic tetrahedra and iron octahedra.

Each channel, approximately 3.5 Å in diameter, is occupied by charge neutralizing K⁺ extra-framework cations and H₂O molecules (Yakubovich et al., 2008). All the structural sites can be occupied by many other elements: Al, Fe, Ge, Mo, Ti at the octahedral sites, and As, Ge, P, Si at the tetrahedral sites (Baur, 2003). The extra-framework cations can be Ag, Ba, Cs, H, K, Li, Na, NH₄, Pb, Rb and Tl. This makes possible the existence of many microporous inorganic compounds, isostructural with pharmacosiderite and characterized by remarkable ion-exchange properties. Buerger et al. (1967) investigated a synthetic Cs-pharmacosiderite obtained treating natural pharmacosiderite with an aqueous solution of CsOH at room temperature.

However, until now the occurrence of a natural Cs-pharmacosiderite was not yet observed. If confirmed, the observed Cs K⁺ cationic exchange will imply the definition of a new mineral belonging to the pharmacosiderite group. Moreover, the occurrence of a new Cs-bearing natural phase would be relevant to the search for new materials that can be used as selective absorbers for the 137Cs isotope from solutions of radioactive wastes and as containers for disposal of radioactive metals (Behrens et al., 1998).

Bioavailability concepts originate from the knowledge that adverse effects in exposed humans and ecological receptors are not caused by total concentration of chemical compounds released into the environment but only by a certain fraction that is biologically available.

From the toxicological point of view, the concept of bioavailability implies that the danger represented by a substance is explained simply in terms of the fraction that can interact with a specific biological site.

In the environmental studies the concept of bioavailability assumes very different meanings that range from the fraction of a substance available for absorption by a living organism, to the amount that can be released from the solid phase of an environmental matrix. Naturally the various aspects of bioavailability are interrelated and in order to understand the complexity of the issue as regards interactions between organism and environment, we tend to refer to processes of bioavailability. By this we mean a combination of reactions that identify not only the different aspects, but also the different temporal stages involving the processes that define bioavailability in a specific situation for a specific organism.

Bioavailability is the key to understand the environmental behaviour of heavy metals, the hazards deriving from pollution and to define appropriate strategies of remediation.

Clean up procedures, at heavy metal contaminated sites, are often very laborious and expensive. For a better use of the limited resources available for remediation the use of knowledge of bioavailability processes can be of noteworthy utility. Bioavailability may be a key component of exposure evaluation which has significant implications for the preparation of the conceptual model and the technology selection.
HEAVY METALS IN CONTAMINATED SOIL:
“PASSIVE APPROACH” AS A TOOL FOR REMEDIATION

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Human and ecological risk assessment of metals in contaminated soil is a powerful mean to evaluate environmental quality objectives in the remediation of contaminated sites.

Risk based clean up procedures are carried out by a tiered methodology, which consider sources reactivity and mobility of metals in the soil environment. Among the exposure pathways which link the source of contamination to the potential receptor, the transfer of heavy metals from soil to plant, and by food chain to human beings is greatly influenced by the processes of bioavailability.

Bioavailability is the key to understand the environmental risk derived by metals, since adverse effects only occur when related to biologically available forms of these elements.

Extraction test generally used in soil chemistry were originally developed to predict metal deficiencies, and tend to be fairly aggressive to simulate plant behaviour.

The action of plant in the rizosphere is not particularly aggressive, so “passive approach” have been developed. They include the collection and analysis of pore water with different means, (artificial roots, field lysimeter) or the use of passive extraction, water or neutral salts are generally used to mimic plant uptake of metals from soil which occur only via soil solution.

Coupling passive approach with bioassay in which plants growing in the contaminated soils, are used as an extractant, seems to provide a powerful tool to use in the risk assessment procedure. Moreover the results can be utilized to select the best remediation technologies for metal contaminated sites.
COMBINATION OF LEACHING AND COLUMN TEST FOR THE ASSESSMENT
OF AMD GENERATION FROM THE HOP WASTE-ROCK DUMP
(ROȘIA MONTANĂ, ROMANIA)

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The production of Acid Mine Drainage (AMD), as a result of the oxidative dissolution of sulphides, and the release of hazardous elements in the environment are main pollution problems affecting natural watercourses in mining areas, with sulphide-rich residues. An important tool for geochemical assessment of abandoned mine areas are kinetic tests, as they provide an insight into the behaviour of the waste-rocks during the interaction with meteoric waters, giving also useful indications of metal mobility and chemical composition of the run-off waters.

In this study two different kinetic tests were applied to assess the generation of AMD from the run-off water of the Hop waste-rock dump, at the Roșia Montană ancient mining area (Apuseni Mountains, Romania). This hydrothermal ore deposit is hosted in andesites and dacites of Neogene age, piercing the prevolcanic sedimentary basement as breccia pipes (Rosu et al., 2004). They host polymetallic sulphides and Au-Ag-Te mineralisations and the ore deposit was mined both underground and in open pit for more than 2000 years. Intensive alteration due to AMD processes is testified by acid sulphate waters.

The eastern side of the Hop waste dump (2.5 ha area), where the waste has been piled up between 1998 and 2000 from Cetate open-pit, was subdivided in a 30×30 m grid to obtain a final collection of 27 samples. First, the Modified E.P.A. Method 1312 (SPLP) (U.S. EPA, 1994) was applied to 20 of them: the < 2 mm grain-size fraction of the solid material was shook for 18 hours in a rotary agitator, together with a slightly acidified de-ionized water, that simulated natural precipitation (water:solid ratio 20:1). The pH value, Electrical Conductivity, sulphate concentration and by ICP-AES total Cu, Zn and As content of the solutions were analyzed.

One sample was then chosen for further investigation: a modified column test (Perez-Lopez et al., 2007) was applied to study the different behaviour of the grain-size fraction < 1, 1-2 and > 2 mm. A different weight of each fraction, representing an area of about 100 m², was separated and put in a PET column with 100 ml of tap water. Every week for one month an aliquot of the solution was taken for the same analyses performed with the previous method.

SPLP results showed that eco-toxic elements content in filtered solutions is generally low: Cu ranges from 0 to 98 ppb (mean 14), Zn ranges from 21 to 570 ppb (mean 155) and As ranges from 1 to 7 ppb (mean 2.5). These data are in agreement with the results of bulk waste-rock material chemical composition, whose metal concentrations are in the range of tens of ppm with the exception of As, that shows a content one order of magnitude higher (Azzali et al., 2010). The pH values vary greatly from 2.9 to 8.9, according to mineralogical and geochemical composition of the waste material. The sulphate content ranges from 13.5 to 475 ppm and exceeds the European limit for drinking waters (250 ppm) in 6 samples. A significant positive relationship between sulphate content and EC was found.

Modified column test results showed that geochemical features of the solutions tend to stabilized after 3 weeks: pH values grow from 2.5 to 2.7 (mean values) while EC values and sulphate concentration, though highly variables for the three different grain-size samples, clearly decrease. The fraction 2-4 mm is the more reactive one, with a final Cu content of 720 ppb, Zn 880 ppb and As 25 ppb.

The comparison between the two methods allowed to suggest that the first is more useful for materials with fine and homogeneous grain-size, as tailing samples. On the other hand, the column test can be successfully applied on waste rocks, made by heterogeneous grain-size materials.

Mercury (Hg) is a heavy metal of environmental concern as it is highly toxic to living organisms. The most toxic Hg compound is methyl-mercury (MeHg), which is a neurotoxin that biomagnifies in the food chain. Of particular concern around Hg mines is the conversion of inorganic Hg (e.g., cinnabar and elemental Hg) to MeHg, which is primarily by the action of bacteria in the sediment column. Fish accumulate MeHg, thus, representing the dominant pathway of Hg to humans who consume fish. As a result of historical exploitation of Hg deposits worldwide, downstream ecosystems are potentially contaminated by Hg and MeHg, both in abiotic and in biotic compartments. The Monte Amiata Hg district, located in Southern Tuscany, represents one of the world’s largest Hg deposits. About 102,000 t of Hg were produced between 1850s-1980s, ranking it as the 4th largest Hg district worldwide. Mine waste calcine deposits, resulting from Hg ore roasting to extract Hg, are located proximal to the abandoned Hg mines, thus, representing the dominant source of Hg to the surrounding environment in this area. The Paglia River drains the east side of Monte Amiata, which hosts the largest Hg mine of the Tuscan district, the Abbadia San Salvatore mine (ASSM). Detailed studies of Hg transport in the Paglia River ecosystem and of Hg speciation are lacking. Therefore, the main objectives of this study are to evaluate: 1) the transport and distribution of Hg in the Paglia River ecosystem, 2) the formation of MeHg in the downstream environment, and 3) Hg concentrations in local freshwater fish.

Samples of stream sediment and water were collected from the Paglia River both upstream and downstream the Hg mines. In addition, calcine samples were collected from mine wastes located in and around ASSM. Regional baseline concentrations of Hg were established by stream sediment and water samples collected distal from the ASSM. Concentrations of Hg in stream sediment samples range from to 0.10 to 14 μg/g, whereas Hg in water ranges from 3.2 to 1360 ng/l. Elevated Hg concentrations in stream sediment are found downstream from the ASSM at a distance of 5 and 20 km (14 and 10 μg/g, respectively). Significantly lower Hg concentrations (0.35-0.79 μg/g) were found in stream sediment collected 7.5-12 km from the ASSM. A similar trend is shown in stream water, with the highest Hg concentration (1,350 ng/l) found at a distance of 5 km from the ASSM. Mine waste calcine samples contain elevated concentrations of Hg (up to 1,500 μg/g).

Concentrations of MeHg range from 0.04 to 6.4 ng/g in stream sediment and from 0.10 to 3.0 ng/l in water samples. Concentrations of MeHg as high as 22 ng/g were found in calcine samples. The ratio of MeHg/Hg is higher in stream sediment (0.01-0.44%) as compared to that in calcine (0.00-0.02%), but was found to be highest in stream water (up to 9.1%). Historical mining of the ASSM has affected the surrounding Paglia River ecosystem, where concentrations of Hg and MeHg are elevated above baselines both in stream sediment and stream water. More than 40% of the stream sediment samples exceed the 1.06 μg/g Probable Effect Concentration (PEC) for Hg, the concentration above which harmful effects are likely in sediment-dwelling organisms. However, only one stream water sample contained a Hg concentration exceeding the 770 ng/l limit established by the USEPA to protect against chronic effects to aquatic wildlife. The presence of significant concentrations of MeHg in sediment and water of the Paglia River ecosystem suggests methylation of Hg in the sediment column, which is then transferred to water and eventually to biota, such as fish. Most important are Hg concentrations in fish muscle as generally greater than 90% of Hg in fish is MeHg. Studies of Hg in fish are in progress to evaluate any adverse effects of Hg to fish as a result of Hg runoff from the ASSM.
ZINC ISOTOPIC FRACTIONATION DURING PRECIPITATION OF HYDROZINCITE, RIO NARACAULI, SARDINIA, ITALY

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In southwestern Sardinia, Italy, the rio Naracauli drains an area of abandoned mines that produced zinc and other metals until 1968. The stream has near-neutral pH, Zn concentrations exceeding several 100’s of mg/l, and seasonally high alkalinity (De Giudici \textit{et al.}, 2009). These conditions contribute to the biologically mediated precipitation of hydrozincite \{Zn\(_5\)(CO\(_3\))\(_2\)(OH)\(_6\)\} (Podda \textit{et al.}, 2000). As the hydrozincite precipitates, the concentrations of Zn and co-precipitated metals (Pb, Cd, etc.) decrease dramatically in the stream water. Streamwater samples were collected from rio Naracauli from October to December, 2009, using standard sampling methods. At the same time, samples were collected of the hydrozincite that was in contact with the stream water. We also collected several samples of sphalerite from mine dumps in the area to check the isotopic composition of the Zn source. Zinc was separated from all samples using the chromatographic separation methods of Borrok \textit{et al.} (2007) and Pribil \textit{et al.} (2010). Purity of separates was checked with conventional ICP-MS analysis, and Zn isotopes were measured on a Nu Instruments high-resolution MC-ICP-MS, using standard-sample bracketing to correct for instrument drift and mass bias. Multiple replicate separations and MC-ICP-MS analyses were used to check the quality of the results. Zinc isotope compositions of the samples are reported as ratios of either \(^{66}\text{Zn}\) or \(^{68}\text{Zn}\) relative to \(^{64}\text{Zn}\) using the standard notation, against the isotopic standard JMC 3-0749-L. Precision of the measurements is generally better than ± 0.1‰. Values of \(^{66}\text{Zn}\) in all samples (solids and water) ranged from -0.6 to +0.3 ‰; \(^{68}\text{Zn}\) ranged from -1.00 to +0.8‰ relative to the JMC standard. A plot of \(^{66}\text{Zn}\) vs. \(^{68}\text{Zn}\) has a slope of 1.98 and r\(^2\) = 0.97, indicating that all fractionation of Zn in this sample suite is mass dependent. Sphalerite had \(^{66}\text{Zn}\) values near -0.1 ‰, with almost no variation between samples. In the highest headwater samples, dissolved \(^{66}\text{Zn}\) was around -0.2 to -0.3 ‰, with a trend towards slightly lighter values downstream. If sphalerite is the main source of Zn to the stream, then the dissolved \(^{66}\text{Zn}\) should be closer to the sphalerite (Fernandez and Borrok, 2009). The fact that dissolved Zn in rio Naracauli headwater samples is 0.1 to 0.2‰ lighter either suggests a different Zn source or some in-stream process that modifies the Zn isotope ratio. The \(^{66}\text{Zn}\) values of hydrozincite samples were 0.25 to 0.3‰ heavier than the waters with which they were in contact, which would explain the lighter \(^{66}\text{Zn}\) values in water samples. Continued precipitation of hydrozincite also would explain the progressive decrease in \(^{66}\text{Zn}\) values for downstream water samples. It is known that the formation of the hydrozincite is biologically driven (De Giudici \textit{et al.}, 2009), but the exact mechanism of Zn fractionation is as yet unknown.

Sessione tematica D5:
Inquinamento ambientale da rocce serpentinitiche:
analisi del rischio e metodi di bonifica

Conveners:
Elena Belluso (Università di Torino)
Chiara Boschi (IGG, CNR, Pisa)*
CHROMIUM (III) AND CHROMIUM (VI) IN SERPENTINITE-HOSTED SPRING WATERS FROM TUSCANY (ITALY)

I.G.G. - C.N.R, Pisa

Serpentinites and serpentine soils in Tuscan area display high concentrations of Cr, dominantly in the form of Cr (III), as well as other potentially toxic elements including Ni. Geochemical interactions during serpentinite weathering and soil formation may provide oxidative pathways allowing the formation of Cr (VI). In fact, spring waters in serpentinites along coastal Tuscany may have high Cr (VI) contents, indicating a possible remobilization of Cr into groundwaters. Despite the availability of measurements from different systems (rock, soil and water) in Tuscany, the pathway of release of Cr (III) from the serpentinites and its oxidation to Cr (VI) is not assessed. RESPIRA project aims to characterize the Cr-bearing phases within serpentinites and serpentine soils (see Langone et al., FIST 2011) and to assess the processes of release and/or oxidation of Cr from rock to near-surface waters. Our multidisciplinary approach, that combines field, analytical and laboratory studies in solid and water samples, is also necessary to define whether or not serpentinites and serpentine soils are sources of non-anthropogenic Cr (VI). Springs from serpentinite outcrops and from a serpentinite quarry in the coastal Tuscany were sampled for Cr (III) and Cr (VI) analysis, separating the two forms directly and immediately in the field using cation-exchange cartridges. All the spring waters are fed by Cr-rich ophiolite host rocks, however they exhibit different content in Cr (III) and Cr (VI). The study sites are far away from potentially anthropogenic pollution sources.

The springs emerging directly from serpentinite quarry (Santa Luce) are Mg-bicarbonate and show alkaline pH values (8.1±0.1) as a consequence of the interaction with ultramafic rocks. The magnesium content in samples collected during dry season is higher than during rainy season when the discharge of the springs increases, indicating a different degree of interaction with the host rocks. The total chromium content is about 5 ppb and the prevailing form is Cr (III), even if slightly basic pH values indicate that the conditions are potentially favourable for both Cr (VI) and Cr (III) forms. Spring waters collected from the surroundings and circulating within ophiolites are Mg-bicarbonate with pH values around 7.5, while groundwaters circulating in carbonates and marls (sedimentary cover of ophiolites) are Ca-bicarbonate with slightly acid pH (6.8±0.2) and higher pCO2 (from 2.3E-2 to 1.0E-1 atm). Differently, high Cr concentrations were measured in Querceto spring waters (50 ppb), almost entirely in the Cr (VI) form. As well, a spring in San Dalmazio site has about 15 ppb of Cr (VI).

All the spring waters circulating in serpentinites are Mg-bicarbonate with pH values around 8. However Ca/Mg molar ratio in Querceto (0.7) is higher than in Santa Luce (0.03) and in San Dalmazio (0.06). In the same area Cr contents in serpentinite groundwaters are lower (less than 15 ppb), essentially in the form of Cr (III), and TIC content is higher. First results highlight differences in Cr (VI) and Cr (III) contents in spring waters discharging from serpentinites. It has been noticed that in Querceto and San Dalmazio Cu-Fe sulphide ores occur close to the springs. This point out that correlating the geochemistry of the water and the mineralogy of the serpentinites and their alteration products should be essential to evaluate distribution and concentration of Cr in waters. Further analyses of trace elements and organics (e.g. humic and fulvic acid, sulphides, ammonia and nitrate) should be fundamental to better understand oxidation and complexation pathway of Cr.
CHROMIUM BEHAVIOR DURING WATER-SERPENTINITES INTERACTION: FIRST RESULTS FROM PETROGRAPHIC AND GEOCHEMICAL STUDY OF SERPENTINITE SOILS AND SERPENTINITES IN A TUSCAN QUARRY (ITALY)

I.G.G. - C.N.R, Pisa

Serpentinite outcrops, such as the altered ophiolites cropping out in the Tuscany (Western Italy), bear high level of Cr (and Ni) that can be released into ecosystems during weathering. Cr is predominantly contained in spinel-group minerals, such as chromites (Chr), that are highly resistant to weathering causing their accumulation within the soil. The role of chromite as source of Cr in the environmental processes is still under debate. Some authors argued that Cr-spinel is not a significant source of Cr in serpentinite soils, particularly compared to Cr-bearing silicates. Other authors demonstrated that Chr, which may underwent a chemical modification during weathering/pedogenesis, could represent a diffusive minor source of Cr due to its high concentration in soils and its slow weathering with time. Regardless to the composition of the hosting minerals, Cr is generally present in the not bioavailable trivalent state which may be oxidized to the highly toxic hexavalent form (Cr(VI)). RESPIRA project, financed by EU and Regione Toscana, aims to study processes that promote the leaching of chromium from primary (peridotite) to secondary minerals until to the groundwater, following a multidisciplinary approach.

A serpentinite quarry in the coastal Tuscany was chosen due to the favorable rock exposure, the occurrence of well-developed soils at the top of the quarry, and spring waters at the bottom of the quarry.

XRF analyses of two soil profiles revealed a weak variation in Cr from values comparable with serpentinite bedrock (3100 ppm; deepest horizons) to depleted values in the uppermost horizons (2765 ppm). This variation reflects the mineralogical composition of the soils horizons: Cr-bearing phases occur preferentially in the deepest horizons.

Preliminary FEG-SEM and EMP results revealed that Cr is mainly hosted by spinel-group minerals, such as Mg-Chr. Cr$_2$O$_3$ content of Mg-Chr vary from ~ 23 to 43 wt. %, with the lowest and highest values relative to crystals from soil samples. Mg-Chr is generally replaced by Fe-Chr and magnetite towards the rims and/or near fractures. In several cases, the alteration products of the Mg-Chr may contain variable amounts of SiO$_2$ (5-27 wt.%) inversely correlated with Cr$_2$O$_3$ contents (11-24 wt.%). The SiO$_2$ values apparently give a measure of the extent of Mg-Chr alteration during serpentinization and suggest the presence of fine-grained silicate aggregates. Indeed, locally these alteration products show a microporosity. Apprecciable Cr contents (0.5 wt.% < Cr$_2$O$_3$ < 1.5 wt.%) have been obtained from the rare relicts of the minerals of the peridotitic paragenesis (e.g. piroxenes). Generally, the Cr contents of serpentine group minerals is low (< 0.2 wt. %) with the exception of serpentinite analysed from bastite pseudomorphic textures and late veins, where Cr$_2$O$_3$ may reach 1.70 wt.%. Garnet and chlorite are secondary phases containing less than 1.0 and 1.3 wt. % of Cr$_2$O$_3$, respectively.

Two springs emerging directly from serpentinites were sampled and preserved for Cr (VI) and Cr (III) analyses. These waters are Mg-bicarbonate and show alkaline pH values (8.1±0.1) as consequence of the interaction with ultramafic rocks. Spring waters collected from the surroundings, and circulating within ophiolites are Mg-bicarbonate with pH values around 7.5 and pCO$_2$ from 3.8$^{-3}$ to 7.20$^{-3}$ atm. Groundwater circulating in carbonates and marls (sedimentary cover of ophiolites) are Ca-bicarbonate with slightly acid pH (6.8±0.2). Their pCO$_2$ range from 2.3$^{-2}$ to 1.0$^{-1}$ atm. The total chromium content in groundwater and in the two springs from quarry is about 5 ppb and the prevailing form is Cr (III). They show an enrichment of Mg related to the degree of interaction with the rock.

These preliminary results reveal that integrating geochemistry and petrography should be successful to model the Cr mobility from natural outcrops and quarries. Further investigations will improve our results.
SOIL CONTAINING ASBESTOS: ANALYSIS AND PROBLEMS

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The goal of this work is to emphasize the various problems that exist concerning asbestos in nature and how these problems are often difficult to solve. An example of this concept is the analysis of contaminated soil, encountered during the excavation of the foundations of a building in the village of Sommarese, 3 km from Emarese (the Aosta Valley), a site of national interest because of the presence of asbestos.

The soil has been analysed by means of optical microscopy in phase contrast (PCOM), adopting a particular methodology with the aim of obtaining a direct weighing of the asbestos fibres: the sample was divided into granulometric classes, the granular fraction was separated in wet conditions, and the wood fraction, present in a high percentage, was partially or totally burnt in a muffle furnace.

The indirectly weighed asbestos was measured according to Italian regulation on the fibres, adopting SEM counting (Ministerial Decree 06/09/94); then the semi-quantitative grades were obtained taking into account the mineral volumic mass.

The results have shown the presence of asbestos in a quantity that almost reaches the threshold value dictated by Italian regulations concerning ground, (Legislative Decree 471, 1999) that is, 1000 mg/kg.

The ground in the old village of Sommarese is therefore polluted naturally. Some questions therefore arise: should the ground be disposed of in an asbestos dump or it is better to leave it where it is, where all the unexcavated soil has the same level of contamination? And if so, what interventions should be made to make the site safe?
ASBESTOS MINERALS IN SERPENTINITES: MAPPING AND RISK ASSESSMENT IN THE OPHIOLITIC BODIES OF TUSCANY, ITALY

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The six minerals grouped under the name of asbestos are universally recognized as dangerous for human health due to their fibrous shape. The asbestos minerals are generally found as common weathering products in peridotite, gabbro and basalt, typically associated in ophiolitic sequences. The circulation of fluids in these oceanic sequences cause a variably intense and penetrative hydrothermal weathering of pre-existing magmatic minerals such as olivine and pyroxene.

No matter their peculiar chemical and physical characteristics, the industrial use of asbestos minerals has been completely eliminated from production and use in many countries. However, the asbestos fibres still represent an ubiquitous pollutant, not simply because of the number of industrial products still present in urban areas, but also because of the tendency, in asbestos-bearing rocks and soils, of fibres to be released naturally (landslides, erosion, weathering) or by human activities (mining, earthworks, excavations, tunnels). Therefore, the control of the risk of environment contamination in areas where ophiolitic sequences crop out, still represents a relevant societal problem that require a precise estimate of the nature and abundance of fibrous minerals. This assessment can be performed with a multiscale and multidisciplinary geological study that allows a characterization of the asbestos from the mineralogical point of view (different degrees of risk for human health are related to different asbestos minerals).

We show here the main scientific and technical lines of a project of asbestos-related risk assessment developed by the Dipartimento di Scienze della Terra (Pisa University) and the Alitec S.r.l. and Pivot Consulting S.r.l. companies, funded by the FSE (Fondo Sociale Europeo) through the Tuscany Region administration.

The main goals of the CaMAm (Caratterizzazione e Mappature Amianto) project is in fact the mapping and characterization of the asbestos-bearing ophiolitic rocks in the area of the Region of Tuscany. The main phases of the project comprise a complete lithological and structural characterization of the outcrops with asbestos-bearing lithotypes as well as a qualitative and quantitative assessment of the amounts of these minerals.

All the collected field-based information will be stored and elaborated in a GIS (Geographic Information System) database. This database will contain a directory of areas where asbestos-bearing lithotypes are outcropping and the related qualitative and quantitative information. The database will be constructed starting from that already existing of the geological cartography, recently performed by the Tuscany region administration. The mineralogical characterization of asbestos phases will be performed by various techniques typically used in the context of fibrous minerals, such as XRD analyses, Raman spectroscopy and, where possible, TEM techniques. As much as possible an attempt will be made to check on possible relationships between the type of mineralizing phase and the structural, mineralogical and petrographical features of the lithotypes or fracture systems containing those phases.

In particular, with this project we aim to test a quantitative estimate of fibres by multi-scale image analyses of the outcrops and their mineralized fracture patterns. Thanks to the cooperation with Pivot Consulting S.r.l. (c/o the Technology Centre of Navacchio (PI)) and Alitec S.r.l. companies, pilot studies in selected areas will be conducted to test the procedures for a quantitative assessment of content asbestos fibres and establish the background level of fibres resealed into the atmosphere. The companies will provide innovative techniques such as (i) the recognition of images through acquisition by drones (Pivot Consulting S.r.l.), and (ii) acquisition of data on the concentration of micro and nano powders dispersed in the air using a portable detector (Alitec S.r.l.).
EXPOSURE TO ASBESTOS FIBERS IN AGRICULTURE:
A CASE OF WORK-RELATED MESOTHELIOMA

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It’s note the correlation between asbestos fibers and pleural mesothelioma which is called the “sentinel event” which highlights a particular exposure to those particular fibers.

This case refers to a farmhand who, during his working life, has always worked in the municipality of Viggianello (PZ) Southern Italy - municipal road Cornaleto-Sant’Elena, where there are ophiolitic outcrops (known as green rocks).

The woman has contracted a pleural mesothelioma. The survey carried out by means of levies of particles of respirable fraction, as well as bulk samples of loose soil - the same type of work - and rock samples in place, has revealed the presence of chrysotile asbestos fiber type in soil. This presence appears to be in agreement with literature data.

This paper illustrates the methods of sampling carried out and the analytical results obtained by using optical microscopy (SEM) and phase contrast (PCOM).
HYDROLOGY, HYDROCHEMISTRY AND WATERBORNE INORGANIC FIBRES AT BALANGERO FORMER MINE AREA, NORTH-WESTERN ITALIAN ALPS

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Water resources have been analyzed in terms of quantity and quality at the former mine of Balangero. The mine, set 30 km north-west of Turin, produced chrysotile since the 1920’s and in the 1970’s became the largest asbestos mine in Europe. In 1990 the mine was closed, although there were still over 18 million tons of asbestos to extract. The mine wasn’t reopened because the Law 257/92 banned the extraction, import, export, marketing and production of asbestos, its products and products containing asbestos.

The study area covers a surface of about 7 km² in the nearby of the former mine and its two landfills of serpentinitic coarse material, resulting from the rock extraction and processing. The former mine is set in the “Balangero Massif”, a geological body mainly consisting of serpentinite.

The research has been carried out in accordance with RSA Company, that deals with the rehabilitation and environmental development of the Balangero site, identified as National Interest Site for remediation by the Law 426/98.

A water balance for the years 2006 and 2007 has been calculated for 5 watersheds covering the whole study area. Precipitation and temperature data of seven meteorological stations have been utilized. In the study area, around 65-70% of precipitation is lost by evapotranspiration. The remaining water (water resources) flows principally as surface water rather than groundwater cause of the low permeability of metamorphic rocks. Infiltration is predominant only at the landfills (22% of the study area).

Also a qualitative characterization of some superficial water samples has been carried out in order to assess the influence of the wide landfill of mine rock residues on the water resources. The waters of the five watersheds have been sampled and analysed at the Turin University Laboratories (Dipartimento di Scienze della Terra and Dipartimento di Scienze Mineralogiche e Petrologiche). Water generally shows a magnesium-bicarbonate facies and secondarily a magnesium-sulphate facies. In some cases, the concentrations of sulphate and nickel exceed the threshold defined by national law. According to literature data, such values are justified by the percolation of rainwater through the serpentinitic materials of the landfill, relatively rich in nickel and sulphides. Regard to the suspended matter in water, only the breathable inorganic fibres (length > 5 μm, width < 3 μm , length/width > 3, as indicated by Italian law) have been researched and analyzed by SEM-EDS. Twenty-two mineral species have been found including three classified asbestos: chrysotile, tremolite-actinolite asbestos and anthophyllite asbestos. Cause of the high dispersion due to the reduced size of the fibres, the highest concentrations of asbestos were detected in samples that drain the landfills, while difficulties have been encountered in the other samples where a generalized low concentration of asbestos fibres probably occur. In order to obtain more accurate data for the other samples, analytical determinations by TEM-EDS have been recommended, as practiced in other countries for analysis of microfibers in water.
PROFESSIONAL EXPOSITION EVALUATION IN THE CULTIVATION OF GREEN STONE QUARRIES IN THE PROVINCE OF PARMA

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The highest concentration of active green stone quarries of Emilia Romagna is located in the province of Parma. Between 2002 and 2004, a regional survey was carried out with the purpose of characterising the extracted materials and defining the exposure to asbestos fibres of workers employed in the mines. In 2009-2010 a further assessment was carried out in order to improve the survey.

The productive sector taken into consideration employs just a few tens of seasonal workers whose number is strongly affected by the market demand for ophiolitic materials. The ophiolitic materials coming from the Apennines are peculiar as the presence of both fibrous and not fibrous serpentine makes the comparison between different microscopic analytical methods interesting.

The 11 mining sites, managed by 8 different companies and employing 30 people as a whole, are homogeneous in terms of kind of activities carried out (with the exception of one quarry only where explosive charges are used): extraction, screening, grinding, loading and transport.

In 4 of these active sites, personal monitoring was carried out on the operators of the typical tasks carried out in the quarry - excavator driver, dumper driver, lorry driver, crusher operator. Despite the limited amount of samples, it is possible to make remarks on the characterisation of the tasks.

The sampling was carried out in accordance with the methodology provided by the UNI EN 589/97 standard. No. 13 persona samples (Cp) were taken, corresponding to 7 exposures during a working shift. As specified by the WHO 1997 method, the following instruments were used:

- calibrated portable pumps (Q = 2 l/min),
- conductive open face sampling heads with cylindrical extension,
- gridded membrane filters (mixed esters of cellulose).

The filters were analysed both in Phase Contrast Microscopy (PCM) and in Scanning Electron Microscopy (SEM), and compared with the Limit value (LV), concentration in ff/cc and/or ff/litre, in order to compare the two methods and to quantify the presence of asbestos fibres.

The data of the personal exposures have been statistically processed to check the enforceability of UNI EN 689/97 standard. Log-normal distribution, GSD and homogeneity of the group examined were determined and, as a consequence, the exceedance probability of the LV (% Pn) with its confidence interval was calculated using the application software ALTREX.

Regressions were performed so as to make a comparison between the analytical methods and to count the quantity of asbestos fibres and of fibres as a whole.

The results of the survey lead us to consider the extraction process of green stones a situation to be kept under control (ORANGE level as per Annex D of UNI EN 689/97). In particular it is deemed necessary to assess the way the mining activities are performed at the quarry and how the extracted materials are used (coarse pieces rather than powder).
PROPOSED CLASSIFICATION OF OPHIOLITES DEPOSITS AND USE OF MATERIALS EXTRACTED ACCORDING TO THEIR CONTENT OF ASBESTOS

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As it is widely known and studied in ophiolites (ultramafic rocks of intrusive magmatic origin, partially altered or metamorphosed) asbestos fibers may be found in the form of slow and small veins (those typical of alpine ophiolites, very rare in Apennines) and distributed within the fractures.

Mining, quarrying and processing could release a number of asbestos fibers into the environment, that needs to implement preventative measures of workers protection and local population.

The methods of control of the extracted materials are carried over from the Ministerial Decree (DM) 14/05/1996, which defines criteria for the classification and the use of “green stone” according to their content of asbestos. The excavation is allowed under a certain danger level as defined by the amount of asbestos released from the rocks, where the value of Release Index must be Ir < 0.1.

In addition to this law (exclusive to the ophiolites quarry sector) we can find the provisions of health and safety at work in Legislative Decree n. 81/2009. It stipulates specific analytical measures and controls over all work environments at risk for the presence of asbestos. The law identifies the permissible exposure limit (defined as “VL” Value Limit), beyond which they must take appropriate precautionary measures.

Various objections were raised over the correct application of the Ministerial Decree 5/14/1996, in particular relate to the real meaning of Ir (Release Index). The real ophiolitic danger is related to the chance of rocking crumbler during extraction and subsequent work phases since it is during these activities that rocks can more easily release asbestos fibers.

These considerations were already included in the studies carried out by the Emilia-Romagna Region (Il Progetto Regionale Pietre Verdi - 2004). It proposes a new classification of the ophiolites deposits based on a simple but direct measurement of the release index (called AR “asbestos free or releaseable”) taken before and during the mining activities related to the types of products produced by the quarry.
QUALITATIVE AND QUANTITATIVE DETERMINATIONS OF CHRYSOTILE IN MASSIVE SERPENTINITES THROUGH THERMAL ANALYSIS METHODS

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One of the main problems in the study of serpentinitic rocks is the accurate determination of serpentine mineralogy, because of the typical coexistence of different serpentine polymorphs in ultrafine, poorly crystalline assemblages, difficult to investigate by conventional methods, such as X-ray diffraction or microanalytical approaches.

In this study, we have collected thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) data for carefully checked serpentine samples, finding that lizardite (lz), antigorite (atg) and chrysotile (ctl) have distinctive thermal behaviour, with main differences in the dehydroxylation range (500 - 800°C). DTG and DTA peak temperatures progressively decrease from antigorite (720 and 715°C, respectively) to lizardite (708 and 714°C), polygonal serpentine (685 and 691°C) and chrysotile (650 and 654°C). Antigorite has a further diagnostic signal at ~740-760°C, always absent in the other serpentines.

TG, DTG and DTA data have been also collected for lz + ctl and atg + ctl mixtures, obtained by combining known amounts of the previously investigated reference samples. Deconvolution processing of DTA endothermic signals revealed good linear correlation between peak area ratios (for both ctl/lz and ctl/atg mixtures) and chrysotile content (with \( R^2 \) of 0.99 and 0.96, respectively). The DTA correlation curves have been used to estimate the chrysotile content in two unknown samples (massive serpentinites with lz + ctl pseudomorphic textures), revealing surprisingly high chrysotile content.

Based on the above results, we suggest that thermal analysis may represent a promising and straightforward method for qualitative and quantitative mineralogical determinations of bulk massive serpentinites, with important petrological and health-related implications.
Sessione tematica D6: Stoccaggio geologico e mineralogico della CO₂: stato dell’arte e prospettive

Conveners:
Chiara Boschi (IGG-CNR)
Luigi Dallai (IGG-CNR)*
Fedora Quattrocchi (INGV)
SUITABILITY OF DEEP SALINE AQUIFERS FOR UNDERGROUND STORAGE OF METHANE AND CARBON DIOXIDE

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Storage of Methane (CH₄) and Carbon Dioxide (CO₂) in deep saline aquifers is a proven technique and a promising strategy to respectively address mitigation of climate change and energy security regarding additional Methane demand during cold weather. These themes are attracting growing interest within both scientific and industrial communities.

According to one of the leading scientific research bodies in geosciences in Italy “Deep saline aquifers offer the largest storage potential of all the geological CO₂ storage options, and are widely distributed throughout the Earth”. Moreover, according to the International Gas Union, “The sciences and technologies that UGS (Underground Gas Storage) operators use for Methane storage, specially for aquifers storage, are a solid basis for CO₂ sequestration projects”, highlighting in an authoritative way the strong technical interconnection between these two industrial sectors. In Italy, several storage projects in deep saline aquifers are underway.

A major underground Methane storage site (Rivara Project) is being planned in a fractured carbonate reservoir in Italy’s Po Valley. Rivara’s working capacity is estimated at approximately 3.2 billion cubic metres (bcm), which would make it one of largest and potentially best performing gas storage facilities in Italy and in Europe. Additionally, several sites in naturally fractured carbonate aquifers are being evaluated for potential CO₂ storage, among which a site offshore under the continental platform of the Tyrrhenian Sea. Major efforts are in progress to properly characterise these storage sites and to plan their safe operation ahead of the beginning of the construction phase, including reservoir and caprock stratigraphy and structure, geomechanics, reservoir engineering, geochemical and seismological monitoring.

An innovative, multidisciplinary and integrated work flow has been identified to document the suitability of these sites. The work programme is designed to determine the feasibility and the safety of the gas storage project, either CH₄ or CO₂. This includes two main phases, namely an Initial Phase, followed by the Appraisal Phase, which repeats the cycle in more details. Each phase involves the following integrated sequential stages:

- Analysis of pre-existing data (wells, seismics, subsurface data, seismological data);
- 3D geologic modelling;
- 3D reservoir modelling;
- 3D geomechanic modelling. The Initial Phase involves all the data gathering activities that can be implemented without a specific licence, while during the Appraisal Phase the activities include the acquisition of geophysical data and the drilling of wells, which require specific ministerial authorization and license.

The key elements of the Appraisal Phase, in fact, are the acquisition of a new 3D reflection seismic campaign and the drilling of the necessary appraisal wells with the associated specialized activities (cores, logs, reservoir test). Before the beginning of the construction phase, it is also important to implement a multidisciplinary monitoring programme ante-operam, in order to have the basic elements for detecting any change that may occur after the beginning of the site operations. While underground Methane storage (UGS) activities are fully regulated in Italy, and an aquifer specific European Standard (UNI-EN-1918-1) exists, underground storage of CO₂ is not yet currently regulated. Italy is however about to adopt European Directive 2009/31/CE of 23 April 2009 on the geological storage of carbon dioxide. Independent Gas Management is a competent specialized operator for the safe development of suitable CH₄ and CO₂ underground storage sites in deep saline aquifers hosted in naturally fractured carbonate rocks.
FLUID GEOCHEMISTRY AND MINERAL CHEMISTRY OF HIGH $p$CO$_2$ SYSTEMS: A LESSON FROM THE PSS1 BORE-WELL AT CAPRESE MICHELANGELO (EASTERN TUSCANY, ITALY)

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Carbon capture and storage (CCS) is considered a valid option for reducing CO$_2$ concentration in atmosphere without a dramatic impact on the economy. The feasibility of many CCS projects worldwide is still under evaluation, although others have already started (e.g. Weyburn pilot project in Canada; Cantucci et al., 2009 and reference therein).

The injection of CO$_2$ underground allows to acquire useful experimental data to be used for geochemical modeling purposes as accurate data and chemical-physical constrains on rock and CO$_2$-rich fluid interactions are needed. Nevertheless understanding if CO$_2$ can safely be stored at depth for long times (thousands of years) can actually be evaluated only by geochemical modeling. Natural analogues are very useful for identifying key mechanisms and processes relevant to long-term stability and seepage mechanisms associated with CO$_2$ geological sequestration. Consequently, these systems are presently representing the easiest way to gather experimental data to be compared with those scenarios provided by geochemical models. A high $p$CO$_2$ system was found located in San Cassiano Basin (Tiber Valley, Eastern Tuscany). Here, in correspondence of PSS1 borewell (Anelli et al., 1994), a relevant fraction (92.2% vol) of carbon dioxide is found at the depth of 3,800 m, presumably located at the top of the main fluid reservoir hosted in “andesitic” (?) volcanic rocks interbedded with the evaporitic Formation of Burano, at P-T conditions of nearly 700 bar (70 MPa) and 120°C respectively, with a density of 860 kg/m$^3$, univocally suggesting the presence of a supercritical fluid (Heinicke et al., 2006).

Fluid chemistry from the bore-well and that discharging at the surface from natural manifestations (bubbling mud pools, springs, stream waters, wells) were studied along with carbon (in CO$_2$) and helium isotopes. Moreover extensive surveys on the altered volcanic rocks, likely corresponding to the top of the reservoir, and the hosted minerals were carried out. Qualitative and quantitative analyses were performed by means of SEM-EDS, XRD and EMP techniques.

The mineral paragenesis consists of Quartz, Ca-Fe-Mg Carbonates, Na-K Illite, Fe-Mg Chlorite and accessory Apatite and Fe-Ti oxides. Fluid inclusion studies showed the presence of H$_2$O-rich and CO$_2$-rich phases. First-type inclusions provide information on the physical-chemical features of fluid responsible for hydrothermal alteration, whilst second-type inclusions indicate changes of CO$_2$ densities within the reservoir. Experimental runs at LLB (CEA-CNRS, Saclay, France) at SANS (Small Angle Neutron Scattering) diffractometer PAXE were conducted for retrieving data about the microstructure of porosity of the rocks. The mineral chemistry of Ca-Fe-Mg carbonates (Bicocchi et al., 2011) was studied by applying appropriate statistical methods. The large chemical, physical and mineralogical dataset obtained in the present study will be employed to build up a conceptual model of the fluid-rock interaction processes that affected this geologically complex portion of the central-northern Apennines.

ENI is strongly committed to fight climate change by developing a Carbon Management strategy that combines operational and management initiatives with the development of research into innovative technologies aimed at optimizing the energy efficiency as well as promoting the use of renewable. In the field of Carbon Management, the eni program includes the building of the first integrated pilot project in Italy, exploiting an exhausted gas field at Cortemaggiore (Piacenza) to realize a pilot CO$_2$ injection test. The project forecast the injection of 24,000 tons of CO$_2$ during a three years period and consists of different phases: particular evidence will be given to the criteria applied for the choice of the injection site, the preparatory studies and the monitoring plan - covering a long period before the start of the injection in order to acquire a sound baseline - planned to ensure the safety and effectiveness of the pilot. The start of the CO$_2$ injection is scheduled for mid of 2012.
SPONTANEOUS CO$_2$ MINERALOGICAL SEQUESTRATION IN MINE WASTE MATERIALS: AN EXAMPLE FROM MONTECASTELLI COPPER MINE (TUSCANY)

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The Montecastelli copper mine, close to Pomarance (Tuscany, Italy), has been exploited since the Etruscan time, but it has been during the 19th century that Cu ores (bornite and calcopirite) were extensively cultivated. Copper minerals are mostly concentrated along a shear zone hosted by serpentinite. During exploitation, barren serpentinites as well as low grade ore material extracted in underground works were disposed in a mine dump in front of the entrance of the tunnels. Field observations, and mineralogical investigations, indicate that specific layers of the dump were intensively carbonated. Carbonate precipitates are known from serpentinite mine dumps from many other localities (Wilson et al., 2006 and references therein).

Such a low temperature alteration is a natural analogue of an induced carbon dioxide mineralogical sequestration, spontaneously developed in a very recent time. RESPIRA project, financed by EU and Tuscan Region, aims to study different type of carbonation processes, that led to natural analogues of CO$_2$ mineralogical sequestration. Here, we report the preliminary studies of the carbonation in Tuscany mine tailing, in order to give an estimate for the sequestration capacity of ultramafic mine tailings, and to provide a framework for the development of standard protocol of enhanced mineral sequestration at mine sites. Dumps at Montecastelli mine are composed by a bottom incoherent layer, up to 4m thick, of medium to big size serpentinite clasts (up to 60 cm in diameter), randomly distributed and characterized by the presence of large voids between clasts. The intermediate layer, ranging from 10 cm to 1 m in thickness, consists of small-medium-size serpentinite clasts encrusted by a very fine-grained whitish carbonate-rich material. A 15-40 cm of young soil with an initial accumulation of organic matter (litter, three roots, etc.), alternating with serpentinite clasts, is on the top. On the distal part of the tailing, the bottom layer disappeared, prevailing a greenish serpentinite- and clay-rich layer very-fine grained and incoherent carbonate-rich layer intercalated to a greenish serpentinite- and clay-rich part.

The carbonate minerals are mainly represented by hydromagnesite, occurring as white coatings and crusts with the typical fibrous-radiating texture, and in veins or fracture fillings. Serpentinites are altered to friable mineral assemblage that consists mainly of clay and carbonates. Provided that exploitation/exploration of the Cu ores at Montecastelli definitively stopped after the Second World War, spontaneous mineral carbonation of serpentinite clasts disposed in mine dumps has likely occurred during the last 60 years. Mineralogical, geochemical and isotopic (O, C, Sr) investigations will provide insights to the P,T conditions and fluid composition during carbonate precipitation in mine dumps at Montecastelli.
Today a main challenge in environmental management is to consider some contaminants such as carbon dioxide (CO₂) and reject brines, instead of harmful and dangerous by-products, as valuable sources for several compounds to be involved in diverse industrial processes.

The geological sequestration of CO₂ currently in vogue is considered the most promising method to trap and store this greenhouse gas. We propose alternatively the long-term sequestration of CO₂ in solid form through its mineral sequestering as hydroxycarbonate of magnesium, nesquehonite [MgCO₃·3H₂O], without any potential risks for the environment as it is stable at Earth surface conditions.

Carbonation reactions are common in nature but the idea of developing this process for the disposal of CO₂ based on the chemical fixation of the carbon dioxide in the form of carbonate minerals was only proposed in 90s using calcium in brines, and then by carbonation of magnesium-bearing minerals from ultramafic igneous rocks. There are serious problems with that approach: the reaction kinetics for magnesium silicates tends to be too slow and environmental concerns are associated with mining and processing very large amounts of rocks. Conversely, we developed an innovative and non-traditional use of CO₂ and brines in a process having a dual beneficial objective to reduce the volume of this greenhouse gas to be discharged and mitigate the negative effects of reject brines.

We recently described a carbonation process involving the reaction of gaseous CO₂ with a magnesium chloride solution producing nesquehonite. In order to evaluate the appropriateness of a reaction of CO₂ with Mg chloride solutions as a process for storing carbon dioxide and wastewater, the thermal behaviour of nesquehonite was investigated in situ using real-time parallel-beam X-ray powder diffraction. Nesquehonite appears to be stable up to 373 K suggesting that its storage as “sequestering medium of CO₂ and reject brines” remains stable under the temperature conditions that prevail at the Earth’s surface. At temperature above 373 K the process of thermal decomposition of nesquehonite (via intermediate hydrated magnesium carbonate phases) ultimately produces magnesite in the range 423-483 K. This sequence involves the formation of carbonate minerals thermodynamically more stable than nesquehonite, assuring the stable storage of these hazardous materials for millions of years. Our initial work on the carbonation process involved a relatively dilute solution of magnesium chloride, roughly 7 g/l of Mg, at room temperature.

The reaction rate was found to be rapid, the deposition of nesquehonite being virtually complete in about ten minutes. Nesquehonite removed about 80% of the CO₂ in solution. To test the efficiency of the carbonation process in more concentrated solutions, having salinity more close to that of the reject brines that are industrially available, further experiments have been carried out using solutions with different degree of salinity (16 and 32 g/l of Mg). A comparison of the efficiency of the CO₂ mineralization process among sets of experiments at low and high salinity shows that in more concentrated solutions, the efficiency was reduced to about 65%. The results suggest that the goal of CO₂ sequestration and reject brines discharge seems to be realistically obtained also using the more common wastewater. The sequestration of CO₂ and the disposal of reject brines via carbonation produces a solid material that can be utilized directly in many products such as acoustic panels, non-structural panels, insulation, or agglomerated in concrete as a man made aggregate. Because nesquehonite growths as fibrous and acicular crystals, it improves the microstructures of manufacturing materials.
GEOCHEMICAL BARRIERS IN CO₂ CAPTURE AND STORAGE: A CASE STUDY

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The fate of CO₂ once injected into a saline aquifer can be predicted by means of numerical modeling procedures of geochemical processes and fluid flow properties, these theoretical calculations being one of the few approaches for investigating the short-to-long-term consequences of CO₂ storage into a deep reservoir. In this work the results of a methodological approach for the assessment of the CO₂ injection impact in the reservoir and the cap-rock stability in an offshore reservoir in the Tyrrhenian Sea are shown and discussed. The stratigraphic succession of the investigated area is constrained by a more than 3,500 m deep well. It is characterized by: a thick marly-to-clayey cover succession overlying a calcareous fractured succession. The first geological sequence can be considered as an efficient cap-rock, whereas the last unit represents the reservoir of a huge regional deep aquifer. A re-interpretation of available seismic reflection dataset was performed to build a 3D geological model and to calculate its Gross Reservoir Volume. 3D simulations were performed by the TOUGHREACT code at the theoretical CO₂ injection pressure.

In order to understand the nuances of this complex system, three different simulations were carried out. The first model is a stratigraphic column with a size of 0.11×0.11×4 km and a metric resolution in the injection/cap-rock area (total of 8,470 elements), with the goal to assess the geochemical evolution of the cap-rock and to ensure the sealing of the system. The second simulation is a horizontal model with a size of 99×11×11 m to study the fate of the displaced water at the plume front and the permeability variations as the injected CO₂ has started to promote geochemical reactions. The third simulation is at full scale (13.5×12.75×4 km) in order to predict the CO₂ path from the injection towards the spill point. The most important effect evidenced in these runs is a barrier effect due to the flow of the CO₂-rich acidic water into the carbonate reservoir, originating a complex precipitation/dissolution surface that may have an effective impact on CO₂ sequestration due to the reduction of available storage volume reached by the CO₂ plume in 20 years and/or the enhancing of the required injection pressure. Kinetic modeling suggests a rough dissolution of calcite of about 20% in volume close to the injection well, although precipitation occurs in the reservoir as soon as the effect of the CO₂ plume has disappeared. Basically, as the acidic saline fluid mixes with the alkaline formation waters calcite is precipitating. This implies that at the injection point the permeability increases and a sort of geochemical barrier is produced downstream along the fluid flow path. As a consequence, two key zones can be distinguished: i) inside and ii) outside the CO₂ plume. Calcite behavior may be regarded as “displacement” from the CO₂-rich waterfront to the downstream fluid path and this is likely the main cause of porosity/permeability reduction. This barrier diminishes the outflow velocity of the CO₂-displaced water, producing a lower CO₂ injectivity. The formation of secondary minerals occurs inside the plume where more acidic conditions are encountered, while the CO₂ plume grows as the injection proceeds up to roughly 1 km of radius after the injection of 30 Mt of CO₂ in 20 years.
Dissolution and Carbonation of a Serpentinite: Inferences from Experiments up to 300°C and 30 MPa

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Mineral trapping is a crucial process in a CO₂ sequestration perspective and it can be simplified as the sum of two consecutive processes: 1) dissolution of primary silicate minerals, such as olivine, serpentine, and pyroxenes, which are mainly found in igneous ultramafic rocks, variably affected by alteration processes, and 2) precipitation of carbonates as a consequence of reaction between solutions and CO₂. Several parameters, such as temperature, pressure, salinity of the solution, control the kinetics of the whole process. Thus, the realization of experimental tests taking into account these parameters is essential in either ex situ or in situ CO₂ sequestration projects involving mineral trapping.

An experimental study was performed within the ZEBU (Zero-Emission Biogas Use) project, aimed at increasing the CH₄ contents of biogas emitted from landfills through CO₂ separation and sequestration by serpentinite carbonation. Experiments in order to determine dissolution rates of a serpentinite sample mainly consisting of lizardite (with subordinate orthopyroxene, magnetite, and chromite) were performed under different P-T conditions (up to 30 MPa and 300°C) in aqueous solutions at variable salinity. In particular, at 0.1 MPa and 70°C, serpentinite was reacted with an acid solution (H₂SO₄ 2M) over different times (up to 24h). MgO extraction from the rock turned out to be efficient, varying between 82 to 97%, depending upon the reaction time. Calculated dissolution rates vary from 4.0·10⁻⁹ to 8.5·10⁻¹⁰ mole m⁻² s⁻¹.

Carbonation tests were subsequently performed rising the pH of the solutions up to 9.5 (through addition of NH₃ solution) under a CO₂ flux, but they failed since Mg- and NH₄- bearing hydrated (or anhydrous) sulphates precipitated causing a considerable Mg depletion of the solutions. In contrast, precipitation of a Mg-hydrated carbonate, nesquehonite, occurred upon mixing a synthetic MgCl₂ solution (which simulates acid attack performed using HCl instead of H₂SO₄) with a solution of (NH₄)₂CO₃, obtained through absorption of CO₂ (from synthetic biogas) in ammonia. At higher pressures, the serpentinite was reacted with a NaCl-bearing aqueous solution and supercritical CO₂ at 9-30 MPa and 250-300°C, either in a stirred reactor or in externally heated pressure vessel. CO₂ was supplied from a tank (stirrer reactor) or produced from decomposition of oxalic acid or silver oxalate (pressure vessel).

Serpentinite carbonation occurs after 24h at 30 MPa, 300°C in 100 g/l NaCl aqueous solutions. Under these conditions, Fe- and Ca-containing magnesite crystallized; its amount varies from 5 to 10 wt.%. As regards the sequestration degree, CO₂ uptake attains a maximum of 16 mol% and possibly can be further enhanced by increasing the salinity of the aqueous solution. Assuming the rock to be constituted only by pure lizardite, the calculated dissolution rates under these conditions range from 6.3·10⁻¹¹ to 1.3·10⁻¹⁰ mole m⁻² s⁻¹, and are roughly comparable to the value obtained through acid attack at 0.1 MPa and 70°C for similar experimental duration.

Overall, the results of the experiments indicate that single-step significant carbonation could be (quickly) attained at high P-T conditions avoiding acid attack. Under atmospheric conditions Mg is extracted very efficiently from serpentinite in acidic environment, but the pH of the obtained solution must be adjusted carefully, to avoid the precipitation of non carbonates Mg-containing solids.
La tematica della cattura e stoccaggio del biossido di carbonio (CCS) rappresenta già da alcuni anni uno degli argomenti di maggiore interesse per il mondo scientifico e la ricerca. Su proposta della Commissione europea, il Parlamento europeo e il Consiglio dell’Unione europea, riconoscendo l’importanza di tali tecnologie, hanno emanato la direttiva 2009/31/EC del 23 aprile 2009. La direttiva considera la cattura e lo stoccaggio del biossido di carbonio come una tecnologia ponte che potrà contribuire a mitigare i cambiamenti climatici. L’obiettivo indicato nella direttiva è quello di consentire il recepimento da parte di ogni Stato Membro entro il prossimo 25 giugno 2011. A tale scopo il Ministero delle politiche europee, il Ministero dello sviluppo economico e il Ministero dell’Ambiente hanno costituito un gruppo di lavoro congiunto per la stesura dello schema di recepimento secondo i principi e criteri direttivi stabiliti dalla legge 4 giugno 2010, n. 96 (Legge “Comunitaria 2009”). Attente riflessioni, confronti, analisi degli aspetti tecnici, amministrativi e giuridici hanno portato nel marzo 2011 alla predisposizione finale dello schema di decreto legislativo, il cui testo è stato dapprima discusso e condiviso con le amministrazioni concertanti (Ministero degli Affari Esteri, Ministero della Giustizia, Ministero dell’Economia e delle Finanze) per poi essere sottoposto all’esame del Consiglio dei Ministri, che, in data 23 Marzo 2011, lo ha approvato in via preliminare. Successivamente, in data 12 maggio 2011, il testo è stato discusso durante la Conferenza Stato-Regioni, dapprima per quanto concerne gli aspetti tecnici, mentre, in data 18 maggio 2011, per quanto concerne gli aspetti politici, riscontrando un parere favorevole, condizionato all’accoglimento di alcuni emendamenti. Significativo per il raggiungimento di questi traguardi è stato l’apporto continuo e costruttivo delle regioni, degli enti di ricerca nazionali e delle associazioni di categoria degli operatori. Le attività future, previste nei prossimi giorni, necessarie a concludere l’iter di recepimento riguarderanno la predisposizione del testo finale e l’invio alle varie commissioni parlamentari, chiamate a pronunciarsi in materia.
STRATEGIC USE OF UNDERGROUND FOR AN ENERGY MIX PLAN: 
THE EXAMPLE OF LATIUM REGION (CENTRAL ITALY)

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The world-wide energy demand has been growing so much that there is the need to develop a strategic mix-energy plan to supply low GHG (GreenHouseGas) emissions energy and solve the problem of CO₂ emission increasing. A study published in 2006 by the European Commission shows that if the existing trends continue, by 2050 anthropogenic CO₂ emissions will be unsustainably high: 900-1000 parts per million by volume.

A first useful step to solve this problem can be to evaluate the synergies and/or conflicts between reliable technologies that can produce clean energy involving deep geological structures, namely: 1) clean coal combustion, jointed to CCS (Carbon Capture and Storage); 2) CH₄ storage in natural reservoirs; 3) renewable energies as geothermal energy. These three technologies could coexist in a strategic use of the underground, especially in densely populated country as the Italian territory. In this framework, the preliminary underground screening for a strategic energy use must also consider the presence of potentially suitable areas addressed in the past by dedicated agency for instance to nuclear waste disposal. Selection of these sites is in fact based on more rigid criteria with respect to gas storage or geothermal energy. Therefore, areas selected for nuclear waste disposal represent a peculiar factor that should be take into account for a correct energy plan evaluation.

CCS is considered one of the main technology able to stabilize and reduce the atmospheric concentration of anthropogenic CO₂. Nowadays CCS market is mainly developed in USA and Canada, but still less accounted in Europe. In Italy there aren’t active CCS projects, even if potential areas have been already identified. Traditionally, CH₄ has been a seasonal fuel. The demand of this gas is usually higher during the winter because used for heat spacing. Storing natural gas is actually strategic for two reasons: to fill the seasonal requirements and to have a strategic energy reserve. Many CH₄ storage sites are located in Northern America, while other are present also in Europe and Italy, but the number of sites is limited despite the huge underground potentiality.

Geothermal Energy is a renewable, clean and sustainable energy which can be used indirectly for power generation and directly for numerous applications such as: space and district heating, water heating aquaculture, horticulture and industrial processes. In Italy the power generation from geothermal energy is about 5,400 GWh/year. It comes exclusively from Tuscany (Larderello-Travale and Mt. Amiata geothermal fields) despite the already evaluated huge potentiality of other regions as Latium, Campania and Sicily. Nowadays, new technologies as EGS (Enhanced Geothermal Systems) and Binary Cycle Plants permit the development of the geothermal energy also in areas considered unproductive in the past, due to low underground temperatures and/or absence of fluids.

Here we present preliminary data concerning this work on the whole the Italian territory, starting from Lazio Region. Results show that in this area the three technologies can coexist despite the general complex geological setting. Therefore we are developing a self-sustaining Dedicated Geographic Information Systems (D-GIS) necessary to organize and manage a reliable Mix-Energy plan relative to the entire Italian territory. It includes geological strategic data and also environmental and infrastructure information. The development of D-GIS can represent a useful planning tool to evaluate synergies and/or conflicts among different deep underground uses (500-5000 m depth) and correlated technologies. Products of this study can finally represent an useful tool not only for the scientific community but also for the policy makers to improve the guidelines for sites selection.
FLUID GEOCHEMISTRY OF SHALLOW AQUIFERS AND SOIL GAS SURVEYS FOR THE ENVIRONMENTAL IMPACT ASSESSMENT OF A POTENTIAL NATURAL GAS STORAGE SITE IN PO PLAIN

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A geochemical survey in soils and shallow aquifers was carried out as part of the feasibility study of a potential natural gas (CH₄) storage site in a deep saline aquifer of Modena Province, Northern Italy. This paper discusses the areal distribution of CO₂, CH₄ and other geo-gases (Rn, He, H₂, N₂) both in soils and shallow aquifers above the proposed storage reservoir.

Soil and dissolved gas, joined with isotopic analysis, allows to distinguish between shallow and deep origin fluids. This approach is used also to identify the presence of anomalous leakage of deep fluids towards surface, and therefore the presence of tectonic discontinuities by means distribution of pathfinder elements as ²²²Rn, He e H₂.

This methodology is based on the previous experience gathered in other projects aimed to i) water and soil gas surveys in active fault areas; ii) natural gas risk assessment and iii) CO₂ geological storage. In particular, the goal of this survey is to characterize the composition, distribution and behavior of the geo-gas (CH₄, Rn, He, CO₂, H₂, etc.) in the geological layers closer to the surface, defining their baseline or background values, their origin, pathways and carrier roles. The geochemical and isotopic characterization of the ground waters circulating in the first 200 meters has been carried out to investigate the origin of the circulating fluids, the gas-water-rock interaction processes, the amount of dissolved gases and/or their saturation status.

In the first 200 m, the presence of reducing waters enriched in CH₄ could be related to organic matter (peat) bearing strata which generate shallow-derived CH₄, as elsewhere in the Po Plain. No hints of thermogenic CH₄ gas leakage from deeper reservoirs have been envisaged. The acquisition of pre-injection data is very important for the future natural gas storage development project and it is strategic as baseline for future monitoring during the gas injection period. Our study could be considered as a monitoring guideline applicable both to other gas storage sites before, during and after the injection and to natural analogues.
**BIOGEOCHEMICAL APPROACH TO THE MONITORING OF BASELINE LEVELS OF CO$_2$ AT THE SEDIMENT-WATER INTERFACE FOR CCS PURPOSE**

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Capture and Storage (CCS) is the CO$_2$ injection in the sub-seabed deep saline aquifers. In the sub-seabed CCS a reliable monitoring of possible CO$_2$ seeps is required in order to assure safety, containment lifetime and biological impacts.

A useful CCS monitoring approach (the experimental biogeochemical approach) is to determine, before the geological storage, natural baseline levels and benthic fluxes of dissolved inorganic carbon species (pCO$_2$ and DIC) and of other connected parameters (alkalinity, pH and $\delta^{13}$C DIC) in seawater in order to characterize the marine carbonate system from a chemically point of view and regarding its natural or anthropogenic origin. Furthermore, the study of the early diagenesis processes generating the observed benthic fluxes is a useful complementary aspect of the CCS biogeochemical monitoring approach. The knowledge of the natural baseline levels and benthic fluxes, before the CO$_2$ injection, will allow the comparison with data obtained after the storage operations so that possible occurrences of unexpected leakages of the CO$_2$ injected in the geological formations under the sea bottom can be verified. This approach could also be useful employed as an “early warning” system in case of possible failure of the CO$_2$ storage. The best method to determine dissolved benthic fluxes is the “in situ” measurement by benthic chamber deployments.

The biogeochemical approach is particularly sound in the northern and central Adriatic Sea where numerous previous DIC and other carbonate system connected chemical benthic flux data, various early diagenesis studies and also up to date and appropriate monitoring technologies (automated benthic chamber and on deck laboratory), able to measure “in situ” benthic fluxes, are available and where CO$_2$ sub-seabed storages can be carried out. Previous researches allowed the definitions of nine different diagenetic environments in the northern and central Adriatic Sea; each environment is characterized by: 1) homogeneous particulate matter and dissolved nutrient continental inputs; 2) distances from main sediment sources; 3) bottom sediment composition; 4) organic matter; 5) depths; 6) oxygenation of water column. In each diagenetic environment a natural background value of DIC, alkalinity and pH sediment-water fluxes has been assigned.

These background values can be used as natural baseline in the CCS to monitoring possible seeps after the injection of CO$_2$ in depth. At present, various researches are in progress in the Adriatic Sea for the acquisition of new data of DIC and other dissolved chemical sediment-water fluxes and on early diagenesis studies, in order to increase the background knowledge in areas or seasons not covered by previous researches.

In particular, in fall 2010 and winter 2011 two cruises have been performed to measure benthic fluxes of dissolved inorganic carbon species and to determine the early diagenesis processes that origin the fluxes in the two extreme seasons in the central-western Adriatic Sea. In these last cruises benthic fluxes have been measured “in situ” by deployments of the ISMAR-CNR and RSE “self-made” benthic chamber and using an on deck laboratory. Furthermore, a technological development research is now being carried out by ISMAR-CNR and RSE for the set up of a full ocean depth (6,000 m depth) Lander equipped with three benthic chambers and one micro-profiler.
Sessione tematica H1:
Anatessi crostale: evidenze naturali, esperimenti, modelli (CANEM)

Conveners:
Roberto Braga (Università di Bologna) *
Antonio Langone (Università di Bologna)
Filippo Ridolfi (Università di Urbino “Carlo Bo”)
MELT PRODUCED DURING ANATEXIS OF THE CONTINENTAL CRUST: COMPOSITIONAL CONSTRAINTS FROM EXPERIMENTAL HOMOGENIZATION OF MELT INCLUSIONS IN PERITECTIC GARNETS OF MIGMATITES

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Recently, Cesare et al. (2009 and 2011) showed that peritectic minerals in migmatites and granulites can trap droplets of anatectic melt that were formed by incongruent melting reactions during high-temperature metamorphism and granite formation. Detailed geochemical studies on these melt inclusions (MI) have shown that they can represent a window of information into the prograde history of partially melted rocks (Acosta-Vigil et al., 2010). However, the recovery of this information is not straightforward as remelting and homogenization of MI at ambient pressure with the routine technique in igneous petrology produced inclusion decrepitation, interaction with host mineral and volatile loss (Cesare et al., 2011). To avoid these problems, we performed the experimental remelting of MI using a piston cylinder apparatus. MI are located within peritectic garnets, hosted in the metasedimentary migmatites from Ronda (Betic Cordillera, SE Spain). These garnets contain primary 2-10 µm MI that range from totally glassy to fully crystallized (nanogranite, Cesare et al., 2009). Partially crystallized MI are very common and generally contain quartz, biotite, muscovite and, more rarely, plagioclase, along with variable proportions of glass. Raman spectroscopy has documented the presence of liquid H2O-filled micropores in nanogranites, in agreement with the presence of a micro- to nano-porosity observed by SEM investigation. Piston cylinder remelting experiments led to the complete rehomogenization of crystalline MI at conditions (700°C, 500 MPa) close to those inferred for anatexis. Remelted MI have a peraluminous, granitic composition with high (up to 7.5 wt.%) H2O content; they overlap the composition of glassy MI, but differ from the composition of leucosomes in the host rock. Some CO2 bubbles are present after remelting experiments, suggesting fluid present, qH2O ≤ 1 conditions, in agreement with graphite being present in the protolith. Our study shows that partially crystallized and nanogranite inclusions in peritectic minerals from migmatites can be successfully remelted and analyzed, and that this experimental approach may become an ordinary procedure for future studies on MI in anatectic rocks worldwide. We have identified the natural anatectic melt composition and fluid regime at the onset of crustal melting for this case study, otherwise unknown. Hence, MI in migmatites represent a unique tool for the in situ characterization of anatexis in its early stages, and provide the only means of determining the volatile fluid content of anatectic melts.

Cesare, B. et al. (2009): Geology, 37, 627-630.
CRUSTAL XENOLITHS FROM TALLANTE (BETIC CORDILLERA, SPAIN): INSIGHTS FOR AN INTERLAYERED CRUST-MANTLE BOUNDARY?

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The geology of the Betic area has been characterized by several tectono-magmatic episodes related to multiple orogenic cycles and extensional phases (Puga \textit{et al.}, 2011; Bianchini \textit{et al.}, 2011 and references therein) ultimately leading to widespread subduction-related and anorogenic volcanism. The last magmatic phase (Pliocene) is represented by Na-alkaline basalts at Tallante that entrained and exhumed abundant deep-seated xenoliths of both mantle and crustal provenance. These xenoliths attracted an intense petrological interest testified by an impressive number of scientific papers. Unfortunately, most of these studies focused on the ultramafic xenoliths ignoring the crustal lithologies that were investigated only by the paper of Vielzeuf (1983).

In this contribution we present new data on felsic (\textit{i.e.} crustal) xenoliths from Tallante that integrate the petrological information provided by the ultramafic parageneses, highlighting the deep lithosphere stratigraphy of the area as well as constraints for the interpretation of geophysical data and models. The felsic xenolith is characterized by a metamorphic peak assemblage composed of quartz + spinel + sillimanite. The occurrence of cordierite rims between spinel and quartz is related to post-peak metamorphism. To obtain P-T information from this texture, we calculated a P-T pseudosection for the specific mineral reaction texture spinel + quartz = cordierite. The microbulk composition was modeled in the SiO$_2$-Al$_2$O$_3$-FeO-Fe$_2$O$_3$-MgO system. Water has not been taken into account in order to simulate the likely anhydrous conditions occurring during the peak metamorphic stage.

The observed paragenesis Spinel-Quartz-Sillimanite indicates temperature around 1000°C for pressure of 7 kbar, increasing to 1125°C at 9 kbar. The formation of cordierite rims between quartz and spinel requires, in the chosen system, decompression down to \(<\) 6 kbar (\(T < 950°C\)). This evolution was accompanied by partial melting testified by glasses films and blebs. Therefore, felsic xenoliths from Tallante attained P-T condition overlapping those recorded by the ultramafic xenoliths of mantle provenance that are represented by spinel-plagioclase peridotite. This suggests that an intimate association of crust and mantle lithologies with pervasive interlayering and interfingering at metric to hectometric scale characterizes the Moho discontinuity in this area.

Melting preferentially occurred in the crustal domains (characterized by lower solidus conditions) generating silica-rich magmas that veined the surrounding peridotite domains, also inducing orthopyroxene-rich metasomatic aureole. The proposed petrological scenario is discussed taking also into account the investigations on the neighboring massifs of Ronda and Beni Bousera where the fossil crust-mantle boundary is exposed, providing fresh insights for the configuration and evolution of the Moho discontinuity in collisioned plate boundaries, that are widespread throughout the peri-Mediterranean realm. The hypotized eteropic crust-mantle boundary would represent a suitable source region for exotic magma types such as lamproites that are common within the Mediterranean area (Tommasini \textit{et al.}, 2011).

Despite granite magmatism represents the major mechanism for past and ongoing large-scale crustal differentiation and it is, therefore, central to understand the evolution of the continental crust, the processes that produce the chemical and isotopic variations displayed by granites remain poorly constrained. Miocene to Pleistocene granites from Tuscan Magmatic Province have been studied since XIX Century but it is during the last two decades that a large number of geological, geochemical and isotopic data have been published (see Dini et al., 2009 and references therein). Theories about the origin of these granites changed through time, from the early highly speculative idea of a pure crustal anatexis (e.g. Marinelli, 1967) to the much more constrained hypothesis of mingling-mixing between crustal- and mantle-derived magmas (e.g. Poli, 1992). The involvement of mantle-derived magma (thermal source for overstepping of breakdown reactions in lower crust as well as a geochemical end-member in mingling-mixing processes) has been largely accepted for many Tuscan granites although in some cases (e.g. granites cored in the Palaeozoic basement of the Larderello geothermal field; Dini et al., 2005) its role has been considered relevant only in providing extra heat for the partial melting of the crust. In previous works (van Bergen et al., 1983; Poli et al., 2002), the micaschists from the Larderello basement, due to their fertile mineralogy, have been assumed to be a potential source of the Tuscan granites. However, available Sr-Nd isotope data for these Palaeozoic rocks do not fit the isotope composition of granites and different crustal sources (not exposed and/or unsampled) have been invoked. It is worth noting that the lack of appropriate sources in terms of isotopic composition is a common feature in Hercynian plutonic complexes (Pyrenees, Central Spain, Armorican Massif, Bohemian Massif, etc.; Villaseca et al., 1998). A detailed geochemical and isotopic study of metaigneous and metasedimentary rocks from the Palaeozoic Tuscan basement (exposed: Apuan Alps, Elba Island; buried: Larderello geothermal field) was performed in order to characterize the potential crustal sources of Larderello granites. Metaigneous rocks are represented by metabasites and metarhyolites (porphyrovids), while studied metasedimentary rocks are mainly micaschists. In some studied outcrops and cores (Larderello, Elba Island), amphibole-rich metabasites are interlayered with biotite-rich micaschists. Sr and Nd isotope data indicate the existence of three distinct isotopic crustal reservoirs: metasediments ($^{87}$Sr/$^{86}$Sr $\approx$ 0.730; $^{143}$Nd/$^{144}$Nd $\approx$ 0.5119); metarhyolites ($^{87}$Sr/$^{86}$Sr $\approx$ 0.750; $^{143}$Nd/$^{144}$Nd $\approx$ 0.5122); and metabasites ($^{87}$Sr/$^{86}$Sr $\approx$ 0.716; $^{143}$Nd/$^{144}$Nd $\approx$ 0.5126). These reservoirs do not fit the isotope composition of Larderello granites but partial melting of a metabasite-metasediment layered source can explain both the observed geochemical and isotopic variation in granites. The existence of Palaeozoic interlayered domains at depth could explain the apparent lack of appropriate anatetic sources, providing alternative mechanisms for the origic of Tuscan granites.

PERITECTIC PHASES ENTRAINMENT AND MAGMA MIXING: THE ORIGIN OF THE CHEMICAL VARIABILITY OF THE LATE MIOCENE GRANITIC COMPLEX FROM ELBA ISLAND (ITALY)

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The comparison between the chemical variability exhibited by the granitic rocks of the Elba Island granitic complex (Italy) and the composition of fluid-absent experimental melts indicates that these rocks have Fe+Mg, Ti and Ca contents that are too high to represent pure crustal melts. Therefore, their origin demands the addition of a ferromagnesian, Ti- and Ca-rich component to an anatectic melt. Various authors, on the basis of textural and chemical data, have interpreted the chemical variability exhibited by the Elba Island granitic rocks as reflecting the progressive hybridization of an original crustal melt with mantle-derived magma(s). However, a simple mantle-crustal magma mixing hypothesis is challenged by the observation that some elements (e.g. Ti and Ca) are highly correlated with Fe+Mg, while others (e.g. Sr, K, Na) are not, as well as by the scattered major and trace element composition of the mafic microgranular enclaves.

This contribution focuses on reconsidering the role of mantle-derived magmas in the petrogenesis of the Elba Island intrusive system from the perspective of the constraints imposed by crustal melt compositions. On the basis of the major- and trace element geochemical data, as well as petrographic data such as amphibole clots replacing former pyroxene and garnets in some of the Elba granitic rocks (possibly representing evidences for the occurrence of entrained peritectic phases), we propose that at least part of the compositional variations displayed by the Elba Island intrusive complex is primary, i.e. reflect the magma composition that ascended directly from the source.

Following this hypothesis, the final composition of magmas may be controlled by two main factors: (i) the stoichiometry of the melting reaction(s) and the composition of reactant phases in the source, that control the composition of the anatectic melt; (ii) the degree of entrainment of peritectic mineral phases, whose nature will be dependent by (i), as well as by the P, T conditions of melting. The magma mixing relevant to the bulk of the Elba igneous products then occurred between successive (different?) magma batches generated by anatexis of heterogeneous source rock volumes. Mantle-derived magmas are only involved in the genesis of the most mafic magma batches.
THE ROLE OF HEATING VS. DECOMPRESSON ON PARTIAL MELTING IN THE BARUN GNEISS (EASTERN NEPAL HIMALAYA)

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Partial melting of deep continental crust may occur during either prograde heating or decompression. Although the effect of temperature on crustal melting has been widely investigated, only few experimental studies address the question of the influence of pressure on crustal anatexis, and the effectiveness of decompression melting in the production of large amounts of melt in the deep crust is still far from being universally demonstrated.

In the eastern Himalayan chain, partial melting is widely documented in the Higher Himalayan Crystallines (HHC), a high-grade, 5-6 km thick lithotectonic unit located at the higher structural levels of the Himalayan belt. Crustal anatexis in the HHC has been generally ascribed to decompression melting (e.g. Harris & Inger, 1992; Harris & Massey, 1994; Patiño Douce & Harris, 1998; Harris et al., 2004; Streule et al., 2010; Searle et al., 2010), and gave rise to significant amounts of granitic bodies and dykes crosscutting widespread migmatites and granulites. The HHC thus represent an ideal natural laboratory in which to investigate the actual influence of decreasing P on partial melting processes.

In this study we have investigated in detail the P-T evolution of two garnet-K-feldspar-kyanite-sillimanite anatectic gneisses from different structural levels of the same Unit (Barun Gneiss) in the lower portion of the HHC (Arun-Barun valley, eastern Nepal). Although the mineral assemblage is identical (Qtz+Pl+Kfs+Bt+Grt+Ky/Sil+Rt), several microstructural and minerochemical features, combined with the results of P-T pseudosection modeling, suggest that the two samples experienced a different P-T evolution, dominated by decompression (sample 07-16) and heating (sample 07-35) respectively.

P-T pseudosection modeling shows that the melt productivity, related to the muscovite- and biotite dehydration melting reactions, depends on: (i) the slope of melt isomodes in the P-T space (which in turn is an expression of the slope of the reaction curve), and (ii) how the P-T trajectory crosses the melt isomodes. For the two studied samples, given the constrained P-T paths and their relations with the main melt-producing reactions in the P-T space, it can be concluded that melt production was mainly triggered by heating, with or without the combined effect of decompression. Decompression alone is not able to explain the production of large amounts of melt, in contrast to what is often suggested for the HHC.

In addition, metamorphic and petrologic data derived for the Barun Gneiss match well with the predictions of the “channel flow” model, one of the most popular paradigms to explain the tectonometamorphic evolution of the Himalayan-Tibetan orogen.

LOW-PRESSURE ANATEXIS IN THE HIGHER HIMALAYAN CRYSTALLINES OF EASTERN NEPAL REVEALED BY CORDIERITE-BEARING LITHOLOGIES

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In the eastern Himalaya, partial melting is widely documented in the Higher Himalayan Crystallines (HHC), a high-grade, several km thick lithotectonic unit located at the higher structural levels of the Himalayan belt (e.g. Goscombe et al., 2006; Searle et al., 2008). In the lower structural levels of the HHC, anatexis occurred at medium to high-P (8-12 kbar) and is recorded in Ky-bearing granulites (Barun Gneiss and Jannu-Kangchenjunga Gneiss). Toward structurally upper levels of the HHC, peak-P significantly decreases down to 4-5 kbar, as revealed by the widespread occurrence of Crd-bearing and Ky-free gneisses (e.g. Imayama et al., 2010; Streule et al., 2010; Mosca et al., 2010), locally named Namche Migmatites and Black Gneisses (e.g. Bordet, 1961; Lombardo et al., 1993).

This contribution focuses on the cordierite-bearing lithologies occurring at the higher structural levels of the HHC, by describing in detail three Crd-bearing gneisses (samples 09-29, 07-26 and 05-17) from different geological transects in Eastern Nepal from Everest to Kangchenjunga. The studied samples differ in terms of bulk composition, likely reflecting different sedimentary protoliths (from pelite to psammite), though they all consist of quartz, K-feldspar, plagioclase, biotite, cordierite and sillimanite in different modal percentages. Garnet occurs in two samples, as a relict phase in very low modal amounts. In all the studied samples cordierite is spectacularly well preserved. Most of the observed microstructures may be interpreted in terms of melt-producing or melt-consuming reactions, such as for example: (i) Crd porphyroblasts including Sil and Bt never in mutual contact, suggesting that Crd is a peritectic phase grown at the expenses of both Sil and Bt; (ii) coarse-grained Kfs poikiloblasts containing abundant inclusions of Bt, rounded Pl and Qtz, and minor Sil, suggesting that Kfs is a peritectic phase grown at the expenses of Pl, Bt, Sil and Qtz; (iii) thin films of Qtz, Kfs or Pl with cuspaté shape locally occurring between adjacent grains of Qtz, Bt or Kfs possibly interpreted as pseudomorphs of liquid-filled pores (e.g. Holness & Sawyer, 2008), thus suggesting that some melt crystallized in the interstices between grains.

The lack of retrograde rehydration suggests that either the studied samples experienced a significant melt loss so that the interactions between melt and solid phases during cooling were limited, or the amount of melt produced was scanty. The results of P-T pseudosection modeling suggest that the first hypothesis is the most likely for the metapelitic samples 09-29 and 07-26, whereas the second hypothesis applies well to the metapsammitic sample 05-17.

The P-T evolution of the studied samples, reconstructed combining microstructural observations, mineral chemical data and pseudosection modeling, is discussed in the framework of the “channel flow” model, which is one of the most popular paradigms to explain the tectonometamorphic evolution of the HHC and, more generally, the first-order geologic features of the Himalayan-Tibetan orogen.

We have studied fine-grained stromatic metatexites occurring c. 400 m below the contact with the Ronda peridotite (Ojén unit, Betic Cordillera, SE Spain). These rocks contain Qtz + Pl + Kfs + Bt + Fib + Grt + Ms + Ap + Gr ± Ilm and have a main foliation defined by alternating layers of biotite and fibrolite and thin (~ 0.5 cm) leucosomes. Garnet occurs in very low modal amount (< 1%). Muscovite is an armored inclusion or texturally retrograde.

Microstructural evidence of melting in the migmatites includes pseudomorphs after melt films, euhedral feldspars, and nanogranite inclusions in garnet. Remelted nanogranites show granitic compositions. The latter microstructure demonstrates that garnet crystallized in the presence of melt.

We have constructed two pseudosections: one for the bulk rock in the MnNCKFMASHT system, and the other for the composition of the remelted nanogranite inclusions in the NCKFMASH system. Calculated isopleths for chemical parameters of garnet (XMg, XGrs), biotite (XMg, XTi) and plagioclase (An content) in the Qtz-Pl-Kfs-Bt-Grt-Si-melt field match the actual values in the rock. The P-T conditions of equilibration were estimated at 4.5-4.8 kbar, 680-700°C. These P-T conditions overlap with the low-T tip of the melt field in the pseudosection for the nanogranite composition. They are also consistent with the complete experimental remelting of nanogranites at 700°C.

These results indicate that nanogranites represent the anatectic melt generated at, or soon after, muscovite melting, and that garnet is able to trap melt inclusions also at temperatures lower than those of biotite breakdown melting.
Sessione tematica H3:
Pre-Mesozoic evolution of the circum-Mediterranean basements

Conveners:
Rosolino Cirrincione (Università di Catania)
Patrizia Fiannacca (Università di Catania)*
EVIDENCE OF EXTENSION IN THE GRANULITE FACIES LOWER CRUST OF CALABRIA DURING THE HERCYNIAN OROGENY

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Quartz-monzodioritic dykes have intruded the Hercynian continental lower crust of Calabria 323±5 Ma ago, according to zircon spot age data. We have constrained the emplacement depth of these dykes by the construction of pseudosections and the calculation of multiple reactions using the internally-consistent dataset of THERMOCALC. Our calculations show that the quartz-monzodioritic dykes have intruded the metapelitic-migmatitic country-rocks at a depth of about 32 km. After the intrusion the dykes together with country-rocks were deformed under granulite facies conditions. This is supported by microstructural evidence and by the application of geothermometry.

The analysis of fabric elements contained within the deformed dykes and the country-rocks suggests that deformation has occurred in an extensional regime. The onset of deformation can be placed to before 306 Ma, because the deformed quartz-monzodioritic bodies are locally cut by undeformed leucocratic dykes connected to the granitoid masses that intruded the Calabrian crust between 306 and 300 Ma.

Intrusion of these granitoids has occurred during extension at mid-crustal levels. Decompression during extension of the Calabrian crust under granulite facies conditions has been pinpoint so far to the intrusion of these granitoid masses.

We can show that in the lower crust the extension started earlier, suggesting that it was asynchronous within the Calabrian crust, and has propagated with time from deeper to mid- and upper crustal levels. Alternatively, the whole Hercynian crust underwent thinning almost synchronously at different crustal levels.
In situ SHRIMP U-Pb ages have been obtained, for the first time, for detrital zircons from metasedimentary and metaigneous rocks from the Peloritani Mountains (NE Sicily), allowing some firm constraints to be put on the formation age and origins of this still poorly known peri-Mediterranean chain. The greywacke protoliths of the paragneiss forming the most common rock-type in the Peloritani Mountains were deposited at ca. 550 Ma, the age of the youngest detrital zircon population, just before the intrusion of granitoid plutons at ca. 545 Ma.

Large portions of flysch-type sequences including deeper equivalents of the ca. 550 Ma greywackes underwent partial melting, producing large volumes of granitoid rocks now exposed as augen-gneisses in north-eastern Sicily, as well as in southern and northern Calabria. Age spectra of detrital and inherited zircons from paragneiss and augen gneiss, respectively, indicate sediment derivation from the erosion of Neoproterozoic to Late Archean sources. The main components are ca. 540-850, 900-1100 and 2400-2700 Ma and minor ones ca. 1.60, 1.80 and 3.20 Ga. These age groups reflect a peri-Gondwanan affinity and are consistent with deposition in a marginal basin located at the northern Gondwana margin, between an old cratonic area and the Avalonian-Cadomian magmatic arc (Nance et al., 2010 and reference therein).

The high abundance of Grenvillian zircon, together with the occurrence of ca. 1.56-1.80 Ga grains, makes it quite unlikely that the amphibolite facies basement of NE Sicily was derived from the West African Craton, contrary to what is suggested for similar coeval rocks from Calabria. Although Grenvillian zircons are known from various sectors of northern Gondwana, such as the Saharan craton and the Arabian-Nubian Shield, a stronger affinity with Amazonian-derived terranes, such as NE Bohemia, NW Turkey and the autochthons of NW Iberia, is more suggestive of an Amazonian linkage for that part of NE Sicily at the Precambrian-Cambrian transition. Later, the Peloritani Mountains were involved in break-up processes linked to opening of the Rheic Ocean and, finally, in a short-lived Mid-Ordovician orogenic cycle.

Magmatic activity related to this Early Paleozoic evolution is documented, respectively, by Cambro-Ordovician alkali metabasites and Caradocian meta-andesites and felsic porphyroids from the volcanic-sedimentary sequences of the southern Peloritani Mountains (Trombetta et al., 2004; Cirrincione et al., 2005). The depicted nearly continuous geodynamic evolution suggests a basement-cover relationship between the Latest Neoproterozoic basement rocks of NE Peloritani and the Paleozoic volcano-sedimentary sequences of SE Peloritani. Inherited Mesoproterozoic zircon from the Mid-Ordovician porphyroids (Trombetta et al., 2004) supports both the Amazonian provenance and the basement-cover relationship of the northern and the southern Peloritani Mountains.

The results of the present study are in substantial agreement with former models proposed by Acquafredda et al. (1994) and Ferla (2000) and additionally provide the first reliable geochronological information on the real age and early history of the medium-high grade Peloritani basement.

Augen gneisses covering an area of about 80 km$^2$ in the Peloritani Mountains (NE Sicily) have been found to be 570-540 Ma granitoids after SHRIMP zircon U-Pb dating of a representative sample from each of three different areas. Similar coeval rocks are also exposed in Calabria, indicating the presence of a large Ediacaran granitoid province in the Calabria-Peloritani Terrane, currently extending from NE Sicily to northern Calabria. Two of the studied augen gneisses, from the eastern Peloritani, have many zircon grains composed of a thick < 545 Ma melt-precipitated rim surrounding a core ranging in age from Late Archean to latest Proterozoic. These cores are interpreted as detrital grains from sediments that were part of the source of the granitoid magmas, and suggest that that source was largely composed of rocks akin to the protoliths of northern Peloritani paragneisses, which have similar patterns of detrital zircon ages. The third augen gneiss, from the western Peloritani, has a protolith emplacement age of < 565 Ma and contains inheritance-free zircon, implying that the magma was strongly zircon undersaturated and/or high-temperature, or derived from a zircon-poor source.

The Late Ediacaran emplacement ages of the granitoid protoliths of the inheritance-rich augen gneisses, together with typical high-K calcalkaline post-collisional geochemical features and strong evidence for dominantly crustal sources from zircon inheritance and isotopic features, are consistent with the widespread crustal melting and post-tectonic granitoid emplacement at ca. 550-540 Ma reported by many authors (e.g., Murphy et al., 2001; Linnemann et al., 2008; Nance et al., 2010) as marking the transition from subduction to strike-slip tectonics at the northern margin of Gondwana at the end of the Neoproterozoic.

It has been proposed that some of the peri-Gondwanan terranes were formed in back-arc environments located between cratonic (south-American or north-African) and arc-related (Avalonian or Cadomian) domains. After a late stage of arc magmatism at ca. 580-560 Ma, possibly represented in the Peloritani Mountains by the 565 Ma protolith of the western Peloritani augen gneiss, inversion of back-arc basins related to collision of the magmatic arcs with mainland areas led to the deposition of turbidite sequences at 545-540 Ma. In some cases (e.g., Lausitz Group in Saxo-Thuringia; Linemman et al., 2007) these sequences were rapidly deformed before the intrusion, at < 540 Ma, of large volumes of granitoids, probably derived from melting of the same turbiditic greywackes, as suggested by comparable zircon age patterns and geochemical and isotopic compositions.

Many of the ~ 545 Ma igneous rims on zircon from the two studied eastern Peloritani augen gneisses overgrow virtually coeval Ediacaran inherited cores, indicating deposition of the sediments only very shortly before magmatism. This interpretation is reinforced by the ca. 545 Ma deposition age obtained for the metagreywacke protolith of an eastern Peloritani paragneiss. These results may be framed in a model involving rapid erosion, burial, sediment deformation and metamorphism up to partial melting conditions in less than about 10 million years. A similar model has been envisaged by Nance et al. (2010) for the Saxo-Thuringian zone. They proposed that these latest Proterozoic examples of extremely rapid geological evolution were caused by a short-lived regime of high heat-flow linked to slab break-off resulting from ridge-trench collision. In this context, evidence for a mantle contribution to the petrogenesis of the ca. 545 Ma granitoids may be found in their geochemical and isotopic features, and the documented presence of coeval gabbroic rocks in the same region.
GEOLOGICAL EVOLUTION OF THE SOUTH EUROPEAN VARISCAN FRAGMENTS FROM CALABRIA INFERRED FROM P-T COMPUTATIONS AND U-Pb ZIRCON AGES

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In Calabria (southern Italy) fragments of south European Variscan chain consisting of ortho- and para-derivates affected by low- medium- high- grade metamorphism crop out. Ortho-derivates involved by green schist to granulite facies metamorphism characterize middle and deep continental crust units. Metagabbros and metabasites affected by granulite facies metamorphism are associated with felsic granulites and migmatitic metapelites of the lower continental crust unit of the Serre. U-Pb spot analyses on zircon separates (performed by SIMS and LA-ICP-MS) have provided constraints on the ages of protoliths and on chronology of Variscan metamorphism. The age of magmatic protoliths of the orthogneisses and of the metabasic rocks was fixed at ~ 540 and ~ 580 Ma, respectively, representing a bimodal magmatic contribution to Pan-African crust in Early Cambrian-Neoproterozoic times. Mafic and felsic magmas were emplaced in the Pan-African/Cadomian basement preserving memory of older terrains belonging to West African Craton. These peri-Gondwana terrains were reworked by Variscan orogenesis and look like the blocks occurring in the east European chain from the Alps to Turkey.

The effects of Variscan metamorphism depend on P-T conditions and rock chemical compositions. A time memory, step by step, of the Variscan evolution was preserved in rock-types where the re-growth or re-crystallization of zircon happened. So the U-Pb zircon ages together with the petrological data in granulite-amphibolite facies metamorphic rocks of the Serre allow to depict the Variscan evolution. Ages around 450 Ma were recorded in the metagneous rocks which coincide with the age derived from Rb-Sr isochron relative to metasedimentary rocks; this age can be related to an Ordovician tectonothermal activity or to Eo-Hercynian events. Cluster ages of 347-340 Ma, 323-318 Ma, 300-294 Ma and 279 Ma were measured in metagabbros and metabasites from the lower portions of the section. Age peaks around 323, 300 and 270 Ma are recorded in overlying migmatitic metapelites. Undated thin luminescent rims of zircon are the only evidence of post-Ordovician events in orthogneisses interleaved with migmatitic metapelites. Conventional thermobarometer, Thermo calculations and pseudosections indicate clockwise trajectories Ky-Sil-And-Ky and Ky-Sil-Ky for the migmatitic metapelites and metabasites, respectively, from the deep continental crust unit of the Serre. The P-T conditions in the metasbic portion indicate a possible P peak (P ≥ 1.08 GPa and T < 850°C) predating the T-peak (T = 850-900°C and P ~ 1.08 GPa) at 347-340 Ma, probably followed by quite isothermal decompression (P = 0.8 GPa) at 323-318 Ma and successive decrease of T (~ 750°C); a new decompression at P about 0.65 GPa around 300 and 280 Ma ago, occurs. During the decompression stages pervasive partial melting episodes, producing leucogranitic and trondhjemitic melts, interested these rocks in which luminescent overgrowths mantle primary zircon cores. The re-constructed P-T path shows even for the upper migmatitic metapelites, P-peak at 0.9 GPa and T = 650°C pre-dating T-peak (750°C) under quite isobaric conditions 323 Ma ago and a multistage decompression at 300, 280 Ma up to 270 Ma with incremental partial melting episodes. An integrate approach involving U-Pb analyses on zircon and REE distribution in garnet orthopyroxene and zircon on thin section, relatively to the mafic granulites better constrain the Variscan evolution.
The Peloritani Mountain belt is a segment of the European Alpine orogen that preserves pre-Alpine basement relics. Very low to high grade metamorphic rocks are exposed in the present-day tectonic stack of the chain. Up to now very few PT paths are available for the basement tectonic slices of the Peloritani Mountains, due to the common absence of suitable parageneses in the low and very low grade metamorphic rocks, as well as to the pervasive late Hercynian thermal re-equilibration in the medium-high grade metamorphic rocks. In this view, to estimate the relic peak PT conditions of the Hercynian evolution of this southern Alpine chain sector, phase diagram calculation method was applied, modelling the upper greenschist facies garnet-muscovite-chlorite schists outcropping in the uppermost levels of the Mandanici Unit.

The investigated fine-grained metapelite are characterized by a dominant lepidoblastic texture, with ilmenite and poikilitic garnet porphyroblasts surrounded by alternating muscovite + paragonite + chlorite and minor quartz + plagioclase layers, with apatite, monazite and zircon as accessory phases. Three schistosity surfaces were recognized: S1 consists in a partially obliterated isoclinal folding schistosity developed during the first identifiable deformational stage (D1); S2 is related to a penetrative microfolding (D2) producing pervasive crenulation schistosity; S3 is consequent to an extensional-shearing event (D3). Porphyroblast-matrix relationships, investigated via optical and electronic microscopy allowed the blasto-deformation sequence to be reconstructed.

The attention was focused especially on garnet zoning pattern analysis. Garnet porphyroblasts have cores characterized by quartz and rare ilmenite inclusion trails with folding pattern linked presumably to the D2 event. Idioblastic rims grow over the crenulated garnet, thus representing a late to post-D2 growth stage. Fe-Mn-Mg-Ca X-ray maps and compositional profiles outlined a weak compositional growth zoning, consisting in a bell-shaped profile, with increasing almandine and decreasing spessartine contents toward the rims.

P-T pseudosection was calculated in the TiMnNCKFMASH system, using the XRF bulk-rock composition of metapelite samples mainly exhibiting assemblages consistent with peak or near-peak conditions. Retrograde evolution is locally represented by garnet breakdown to chlorite. Garnet inner core isopleths intersections indicate T of 510°C at P of 0.483 GPa, just nearby the garnet-in curve, in agreement with pyrophanite isopleths composition of porphyroblastic ilmenite.

Garnet rim isopleths intersections define similar P-T conditions of T = 525°C and P = 0.485 GPa. These P-T estimates are linked to the first identifiable metamorphic stage in which isoclinal folding event (D1) and garnet core developed. Garnet rim isopleths intersections gave values of the peak metamorphism at T of 535°C with slightly lower P of 0.430 GPa, attained during the crenulation deformational event which obliterated most of the previous foliation. All the obtained intersections belong to the same pseudosection PT field characterized by chl+ms+pl+ilm+grt+p+pg assemblage, in agreement with the observed mineralogical assemblage. Subsequent retrograde evolution is depicted in the pseudosection PT space by garnet breakdown reaction into chlorite with T of 500±20°C at P of 0.32±0.03 GPa, consistent with the observed partial to complete pseudomorphic replacements. PT estimates obtained via garnet isopleths thermobarometry can be interpreted as the peak PT climax of the Mandanici Unit reached during the Hercynian crustal thickening at upper-middle crust conditions, while the following retrograde evolution depicts a typical retrograde clockwise PT trajectory consistent with the initial exhumation stage of the Hercynian orogen.

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Diffuse dyke swarms with intermediate to felsic composition and calcalkaline affinity crop out in the Serre Massif (Calabria, Southern Italy). These are part of the widespread late- to post-collisional magmatism affecting most southern European basements during the waning stages of the Hercynian orogeny. The dykes are andesitic and dacitic-rhyodacitic in composition, with medium- to high-K2O content, and show typical features of subduction-related magmas, such as LILE and LREE enrichment and HFSE depletion.

Chondrite-normalized REE patterns are weakly to strongly fractionated (LaN/YbN = 8.5 to 14.0 for andesites and 2.3 to 16.3 for dacites-rhyodacites) with slightly negative to positive Eu anomaly for the andesites and markedly negative Eu anomaly for the dacites-rhyodacites. The petrogenesis of the late- to post-Hercynian calcalkaline rocks is usually linked to an extensional post-collisional setting involving thinning of the continental lithosphere and progressive upwelling of the asthenospheric mantle. In such a context, both pure mantle, crustal and hybrid melts are likely to be generated.

The andesitic dykes show mineral and whole-rock major and trace element composition resembling boninitic rock associations (anomalously high MgO, Mg#, Cr and Ni, coupled with high SiO2, relatively low TiO2, high Mg# in clinopyroxene, high Al2O3/TiO2, high Zr/Hf, moderate LREE enrichment, low HREE and negative Nb-Ta troughs in primitive mantle-normalized diagrams). Petrological investigations suggest that they were probably produced by partial melting of an enriched mantle source metasomatized by crustal fluids/melts during former subduction of oceanic lithosphere and then suffered minor, if any, assimilation of lower crustal metapelites. Most dacite-rhyodacites were instead likely derived by hybridization in various proportions of crustal and mantle melts, whereas pure crustal metasedimentary sources, and more or less efficient restite unmixing processes, were involved in the generation of the most silica-rich rhyodacites.
EVIDENCE OF HERCYNIAN HIGH TEMPERATURE RELICS REPLACED BY ALPINE MYLONITIC OVERPRINT: NEW IMPLICATIONS FOR THE TECTONO-METAMORPHIC EVOLUTION OF THE CASTAGNA UNIT
(CALABRIAN PELORITANI OROGEN, SILA PICCOLA MASSIF)

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Petrological and microstructural investigations have been integrated to unravel the tectono-metamorphic evolution of the Castagna Unit. This unit represents a pervasively mylonitised horizon located in the lower-intermediate portion of the northern Calabride continental crust section, sandwiched at the bottom by the low grade metapelite of the Bagni Unit and at the top, by the granulite facies rocks of the Sila Unit. Evidence of Hercynian high temperature relics have been observed for the first time, preserved as low strain domains within the pervasive mylonitic foliation of the metapelite horizons. In this view, petrological, structural and microstructural analysis on mylonitic paragneiss and leucogneiss, allowed to yield reliable P-T constraints aimed to depict the tectono-metamorphic history for this little-know and discussed portion of crystalline basement in the northern Calabrian Peloritani Orogen.

Locally, low strain domains composed of garnet-sillimanite paragneiss, with intermediate to low Ti-biotite and oligoclase-andesine plagioclase, are preserved in the metapelite horizons. The quasi-absent garnet crystal zoning, suggesting the presence of pervasive re-homogenising effects of garnet interiors, represents a petrological evidence of long residence time at high T conditions in the lower crust. The narrow high Mn rim content in garnet depicts an anti bell-shaped profile suggesting a clear evidence of retrograde metamorphism.

Thermodynamic modelling, by means of pressure-temperature (P-T) pseudosection computations, in the MnNaCaKFMASH system, not allowed to yield any reliable P-T constraints about the prograde metamorphic event coeval with the former garnet growth stages. The narrow retrograde rims of this re-homogenised garnet, allowed reliable P-T constraints to be detected, with P ranging from 5.7 to 6.8 Kbar at T of 595°C, consistent with the former stages of the retrograde metamorphic trajectory at upper amphibolite facies conditions. The subsequent pervasive mylonitic retrograde evolution is mainly recorded in the leucogneiss horizons, characterised by ribbon-like quartz levels wrapping feldspar porphyroclasts and low phengite mica fish. Syn-mylonitic white mica shows a bimodal distribution of phengite content: a) an high phengite white mica (e.g. 3.23-3.4 a.p.f.u) can be interpreted as the result of an high pressure mylonitic stage ranging from 4 to 8 Kbar; b) a low phengite one, could represent the relic of a previous mylonitic stage developed at lower pressure conditions.

Quartz c-axis orientation pattern analysis allowed to constrain shearing temperature consistent with lower greenschist facies conditions (i.e. 400-450°C) with subordinate evidence of prism c-slip system activation consistent with higher shearing temperature, both characterised by the same sense of shear. New implications on the evolution of the Castagna Unit suggest as the pre-mylonitic relics preserved as low strain domain in metapelite, can be interpreted as the result of an Hercynian granulite facies mineralogical association, as supported by the re-homogenising effect on garnet interiors, affected by the former stage of retrograde evolution in upper amphibolite facies conditions, constrained by means of garnet rim isopleth thermobarometry. In this view, the Castagna Unit can represent the basal mylonitised and retrocessed portion of the originally granulitic Sila Unit, during a former late Hercynian lower pressure stage. Undeformed aplitic-pegmatitic dikes, linked to the Sila Batholith emplacement, crosscutting the mylonitic foliation, support this interpretation. The subsequent well-developed HP-LT mylonitic overprint, can be interpreted as a pervasive Alpine re-activation. In this scenario, the “Castagna Unit’s shear zone” can be interpreted as a post-Hercynian “detachment zone”, postulated in order to justify the exhumation of the deepest parts of the continental crust, reworked during the building of the Alpine Orogen.
Sessione tematica H5:
Magmatismo e geodinamica:
rifting, plumes di mantello e processi di subduzione

Conveners:
Luigi Beccaluva (Università di Ferrara) *
Gianluca Bianchini (IGG-CNR)
Claudia Piromallo (INGV, Roma1)
GEODYNAMIC IMPLICATIONS OF INTERACTIONS BETWEEN SUBDUCTION-MODIFIED AND INTRAPLATE-LIKE MANTLE SOURCES IN THE GENESIS OF NEOGENE CENTRAL ANATOLIA VOLCANISM

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In Central Anatolia, between Konya and Kayseri, and Eastern Anatolia, in the region enclosed among Adana, Sivas and Diyarbakır, Neogene volcanic rocks largely outcrop: large ignimbrite sheets and continental sedimentary rocks are found along with lava flows, strato-volcanoes, volcanic domes and plateau lavas. Some of these products have calc-alkaline affinity and the typical geochemical characters of subduction-related rocks; they have a compositional range from basalts to rhyolites, without any compositional gap. Some others are alkaline, mostly sodic, are strongly SiO₂-undersaturated and reveal an intraplate-type mantle source: they are basanites, tephrites, alkali basalts and trachy-basalts.

The occurrence of subduction-related and intraplate-type volcanic products in the same region is a common feature with surrounding areas in Aegean-Anatolian region. However, Central Anatolian lavas and pyroclastics have some peculiarities. Indeed, these two kind of lavas may be found in the same area, but have usually different time distribution: for instance in Western Anatolia, Central Aegean and Thrace calc-alkaline products are remarkably older than alkali basalts. In addition, mantle sources of subduction-related and intraplate-type lavas are easily distinguished by their Sr and Nd isotope ratios in Central-Eastern Mediterranean region: alkali basalts usually have ⁸⁷Sr/⁸⁶Sr around 0.7030-0.7035 and calc-alkaline and shoshonitic rocks show distinctly higher values(0.7050-0.7080). Interestingly, in the studied rocks, there is no any clear time and/or space separation between calc-alkaline and alkaline rocks, and no sharp chemical and/or isotopic boundary may be traced. Rather there is a gentle transition, with many samples characterized by intermediate features. As an example, alkaline rocks have ⁸⁷Sr/⁸⁶Sr varying from 0.7034 to 0.7055 and Ba/Nb from 5.0 to 11, whereas the same parameters span in the ranges of 0.7039-0.7056 and 11-163, respectively, in the calc-alkaline basaltic samples. Thus, all the observed data point out for the involvement of two different mantle sources in the genesis of this magmatism, and most samples seem to be derived from interactions of these different sources. Furthermore, the distribution of calc-alkaline rocks is not strictly linked with respect to subduction dynamics.

Large volumes of very young (< 2 Ma) calc-alkaline rocks are found in Kapadokyan region, in Central Anatolia, even if current subduction is very slow, or stopped at all. More to the east, some calc-alkaline rocks, are found both predating and postdating the 15 Ma Arabia-Eurasia collision, either in the upper turkish plate or the Arabian foreland. Alkali basaltic plateau lavas are sometimes remarkably older than calk-alkaline lavas and ignimbrites, as those around Şarkışla, dated at 15.7-14.0 Ma ago, and south of Sivas, which gave K-Ar ages of 5.1-4.8 Ma ago.

The Neogene Central-Eastern Anatolia calc-alkaline rocks are sourced in a subduction-modified mantle wedge. Anyway, the lacking of strict connections with the subduction dynamics and geometry indicate that the metasomatizing event of the mantle wedge may be decoupled from the event responsible for the partial melting.

Intraplate-type magmas are sourced in the underlying asthenosphere, not affected by any subduction imprint. The occurrence of calc-alkaline magmas intimately connected with intraplate-type magmas and the presence of transitional samples point out for a contemporaneous involvement of two different mantle sources, located at different depths. This magmatism may be explained by the peculiar tectonic setting of the region, linked to the North Anatolian Fault and to the East Anatolian Fault. The occurrence of vertical strike-slip faults, as well as pull-apart basins, may explain contemporaneous melt extractions at different mantle depths.
In the southernmost sector of Italy continental within-plate volcanism (e.g. Sicily Channel, Etna, Ustica) occurs in close geographical and geodynamic association with both subduction-related magmatism (e.g. Aeolian Islands) and ocean spreading (Tyrrenian seafloor). Magmatism in the Sicily Channel (Pantelleria and Linosa) is due to the passive up-welling of asthenospheric mantle in response to the development of pull-apart basins related to south-eastward roll-back of the subduction of the Ionian plate with respect to the rest of the subducting African plate. Within the Sicily Channel, Pantelleria, the type locality of pantellerite, is a Late-Pleistocene magmatic system characterised by a bimodal association of alkali basalts and peralkaline rocks (trachytes to pantellerites), separated by a large compositional gap in SiO$_2$ (50-67 wt.%). The relationships between basaltic and differentiated magmas at Pantelleria, and in bimodal magmatic suite in general, have been the focus of debate in the last three decades. In particular the evolved per-alkaline products are interpreted either as derived from basaltic parental magmas by fractional crystallisation or by re-melting of a gabbroic cumulate.

This study presents new $^{238}$U-$^{230}$Th isotope data along with Sr, Nd and Pb isotope ratios and trace element contents of both the mafic and the felsic peralkaline products of Pantelleria volcano. $^{235}$U-$^{231}$Pa disequilibria have also been measured on two samples with basaltic and hawaiitic composition. The aim of this contribution is to investigate i) the melting regimes responsible for the generation of the least differentiated alkali basaltic products, and ii) the relationships existing between mafic and differentiated peralkaline magmas.

Pantelleria mafic products have ubiquitous $^{230}$Th excesses ranging from 7% to 21%. This range is due to a rather wide variation of ($^{238}$U/$^{232}$Th) at an almost constant ($^{230}$Th/$^{232}$Th). A notable exception is constituted by two hawaiitic samples that present comparable $^{230}$Th-$^{238}$U disequilibria with alkali basalts, but at significantly lower ($^{230}$Th/$^{232}$Th) and ($^{238}$U/$^{232}$Th). Hawaiites also display similar ($^{231}$Pa/$^{235}$U), but different Sr, Nd and Pb isotopes with respect to alkali basalts suggesting these two types of magma derive from two distinct mantle sources, but similar melting regimes.

Trachytes and pantellerites also have ($^{238}$U/$^{232}$Th) similar to those of alkali basalts, but slightly lower ($^{230}$Th/$^{232}$Th). This feature argues against the possibility of generating the peralkaline products by re-melting of a gabbroic cumulate, favouring an origin through fractional crystallisation in timescales comparable to the half-life of $^{230}$Th.
The Southern Tyrrhenian subduction system shows a complex interaction among asthenospheric flow, subducting slab and overriding plate. To shed light on the deformations and mechanical properties of the slab and surrounding mantle, we investigated the attenuation and the anisotropic structure through the subduction region. The 3D attenuation results show high-attenuation shallow regions corresponding to the crustal layers, while the slab is imaged as a low-attenuation body bounded by high-attenuation regions located beneath the Aeolian magmatic arc.

Between 100-200 km depth, in correspondence of high concentration of earthquakes, the slab is characterized by a spot of high attenuation. Such a feature could be related to the dehydration processes associated to the slab metamorphism. A high-attenuation anomaly is present in the mantle wedge beneath the Aeolian volcanic arc and could indicate mantle melting and slab dehydration and also to the large-scale serpentinization.

We also investigated the anisotropic structure of the subduction zone by analyzing shear-wave splitting of the slab earthquakes. Seismic anisotropy reveals a complex pattern of anisotropy across the subduction zone. S-rays sample mainly the slab, showing variable fast directions and delay times. Comparison of S splitting measurements to P-wave velocity anomaly at 100-200 km depth shows that where the rays primarily sample the slab the delay times are small. In contrast, where S rays sample the mantle wedge, the delay times are quite high. This across-subduction variation of delay time depicts the slab as a weakly anisotropic region relative to the mantle above and below and suggests that the main source of anisotropy in the subduction zone is the deformation of the mantle above and below the slab induced by the retrograde motion of the slab.
ULTRATITANIFEROUS BASALTS AND PICRITES FROM THE OLIGOCENE ETHIOPIAN PLATEAU: INSIGHTS ON THE PLUME RELATED MANTLE METASOMATISM

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Geochemical and petrological data indicate that the 30 Ma Northern Ethiopian continental flood basalts and picrites were generated in connection with the “Afar plume”. Previous studies (Beccaluva et al., 2009) show that: a) Basaltic lavas appear zonally arranged with Low-Ti tholeiites (LT) in the west, High-Ti tholeiites (HT1) to the east and very High-Ti transitional basalts and picrites (HT2, TiO₂ 4-6.5 wt.%) closer to the Afar triple junction; b) the P-T conditions of magma generation increased from 1.3 GPa / 1200°C to 3 GPa / 1500°C from West to East; that is, from the outer zones (LT) to the core of the plume head where HT2 ultra-titaniferous picrites were generated. Further sampling has been carried out in the inferred plume axial zone (Lalibela area) focusing on picrite rocks, as well in the Yemeni counterpart where analogous HT2 products (including picrites) are recorded in the Manakhah section. The observed parageneses dominated by olivine and clinopyroxene phenocrysts, within a groundmass containing clinopyroxene, plagioclase, Fe-Ti oxides, alkali feldspar, phlogopite and apatite are consistent with the transitional character of these lavas and their overall enrichment in the most incompatible elements and fractionated REE patterns (La/NaYbN up to 26). New isotopic data carried out at the IGG-CNR Institute of Pisa integrated with those available in the literature (Pik et al., 1999). show correlations between TiO₂ (and other incompatible elements) and Sr-Nd-Pb isotopic data, thus defining the isotopic fingerprint of the plume-related metasomatic agents. These metasomatic agents can be envisaged as alkali-silicate melts that integrate various geochemical components (e.g. Titanium and related high field strength elements, low field strength elements, light rare earth elements, H₂O) scavenged and pooled along the plume axis, and derived from heterogeneous mantle materials mixed during the plume rise. Petrological modeling indicate that the resulting metasomatized mantle sources were characterized by hydrous, iron-titanium-alkali rich exotic parageneses including amphibole, phlogopite and Ti-bearing minerals such as ilmenite. A debate is still open on the ultimate origin of the metasomatic Fe-Ti rich fluids, in turn related to depth of the plume convective cell. A direct core contribution is not plausible, and most Authors favor long-term mechanisms of Oceanic Crust (Fe-Ti basalts/gabbros and their metamorphic equivalent, i.e. eclogites) recycling deep in the mantle via ancient subductions (Sobolev et al., 2007). Accordingly, the uprising plume could have remobilized domains from the mantle Transition Zone which may include relics of older subducted slabs. Within these remobilized domains, characterized by the coexistence of peridotite and eclogite and referred to as a “piclogite” association, the eclogites melt preferentially generating Fe-Ti rich melts that infiltrates and metasomatizes the shallower lithospheric mantle. Alternative views, suggested by studies of high-TiO₂ basalts of lunar provenance, hypothesize primordial “magma ocean” stages in which vast mantle zones were molten and subsequently differentiated with the formation of discrete Fe-Ti-rich mantle domains (Shearer et al., 1996; Thacker et al., 2009; Elkins-Talton et al., 2011).

WHAT GOES INTO SUBDUCTION? NEW CONSTRAINTS ON THE LITHOLOGICAL COMPOSITION OF THE WESTERN TETHYAN SLAB

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The lithological composition of subducted lithosphere is likely to exert a first-order control on the generation of the fluids/melts leading to magmatic activity along convergent plate margins. In the Western Mediterranean, the Africa-Europe convergence, which started in the Cretaceous, has been accompanied by magmatism especially active since the Eocene. Plate convergence was accommodated by deformation along plate margins and by subduction of the Western Tethys lithosphere, whose lithostratigraphy can be studied directly in Alpine tectonometamorphic units that underwent subduction to high-pressure depth and were then exhumed.

This study, which focuses on the Zermatt-Saas Zone and the Internal Valaisan Domain in the Western Alps, shows that a significant part of the subducted Tethyan lithosphere consisted of variably serpentinized subcontinental mantle locally overlain by slivers of continental basement and pre-rift continental shelf sediments, prior to the deposition of post rift-deposits.

The Zermatt-Saas Zone, in the Valtournenche area, consists of abundant serpentinized mantle, intruded by Jurassic gabbros and locally overlain by slivers of continental crust and pre-rift sediments, with relatively minor amounts of syn- to post-rift sediments, which underwent Alpine metamorphism at P > 2.5 GPa at ca. 48-44 Ma. The association of continental basement rocks, pre-rift sediments and ophiolites has generally been ascribed to the formation of a tectonic mélange during the Alpine orogeny. However, zircons from Permian plutonic rocks of the Etirol-Levaz continental basement slice show a distinctive phase of growth at ca. 170-160 Ma. High U/Th ratios and zoning patterns suggest that zircons grew as a result of melt infiltration related to the intrusion of mafic magmas, also dated at ca. 170-160 Ma, in the underlying serpentinites. Therefore, the continental basement slices and the oceanic basement rocks were already juxtaposed in the Jurassic and they were probably part of an Ocean-Continent Transition Zone.

The Pointe Rousse-Breuil Unit, which is part of the Internal Valaisian Domain, is located in a more external part of the Western Alps with respect to the Zermatt-Saas Zone. This unit is composed of serpentinized subcontinental mantle in contact with slivers of continental basement and polymictic breccias, passing upward to radiolarian schists and calcschists (Aroley - Marmontains - St. Christophe lithostratigraphic units), which underwent Alpine metamorphism at P > 1.5 GPa at ca. 38-36 Ma. Cataclasites and gouges, developed at the expense of granitic rocks and ultramafics, are commonly found along the interface between mantle and crustal rocks, but no evidence of brittle deformation is found in the overlying meta-sedimentary sequence.

These observations are interpreted as indicating that ultramafics and continental basement were juxtaposed during Mesozoic rifting by the activity of low angle detachment faults, prior to the deposition of the overlying sedimentary cover at the bottom of the Valaisian Basin. Therefore, our results indicate that a significant portion of the Western Tethyan slab, that was consumed during the Alpine orogeny, was markedly different from a typical Oman-type ophiolite. The lithostratigraphy of the Valaisian Domain and of the Piemonte Zone is indeed comparable to the Ocean-Continental Transition Zones that have been described in 50% of present-day rifted margins and in the less deformed / metamorphosed Eastern Alps. Such domains, which can be up to 200 km wide, are characterized by a different lithostratigraphy with respect to typical ‘oceanic’ and ‘continental’ lithosphere, with windows of exhumed serpentinized mantle between slivers of continental crust. Pre-rift sediments (typically dolostones) are present only rarely as extensional allochthons and syn- and post- rift sediments (typically thin radiolarian cherts followed by thick marbles, marls and pelites) seal the extension-related lithostratigraphy.
Pb-Hf-Nd ISOTOPIC DECOUPLING IN PERIDOTITE XENOLITHS FROM MEGA (ETHIOPIA): INSIGHTS INTO THE MULTISTAGE EVOLUTION OF THE EAST AFRICAN LITHOSPHERE

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New Hf and Pb isotopic data from clinopyroxenes from East African Rift (EAR) mantle xenoliths (Mega, Sidamo region, southern Ethiopia), coupled with recently published Nd isotope and trace element compositions, provide compelling evidence for multiple episodes of mantle depletion and metasomatic enrichment.

Radiogenic values ($\varepsilon_{\text{Nd}}$ up to +22.5 and $\varepsilon_{\text{Hf}}$ up to +1076) suggest that mantle domains currently located beneath the Main Ethiopian Rift suffered extreme melting regimes, possibly in the presence of residual (majorite?) garnet, effectively fractionating Sm/Nd, Lu/Hf and Nd-Hf systematics. Positively correlated Lu/Hf and $^{176}\text{Hf}^{177}\text{Hf}$ provide an apparent ingrowth of 1.96 Ga, close to the CHUR model age of the most radiogenic sample (1.95 Ga) and is consistent with other local records of Proterozoic melting events. Pb isotopes are clearly decoupled from the Nd-Hf systematics, displaying $^{206}\text{Pb}^{204}\text{Pb}$ up to 20.1, $^{207}\text{Pb}^{204}\text{Pb}$ up to 15.70, and $^{208}\text{Pb}^{204}\text{Pb}$ up to 39.8.

These data suggest vigorous convection cells, possibly triggered as a far field dynamic consequence of the Afar plume impingement, preferentially occurred beneath this site, where important lithospheric discontinuities exist between the Archean/Early Proterozoic Tanzanian craton and the Late Proterozoic Panafriacan mobile belt. Such deep mantle dynamics may contribute to stabilizing distinct EM1 and HIMU metasomatic components in the EAR lithospheric mantle.
Swarms of diabase dykes and a few sills of the Central Atlantic magmatic province (CAMP) intruded the Piedmont area of the Appalachians and the coastal plains of eastern North America (ENA) between 201 and 199 Ma.

Three different trends were aeromagnetically recognized, radiating from NW (mostly in the south), to N-S (in North and South Carolina) and turning NE to the north. Based on crosscutting relations, an age progression can be defined from NW- to N- and NE-oriented dykes. 70 dykes and a sill were sampled from Georgia to Virginia. ENA diabases grade in texture from ophitic to intergranular or intersertal, with few porphyritic samples, and grain size varies from sub-pegmatitic to nearly aphanitic.

A typical basaltic mineralogy is observed, with ubiquitous plagioclase (An$_{47-84}$), pyroxenes (augite En$_{33-56}$Fs$_{9-30}$Wo$_{17-42}$, pigeonite, and rare orthopyroxene) and Fe-Ti oxides, flanked by either olivine (Fo$_{48-89}$) or micropegmatite, in olivine- and quartz-normative samples, respectively. SiO$_2$ (46.2-54.3 wt.%) and alkali (1.28-4.38 wt.%) contents classify these rocks as basalts and andesitic basalts with tholeiitic affinity, showing a characteristic Fe-enrichment trend with fractionation. A wide range in MgO (4.74-16.99 wt.%), Al$_2$O$_3$ (12.94-18.68 wt.%) and TiO$_2$ (0.36-1.35 wt.%) suggests different degrees of low pressure fractional crystallization for this magmatic suite, controlled mostly by plagioclase, pyroxenes and olivine. Mg-, Cr-, and Ni-enrichments reflect also accumulation of mafic minerals in some samples.

Incompatible trace element contents are fairly homogeneous and generally low, e.g. La$_N$/Yb$_N$ (0.54-2.39), a characteristic typical of melts derived from a quite depleted shallow mantle-source. All the 40 samples analysed for trace elements by ICP-MS share negative Ti, Ta and Nb anomalies, suggesting either a source inheritance or the effect of crustal contamination (though discarded by other observations). Incompatible trace element contents are not correlated with isotopic compositions of ENA dykes, which display a considerable spread in initial isotopic signatures, unlike other CAMP suites, e.g. $^{87}$Sr/$^{86}$Sr$_{200Ma}$ (0.7043-0.7088), eNd$_{200Ma}$ (-6.8-+2.1) and $^{208}$Pb/$^{204}$Pb$_{200Ma}$ (17.41-18.61).

Pb isotopic compositions plot above the NHRL, at positive $\Delta$7/4 (10-17) and $\Delta$8/4 (19-73). Low $^{188}$Os/$^{187}$Os$_{200Ma}$ compositions (0.127-0.144), obtained for 12 selected rocks, argue for negligible amounts of crustal contamination, and coupled with the large range of Sr-Nd-Pb isotopic compositions, they suggest generation from a strongly heterogeneous mantle source for these magmas, probably a metasomatized lithospheric mantle. Moreover, geochemical variations are not systematically linked to dyke trends, basement composition or geographic position of these intrusives, again suggesting small scale heterogeneities in the mantle source.

The alternative hypothesis of a deep enriched and heterogeneous mantle-plume source, is not supported by the crystallization temperatures calculated for high-Fo (up to Fo$_{89}$) olivines (ca. 1350°C), that do not argue for a very hot (i.e. mantle-plume) origin. Geochemical correlations between ENA intrusives and CAMP flows from North America (i.e. flat REE patterns, Ti negative anomaly) suggest that these dykes and sills may have fed extrusives chemically similar to Preakness and Hook Mt. flows (i.e. the youngest flows from the Newark basin and other Triassic rift basins in North America) whereas none of the analyzed dykes yields geochemical compositions similar to the slightly older Orange Mt. basaltic flows.
Recent tomographic models of the central Mediterranean region yield the definition of the Vp and Vs structure in the uppermost mantle. Broad low velocity anomalies are identified along the Tyrrhenian margin of the Apennines at about 50-100 km depth, coherently with the intense stretching and the development of Quaternary volcanism. On the contrary, low velocity anomalies seem to be absent in the southern Tyrrhenian wedge in front of the Ionian slab and underneath the Eolian volcanoes, i.e. where the magmatic signature shows the most clear subduction-related components. These latter volcanoes have localized shallow (40-50 km depth) and small low Vp volumes indicative of isolated magma chambers located at the base of the crust.

This apparent controversy is tentatively explained by a model in which low velocity anomalies in the Tyrrhenian and peri-Tyrrhenian domains represent large asthenosphere up-welling that sustained the stretching of the European lithosphere and the opening of the back-arc basins. In the Apennines, the highly heterogeneous Quaternary magmatism testifies the more recent stage of the stretching process, triggered by the delamination of the Adria continental lithosphere. Conversely, the lack of seismic evidence of asthenospheric up-welling in the mantle wedge of the Ionian slab suggests that the Eolian volcanism is fed by small magma chambers originated before the (local) onset of the stretching induced by the Ionian slab retreat.
ORIGIN AND EVOLUTION OF PONTINE ISLANDS MAGMATISM (TYRRHENIAN SEA, ITALY): GEOCHEMICAL CONSTRAINTS FROM SUBMARINE VOLCANICS

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The spatial-temporal distribution and compositional variability of Plio-Quaternary magmatic products emplaced in the Tyrrhenian and surrounding regions is related to subduction processes and extensional phases, which acted in different ways in the northern and the southern part of the basin. In this framework, the magmatism of the Pontine Islands is very interesting as 1) emplaced at the boundary between the Tuscan and the Roman Magmatic Provinces; 2) strictly related to geodynamic processes involved in the opening of the Tyrrhenian oceanic domain.

Previous studies defined that: 1) Pleistocene volcanic episodes were represented by potassic products, with basic to intermediate rocks in the islands of Ventotene and Santo Stefano and with intermediate to highly evolved rocks (trachytes up to peralkaline rhyolites) in the south-eastern part of Ponza and Palmarola island; 2) Pliocene volcanic episodes are represented by calcalkaline products, with silica-rich volcanic units constituting the dominant products in Ponza and Zannone islands; the latter were characterized by lack of primitive rocks raising questions on the petrological processes as well as on the tectonic mechanisms that triggered magma genesis.

In this contribution we present new data including the investigation of the Pontine submarine portions carried out in four oceanographic cruises (aboard RV Urania), during which seafloor samples were dredged. An important result is that off-shore sampling also recovered less-evolved terms, i.e. basalts and andesites, of the calcalkaline series.

The new sample collection has been characterized through major/trace element data and Sr-Nd isotopic analyses, implementing the data-set already available in the literature to provide better constraints on the genesis of both calcalkaline and potassic series.

Previous studies (Conte & Dolfi, 2002; Cadoux et al., 2005) interpreted the Pontine magmatism in the framework of a transition from subduction-related to intraplate geodynamic settings. The new data suggest that such transition has not been fully accomplished, pointing to ubiquitous and persisting subduction-related signatures in the Pliocene-Pleistocene mantle sources. In particular, geochemical and isotopic characters of the mafic products indicate highly heterogeneous mantle sources, in turn related to crustal components recycled in the mantle via subduction. Further assimilation of crustal materials possibly occurred as result of shallow level processes in the plumbing system, contributing to define the observed isotopic fingerprint.

NEW EVIDENCES OF MANTLE HETEROGENEITY BENEATH HYBLEAN AREA (SICILY) AS INFERRED FROM NOBLE GASES AND GEOCHEMISTRY OF ULTRAMAFIC ENCLAVES

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We carried out a geochemical investigation of the mantle beneath Hyblean area through ultramafic enclaves (peridotites and pyroxenites) found in Miocene age Hyblean volcanics. Major and trace elements, in the whole rock and in the single mineralogical phases and Sr-Nd isotopes in clinopyroxenes were analysed together with noble gases entrapped in CO\textsubscript{2}-rich fluid inclusions hosted in olivines and pyroxenes.

The pattern of REE, the Zr/Nb and \textsuperscript{143}Nd/\textsuperscript{144}Nd ratios highlighted clear compositional differences between the peridotite group (Zr/Nb = < 4; \textsuperscript{143}Nd/\textsuperscript{144}Nd = 0.5129) and the pyroxenites (Zr/Nb = 20; \textsuperscript{143}Nd/\textsuperscript{144}Nd = 0.5130). Also, the REE analyses suggested the presence of cryptic metasomatic events which would have re-fertilized the peridotitic layer previously depleted by extraction of melts. In this context, the metasomatizing agent, namely a deep-seated magmatic liquid intruding the peridotites at different levels, would be represented by the pyroxenites, as suggested also by their finding as veins in peridotitic nodules.

The noble gas analyses confirmed the above compositional difference between the peridotites and the pyroxenites. In particular, we focused our attention on the \textsuperscript{3}He/\textsuperscript{4}He and \textsuperscript{4}He/\textsuperscript{40}Ar ratios because they represent important tracer of mantle processes. The \textsuperscript{3}He/\textsuperscript{4}He and \textsuperscript{4}He/\textsuperscript{40}Ar ranges measured in the fluid inclusions of peridotites (7.0-7.4 Ra and 0.4-8.0, respectively) were in average lower than that shown by the pyroxenites (respectively 7.2-7.6 Ra and 0.6-15). In order to explain the observed mantle heterogeneity in noble gas systematics, we hypothesized a mixing between two end-members:

1) a shallow peridotitic layer having R/Ra of < 7 and \textsuperscript{4}He/\textsuperscript{40}Ar ratio lower than that the typical production range (\textsuperscript{4}He/\textsuperscript{40}Ar < 2-5), due to melt extraction events;

2) a deep pyroxenitic metasomatizing melt characterized by a R/Ra of < 7.6 and with a variable \textsuperscript{4}He/\textsuperscript{40}Ar ratio due to degassing processes connected with the ascent of magma at different levels of the hosted peridotite.

The whole geochemical dataset therefore suggests the presence of two different mantle sources for the above highlighted peridotitic and pyroxenitic groups, respectively a shallower HIMU-type source for the former and a deeper DM-type source for the latter.
In the Bohemian Massif (Czech Republic), the Moldanubian (M) and the Tepla Barrandian (TB) terrains were assembled during Variscan orogenesis. In ancient times, both regions were the site of quite coeval basic intrusions which identified extensional geodynamic contexts. In M such “igneous” rocks are mainly represented by amphibolites and by quite rare transitional slightly metamorphosed dykes with a supposed age of 600-550 Ma (Janoušek et al., 2008). These cut the paleoproterozoic granitoids of the Svetlik formation and suggest an original continental-cratonic setting. While amphibolites appear to be chemically spread, the dykes show a strong elemental OIB (Sun & McDonough, 1989) affinity (Dy/YbCN = 1.3 vs. 1.68; La/SmCN = 2.07 vs. 2.33; La/NdCN = 1.48 vs. 1.86).

In TB, scarcely metamorphosed basic bodies have been intruded by rare dykes swarms (524 Ma; Dörr et al., 2002) showing a fairly cumulitic texture, a quite high silica content coupled with an high Mg#, a N-MORB (Sun & McDonough, 1989) like REE pattern (La/SmCN = 0.54 vs. 0.55; Dy/YbCN = 1.15 vs. 0.97; La/NdCN = 0.61 vs. 0.66) and an evident negative Nb anomaly followed by a positive Ti one.

Differences in the mantle sources involved in the TB and M dyke genesis could be also explained by the La/Ce (0.3 vs. 0.4) and La/Yb (1.0 vs. 1.4), the first being a direct feature of the source and the second a possible consequence of variable amount of garnet in the residual source mantle. Notably, such behavior cannot be easily modified by sub-solidus processes.

To explain the genesis of the TB dykes, an extensional event which immediately followed the evolution of an Island Arc system has been suggested by several authors (Dörr et al., 2002; Zulauf et al., 2004). Indeed, for the M Late Proterozoic magmatism, which outcrops in a region strongly tectonized where the amphibolites were mainly investigated, a clear geodynamic context is also undefined.

Notwithstanding, the supposed ages of the magmatic event and the chemical behaviors of the slightly metamorphosed dykes, could be inserted within the recent 600-500 Ma plate reconstructions proposed by Pisarevsky et al. (2008). So, such magmatic event could be interpreted as a minor occurrence of the plume related continental extension responsible of the Baltica-Amazonia-Laurentia-Avalonia break-up, which should represent the last great extensive-transientive moment between the Rodinia Break-up and the Great-Gondwana assemblage.

THE OXYGEN ISOTOPIC COMPOSITION OF XENOLITHS FROM TALLANTE (SOUTHERN SPAIN): EVIDENCE FOR CRUST RECYCLING INTO THE MANTLE

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Mantle xenoliths from Tallante (Betic Cordillera, Spain) include samples recording a peculiar distinct style of metasomatism that induced orthopyroxene, plagioclase, phlogopite and amphibole crystallization and generated “hydrous” opx-rich mantle domains. The latter are locally crosscut by felsic veinlets containing plagioclase and orthopyroxene ± quartz ± phlogopite ± amphibole. The observed parageneses and available Sr-Nd-Hf isotopic data suggest that metasomatic agents were related to recycling of crust components within the mantle, plausibly in connection with subduction processes occurred during the Cenozoic Betic orogenic cycle.

In this study we investigated representative samples of composite xenoliths consisting of peridotite crosscut by felsic veins (varying in size from centimetric to millimetric) and unveined peridotites, measuring the $^{18}\text{O}/^{16}\text{O}$ ratios of the constituent minerals by laser fluorination. Results show that the narrow O-isotope compositional “typical” of mantle rocks, and the limited oxygen isotope fractionation at mantle temperatures, make oxygen isotopes a powerful tool for identifying recycled crustal material in the mantle. Orthopyroxene and plagioclase of the centimetric vein show $\delta^{18}\text{O}$ values of $+9.8$ and $+10.6\%$, respectively, whereas clinopyroxene of the surrounding peridotite country rock has $\delta^{18}\text{O} = +6.2\%$. Plagioclase of two distinct millimetric felsic veins show $\delta^{18}\text{O}$ of 7.6 and 7.3%.

The $\delta^{18}\text{O}$ values significantly higher than typical mantle ones provide insights to the genesis of the Cenozoic subduction-related magmas of the Betic region that include silica-oversaturated calcalkaline (s.l.) and lamproite products, possibly resolving source vs. shallow level crustal contamination of the magmatic rocks. Moreover, the different O-isotope composition recorded in veinlets characterized by different thickness could provide insights into diffusion-assisted O-isotope reequilibration of mantle rocks, thus constraining the time for “crust digestion” into the mantle.
SMALL SCALE CONVECTION IN THE MEDITERRANEAN MOBILE BELT

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Mobile belts are long-lived deformation zones composed of an ensemble of crustal fragments, distributed over hundreds of kilometers inside continental convergent margins. The Mediterranean represents a remarkable example of this tectonic setting: the region hosts a diffuse boundary between the Nubia and Eurasia plates comprised of a mosaic of microplates that move and deform independently from the overall plate convergence.

Surface expressions of Mediterranean tectonics include deep, subsiding backarc basins, intraplate plateaux and uplifting orogenic belts. Although the kinematics of the area are now fairly well defined, the dynamical origins of many of these active features are controversial and usually attributed to crustal and lithospheric interactions. However, the effects of mantle convection, well established for continental interiors, are expected to be particularly relevant in a mobile belt, and modeling may constrain important parameters such as slab coherence and lithospheric strength.

Here, we compute global mantle flow based on recent, high-resolution seismic tomography, to investigate the role of buoyancy-driven and plate-motion induced mantle circulation for the Mediterranean. We show that mantle flow provides an explanation for much of the observed dynamic topography and microplate motion in the region. More generally, vigorous small-scale convection in the uppermost mantle may also hold the key for understanding other complex mobile belts such as the North American Cordillera or the Himalayan-Tibetan collision zone.
JURASSIC U-Pb ELA-ICP-MS ZIRCON AGES FOR SEGREGATION OF HUGE CHROMITITE LAYERS IN THE FINERO MANTLE BODY: NEW INSIGHTS INTO THE GEODYNAMIC EVOLUTION OF THE SOUTHERN ALPS

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Zone (IVZ), Southern Alps. It consists of a mantle body, surrounded by a mafic-ultramafic intrusive sequence (Siena & Coltorti, 1989), documenting an association of mantle and crustal rocks inferred to be placed at the bottom of the continental crust of the Adria plate before the opening of Ligurian-Piedmontese branch of the Jurassic neo-Tethys. Nevertheless, the Finero complex shows several tectonic and petrochemical differences with respect to those of the central IVZ. For instance, published geochronological U-Pb zircon data constrain the emplacement of the Mafic Complex in the central sector of the IVZ at 280- to-295 Ma (Peressini et al. and references therein). Conversely, the intrusion age of almost part of the Mafic Complex in the Finero area (SHRIMP U-Pb zircon dating) indicate that the External Gabbro, the largest unit forming the Finero Mafic Complex, intruded the bottom of the Kinzigite Formation during Ladinian (Zanetti et al., 2011). A Triassic ages have been also determined for the multiple metasomatic and intrusive events affecting the associated mantle body (Grieco et al., 2001 and references therein). This is mainly formed by harzburgite modally enriched in phlogopite and amphibole and with large LILE contents. Based on the geochemical and isotopic composition, several authors proposed that the growth of phlogopite-bearing assemblages was related to the migration of melts containing significant crustal-derived components. With the aim to place constraints on the timing of melt migration through the Finero mantle body, zircons were separated from three, dm-thick chromitite bands enclosed in huge dunite bodies outcropping along the Cannobino River and on the Mt. Sasso Rosso. U-Pb ELA-ICP-MS data result in concordant ages comprised in the range of 188-186 Ma, which is believed to date the segregation of the chromitite bands during channeled porous-flow melt migration. These ages are significantly younger than that determined through conventional multigrain dating by (Grieco et al., 2001), whose data define an intercept Triassic age of 208±2 Ma. Although the studied chromitite bands do not show primary phlogopite, the major and trace element mineral chemistry point to a cognate origin with the migrating melts forming the phlogopite harzburgite. The finding that the porous-flow ascent of LILE-enriched melts through the Finero mantle unit postdates the emplacement of the Finero Mafic Complex, and the absence in the latter of the record of this magmatic stage, suggest that the Finero mantle unit might have been emplaced tectonically in contact with the lower crust at some time after lower Jurassic. This hypothesis is supported by the observation that the contact between mantle unit and Mafic Complex is always tectonic. As a whole these data confirm that the northernmost part of the IVZ, represented by the Finero complex, cannot be longer considered as a part of the central IVZ, thus suggesting that the entire geological setting of the area should be revised.

U-Pb ZIRCON DATA FOR TUFFACEOUS LAYERS FROM THE SEDIMENTARY COVER OF THE STRONA-CENERI ZONE AND PO PLAIN: CONSTRAINTS ON THE TRIASSIC GEODYNAMIC EVOLUTION OF THE SOUTHERN ALPS

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In the western sector of the Southern Alps, tuffaceous levels are occasionally found in the Triassic sedimentary sequences. The direct age characterisation of these layers is very limited: in fact, a U-Pb zircon age of 245±1 Ma is available only for the tuffites from Mt. San Giorgio area (Lugano, CH: Mundil et al., 1996), which results slightly older than that expected according to the stratigraphic position. Besides, no geochemical information is presently available for these layers and the geodynamic setting of the related volcanism is still matter of debate.

Thus, with the aim to place further constraints of the geodynamic evolution of the Southern Alps in Mesozoic times and increase the accuracy of the age record of the sedimentary sequence, we have performed a mineralogical, geochemical and geochronological study on tuffaceous deposits outcropping within the Anisian-Ladinian succession of the sedimentary cover of the Strona-Ceneri Zone in the Borgosesia area (Carraro & Fiora, 1974; Fantoni et al., 2004) and recovered at the same stratigraphic position in wells of the Villafortuna-Trecate oil field (western Po Plain, Piedmont region, NW Italy: Fantoni et al., 2002). CO₂ concentration was determined by Dietrich-Früling calcimeter. XRD data indicate that such tuffaceous deposits are constituted by a variable mixture of magmatic and sedimentary components.

Major and trace element compositions, assessed by means of XRF analysis, suggest a calc-alkaline affinity for the magmatic component. To provide accurate geochronological constraints, zircons have been separated with conventional methods from four tuffaceous outcrops, namely “Lembo di Sostegno”, “Lembo di Crevaucoure” and “Lembo di Monte Fenera” outcrops, as well as from a buried tuffaceous sample of the Villafortuna-Trecate oil field. Zircons were mounted in epoxy resin and characterised under cathodoluminescence (CL).

Based on colour, morphology and internal structure, they 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. The zircons from the second group are colourless, rounded in shape and with only relics of magmatic zoning, consistent with metamorphic recrystallization. U-Pb ELA-ICP-MS data point to ages of 237±8 Ma and 229±9 Ma for the magmatic growth of the zircons from the tuffites of “Lembo di Crevaucoure” and “Lembo di Sostegno”, respectively, which are in agreement with their stratigraphic position.

The volcanic activity producing these layers might be linked to the intrusive Triassic magmatism documented in the Finero Complex (NE Ivrea-Verbano Zone; Zanetti et al., 2011; Stähle et al., 2001). Conversely, the zircons from the “Lembo di Monte Fenera” and Villafortuna-Trecate oil field produce a very large range of crystallisation-recrystallisation ages, which span from Proterozoic to Paleozoic to the Permian-Triassic boundary, thus indicating a dominant contribution of the crystalline basement to the zircon population.

THE GARROTXA VOLCANIC FIELD (NE SPAIN):
NEW GEOCHEMICAL CONSTRAINTS

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The Quaternary volcanism of the Garrotxa area (NE Spain) developed during the rift-type extensional tectonics affecting the eastern margin of Iberia since the late Oligocene and related to the opening of the Valencia trough. Location of the eruptive centres is controlled by the main NW-SE faults that limit the different elevated or depressed blocks configuring the tectonic structure of the area. The Garrotxa volcanic activity is characterised by small strombolian cones and lava flows formed by very short monogenic eruptions, occasionally phreatomagmatic. As result of this activity, more than 40 volcanic cones and about 30 main lava flows can be recognised in this region.

The volcanic rocks consist of basanites, alkali basalts, and trachybasalts that are aphanitic, vesicular, hipoohialine and porphyritic in texture, in which olivine and clinopyroxene (± plagioclase and oxides) are the main mineral phases.

They show relatively homogeneous geochemical features, with FeO/MgO and Na2O/K2O weight ratios ≤ 1. For most of the samples, major and trace element correlations exclude significant stagnation and magmatic evolution in crustal reservoirs. Primitive mantle-normalized multi-element diagrams are characterized by a typical bell-shaped, OIB-like trend, with progressive enrichment of the most incompatible elements, except for Th, Pb, K and Rb, and significant peaks at Ta and Nb, sharing their geochemical patterns with the whole Cenozoic anorogenic magmatism of the European-Mediterranean area.

Significant variability of 143Nd/144Nd and 206Pb/204Pb ratios in the Garrotxa volcanics testify for a common heterogeneous mantle source, and are likely related to mixing processes occurred between the local lithospheric mantle and a sublithospheric, geochemical enriched component. Sr-, Nd-, and Pb-isotope compositions of the Garrotxa magmas confirm their similarity to the EAR (Enriched Asthenospheric Reservoir)-derived basalts of the Mediterranean region, showing a HIMU (High μ = high 238U/204Pb)- DMM (Depleted MORB Mantle) signature. Noticeable, the Garrotxa basalts display geochemical features that are very close to those of Cape Verde, a key “end-member” in the petrogenesis of the European magmatism since the Cretaceous (Piromallo et al., 2008). In our model, the rift-related extensional tectonics favors upwelling of sub-lithospheric, plume-like mantle into the local lithosphere, originating EAR-type basalts via adiabatic decompression melting.

In conclusion, the Garrotxa volcanic activity must be included within the members of the within-plate Tertiary-Quaternary magmatism of the European-Mediterranean area.

The geochemical and mineralogical compositions of mafic igneous rocks have been classically considered powerful tools to infer the composition of their magma source(s). At the same time, geochemical models (e.g., the existence of the mantle end-members DMM, HIMU, EMI, EMII, EMIII, FOZO, C-, PHeM, LONU, LOMU, HRDM, and so on) have been commonly, and dangerously, translated to physical concepts and specific seismological subdivisions of the mantle (e.g. upper mantle, lower mantle, D'). Despite the vigorous research activity and the wealth of data and hypotheses developed during the last forty years, the thermal state and the chemical composition of the upper mantle are far for being fully understood. Concepts considered well acquired, like the significance of terms like upper mantle, lithosphere and asthenosphere, the rheological behaviour of mantle rocks, the seismic wave velocity perturbations, the presence of olivine-poor lithologies, the chemical reactions and the metasomatic effects of percolating melts in the upper mantle, the origin of non-basaltic melt compositions (e.g., carbonatitic or ultra-potassic) still need profound re-thinking. Often fundamental assumptions (e.g., upper mantle with depleted compositions, presence of active upwelling of deep-rooted mantle plumes, potential temperature, geotherm(s), the definition itself of “ambient”, “normal”, “anomalous” and “exotic” mantle) force the conclusions towards unrealistic results.

The following remarks should be taken in mind when performing petrological models based on geochemical and geophysical arguments:

1) there is no reason to hypothesize a homogeneously depleted upper mantle;
2) the asthenosphere is not necessarily depleted nor fully convecting;
3) tomographic images based on Vs and Vp anomalies cannot be considered as thermometers;
4) positive Vs and Vp anomalies can be related with the presence of less dense material (e.g. depleted harzburgite, seismic lid) and low-velocity anomalies can be dense eclogite;
5) the presence of thermal anomalies in the form of mantle plumes is not required by any discipline;
6) the potential temperature of the mantle is not the classical 1273°C value;
7) the concept itself of mantle potential temperature should be considered in relation to the depth of magma formation;
8) if the composition of the upper mantle is not entirely peridotitic and if olivine-poor lithologies are not volumetrically insignificant, the concept of Mg# to determine the primitiveness of a basaltic magma needs to be rethought;
9) the geochemical similarity of two magma batches cannot be considered as the proof for the derivation from the same physical mantle;
10) a given magma with a particular geochemical signature (e.g., carbonatitic, leucititic, basaltic, alkali sodic) can be generated in different tectonic settings;
11) the geochemical composition of a magma cannot be necessarily considered as a reflection of its mantle source, being very likely the possibility of strong chromatographic exchange reactions en route to the surface;
12) high magma productivity is not necessarily related with high absolute temperatures, but rather to high homologous temperatures or even ambient mantle temperature, which can be higher than MORB temperatures;
13) the geological history of the area where given igneous district is developed can be relevant;
14) shear heating at the base of the lithosphere can contribute to the generation of magmas in intraplate settings.

With these assumptions, the source depth of the Earth’s volcanism can be mostly dominated by the asthenosphere (the upper mantle boundary layer; upper 200 km of the mantle), without a significant signature of the geochemical composition of the deeper levels of the mantle, whose composition remains mostly unsolved. Some of these remarks may seem very obvious, but the scientific literature is full of oversimplifications and of models based on unconstrained and unrealistic assumptions.
SUBDUCTION-UNRELATED / SUBDUCTION-RELATED MAGMATISM IN NORTHERN APENNINES. THE EARLY OLIGOCENE AVETO-PETRIGNACOLA VOLCANICLASTIC SUCCESSION

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During the Early Oligocene, the ~ 800 m thick Aveto-Petrignacola volcaniclastic Formation (APF) was deposited in a relatively short time (~ 32-29 Ma) in the Northern Apennines. The APF volcanic rocks are mostly basaltic andesites, andesites and dacites, with minor rhyolites and gabbroic compositions found as pebbles ~ 0.001-0.5 m³ in size (with average diameter ranging from ~ 5 to 30 cm). This volcaniclastic succession is interpreted as the product of subaerial effusive to explosive arc magmatism and is associated to turbidite sedimentation. Petrographic, mineral chemical, major and trace element content, as well as Sr-Nd-Pb isotopic ratios are all compatible with a calc-alkaline magmatism generated as consequence of the metasomatic modifications of mantle sources related to the subduction of oceanic lithosphere. The APF volcanic rocks are a puzzle in the geodynamic evolution of the Italian area. This Formation is now part of the Apennine thrust system, developed as consequence of the West-directed subduction system that involved recycling of the oceanic lithosphere of the Mesogean/Liguride ocean(s) beneath the southern paleo-continental margin of Europe. Such a subduction system was associated with production of abundant calc-alkaline/arc tholeiitic magmatism starting from Late Eocene/Early Oligocene in SE Spain (Malaga arc tholeiitic dykes), Sardinia (e.g., Calabona microdiorite) and SE France (Esterel microdiorite). During the Middle-Late Eocene, the Alpine Tethys subduction system had already ceased, followed by Adria-Europe continental collision. In other words, during the emplacement of the APF subduction-related volcanic rocks, the Alpine subduction system was already shut down, whereas the Apennines subduction system was fully developing. Notwithstanding this, we propose that the APF volcanic rocks are genetically connected to the Alpine subduction system rather than the Apennines.

We propose that the APF volcanic rocks are generated by a mantle source modified by components of the Alpine slab detached during Middle-Late Eocene, and still wandering beneath the Adriatic lithosphere after the closure of the Piedmontese (Liguride) Ocean. The effects of the “zombie” slab would be a metasomatic modification of the original peridotitic matrix, allowing hydration with the consequent formation of amphibole. Local effects of stress release in the Apennines foreland and in the Alps hinterland would have played an important role to trigger magmatism. Paradoxically, the subduction-related igneous activity in the APF area developed several Ma after the cessation of oceanic lithosphere subduction in an area that, few Ma later, would have been involved in a completely different orogenesis (Apennines tectonics).

In summary, the APF volcano (now completely eroded) would have been generated as consequence of Alpine tectonics, but would have been involved in the Apennines thrusts soon after its formation. According to this view, the APF and the Mortara volcanoes, the latter now buried beneath the Po Plain, would have the same origin. The formation of the Po Plain (representing the foreland of the Apennines and the retro-foreland of the Alps back-thrusts) would have prevented the Mortara volcano from being eroded, leaving it in its original position on the north-western margin of Adria.
The Axum-Adwa sector (Tigray, Northern Ethiopia) is characterized by a transitional basalt-trachyte magmatic complex which took place at the northern periphery of the Oligocene Northern Ethiopian Continental Flood Basalts (CFB), which are related to the Afar plume.

This complex consists of basaltic, trachyandesitic and trachytic flows and subvolcanic dome-shaped syenitic intrusions, the latter mostly occurring around Axum.

These intrusive rocks - quarried by the Axumites as the ideal material to carve their famous obelisks - bear variable amounts of nepheline/aegirine aggregates that probably developed during late- to post-magmatic stages.

Major and trace element modeling by PELE and MELTS software using bulk rocks and constituent minerals, indicates that trachyandesitic and trachytic magmas could derive by shallow fractional crystallization processes from the associated transitional basalts.

Magma vents are set along an ENE-WSW lithospheric fault system that may have favored magma generation deep in the mantle, as well as their differentiation at shallower levels in the crust.

This tectonomagmatic setting, nearly perpendicular to the Red-Sea spreading axis and parallel to that of Gulf of Aden, appears to be geodynamically related to the extensional phases which radiated from the Afar triple junction after the paroxysmal eruption of the Northern Ethiopia CFB.
HIGH TiO₂ PICRITE BASALT / RHYOLITE BIMODAL ASSOCIATION AS INDICATOR OF INITIAL RIFTING AT A “PLUME AXIS”: THE CASE OF NORTHERN ETHIOPIAN PLATEAU

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Voluminous felsic volcanism has been recently associated to 1) mafic Large Igneous Provinces (LIP) where rhyolites are comparable to A-type granites or 2) continental convergent margins Silicic LIP (SLIP) where rhyolites share similarities with S- and I-types granites (Pankhurst et al., 2011). An intriguing petrological debate has concerned the genesis of bimodal silicic-mafic volcanism in continental LIP (Bryan et al., 2002). In several Continental Flood Basalt (CFB) provinces of the Gondwana realm - such as Paranà-Etendeka, Karoo, Ferrar, Deccan, Madagascar, Seychelles and Afro-Arabian region - extensive (10⁴-10⁵ km²) rhyolitic volcanics occur, generally late in the sequence and sometimes interbedded with basalts (Bryan et al., 2010).

In this contribution we present petrological and field data on the high-TiO₂ picrite basalt/rhyolite bimodal association in the north-eastern Ethiopian plateau (Lalibela area) which is considered the axial zone of the 30 Ma CFB activity related to the Afar plume (Beccaluva et al., 2009).

In this area the volcanic sequence consists of ca. 1700 m of mostly very high TiO₂ (4-6.5%) picrite basalts, covering an area of ca. 15000 km², topped by an average thickness of ca. 300 m tick rhyolitic ignimbrites and lavas which discontinuously extend over an area of ca. 10000 km². Petrogenetic modelling, using rock and mineral chemical data and phase equilibria calculations (by PELE and MELTS), indicates that: 1) very high TiO₂ picrite basalts could generate rhyolitic, sometimes peralkaline, residual melts (liquid fraction 9-16%) with persistently high TiO₂ content (0.4-1.0%); 2) by closed system fractional crystallization processes developed at 0.1-0.3 GPa pressure range, 1400-750°C temperature, at QFM fO₂ conditions; 3) the highest crystallization rate - involving 10-13% of Fe-Ti oxide removal - in the temperature range between 1070 and 950°C, represents an “ephemeral” fractionation stage, resulting in the absence of erupted silica intermediate products (Daly gap). The eruption of highly differentiated products capping the basic volcanics implies a rapid change from “open” to “closed” tectono-magmatic system, which favoured trapping of parental picrite basalts and their fractionation in upward zoned magma chambers, ultimately leading to low aspect ratio fluorine-rich rhyolitic ignimbrites and lavas. This tectono-magmatic evolution resulted from the onset of continental rifting at the plume axis, with faulting and block tilting, allowed magma differentiation in shallow - N-S elongated - fissural chambers parallel to the developing Afar Escarpment. In this scenario, rhyolitic eruptions represent the transition between the plateau basalt stage to the incipient rifting progressively evolving to continental break-up and formation of the Red Sea basin.

We analyze P and S wave spectra from moderate- to deep-focus teleseisms recorded at the Retreating-Trench, Extension, and Accretion Tectonics (RETREAT) temporary broadband seismic network to assess the variations of the Earth mantle attenuation in the northern Apennines region (Italy). For each earthquake, we compute the ratio between the spectrum at each station and the average spectrum, in order to estimate $t^*$ residuals ($\Delta t^*$) from the spectral ratio decay.

The number and distribution of the teleseisms useable for the P wave $t^*$ calculation allow for a gross azimuthal analysis; although the ($\Delta t^*$) values at single station display, in most cases, azimuthal-dependent fluctuations, their overall distribution shows a partition of the study region into two main areas, whose gross features remain almost unchanged over the whole azimuthal range. This partition is confirmed by the S wave $t^*$ mean values, computed for each station over the set of useable events. We distinguish a relatively high attenuation area on the western, Tyrrhenian side and a relatively low attenuation area on the eastern, Adriatic side. By correlating our $\Delta t^*$ estimates and the velocity structure derived from the existing tomographic models, we compute the ranges of possible P and S wave Q values in the mantle wedge above the Apennines slab (on the Tyrrhenian side) and in the asthenosphere below the Adriatic region.

Furthermore, the determined attenuation properties are used to draw some inferences on the thermal state of the uppermost mantle and on the physical properties of the tectonic elements, which constitute the subduction system in the region.
PETROPHYSICAL AND PETROLOGICAL FEATURES
OF DEEP-SEATED XENOLITHS FROM MIocene TUFF-BRECCIAS
OF THE HYBLEAN PLATEAU: SUGGESTIONS FOR A
LITHOSPHERIC MODEL BENEATH SOUTH-EASTERN SICILY

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As it is known, deep-seated xenoliths act like an “open window” to the inaccessible portions of
lithosphere, and permit lithological models to be set out with a great detail.

In this work, attention focused on xenoliths collected within Miocene tuff-breccias from the Hyblean
Plateau (south-eastern Sicily, Italy). According to main petrographic features, the studied xenoliths may be
grouped into: a) ultramafic, which consist of spinel facies peridotite and pyroxenite (some garnet bearing); and
b) feldspar-bearing suite, represented by mafic granulite and minor metagabbro and anorthosite.

Spinel facies peridotite rocks (harzburgite and harzburgitic lherzolite) exhibit protogranular to (rare)
porphyroclastic texture; they are constituted by olivine (Fo\text{89-91}), orthopyroxene (En\text{88-91}; Mg\# 90-92),
clinopyroxene (Cr-diopside: En\text{51-54}Fs\text{2-4}Wo\text{44-48}), Cr-rich spinel (Cr\# 23-35). Very rare phlogopite occurrence
testifies that the Hyblean mantle underwent metasomatic event.

Pyroxenite specimens classify into: Cr-diopside websterite (Cr-diopside, Ca-poor pyroxene, Cr-Al spinel
+/- olivine and amphibole); Al-diopside websterite (Al-diopside, Ca-poor pyroxene, Al-spinel, garnet
(Py\text{54.5}Alm\text{25}Gr\text{10.5}). Al-augite pyroxenite (interpreted as igneous adcumulitic products) are composed of
Al-clinopyroxene, Al-spinel, garnet (Py\text{64}Alm\text{25}Gr\text{10}). Finally, feldspar-bearing xenoliths are mostly
represented by mafic granulite (plagioclase, Ca-pyroxene, Ca-poor pyroxene and Al-spinel +/- amphibole).
Metagabbro and metadiorite (plagioclase, Ca-pyroxene, Fe-Ti oxides, apatite) and anorthosite (plagioclase +/-
Al-spinel and pyroxene) occur at a lesser extent.

Pressure-temperature estimates, based on two pyroxene and garnet mineralogical assemblage within
pyroxenite provided equilibration values of 0.98 GPa at 740°C for spinel pyroxenite and 1.32 GPa at 1040°C for
garnet pyroxenite.

In addition, petrophysical investigation was carried out on three selected lithotypes (peridotite, pyroxenite
and mafic granulite), whose large size of collected xenoliths allowed laboratory seismic measurements (Vp, Vs,
Poisson’s ratio, seismic anisotropy) at various P-T conditions (up to 600MPa at 600°C).

Since investigated xenoliths are considered to be representative of large scale lithological units,
petrophysical results combined with petrological information permit available geophysical data to be constrained
and interpreted at a better extent and may provide useful suggestions for a lithospheric model underneath the
Hyblean Plateau.
TRIASSIC THOLEIITIC AND ALKALINE BASALTIC MAGMATISM IN WESTERN-CENTRAL SICILY (SOUTHERN ITALY): GEOCHEMICAL AND ISOTOPIC CLUES TO MANTLE SOURCES INVOLVED DURING EARLY CONTINENTAL RIFTING

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During Early Mesozoic, a diffuse magmatic activity developed in western-central Sicily in relation to the extensional tectonics associated with the opening of the Neotethys Ocean. In this work, we report and discuss geochemical and Sr-Nd isotopic data for Sicilian Triassic tholeiitic and alkaline volcanic rocks.

Tholeiitic basalts from western Sicily are characterized by relative HFSE enrichment, high HFSE/LILE ratios, flat REE patterns (LaN/YbN = 2.27-2.48), Ti, Sr and K negative anomalies and Pb peaks in primitive mantle-normalized diagrams. The Sr (87Sr/86Sr = 0.707-0.708) and Nd isotopic compositions (εNd = from -1.7 to -2.2) are compatible with an origin from enriched mantle sources. Additionally, the relatively high Sr isotopic ratios and diagnostic trace elements ratios, such as La/Nb (~ 17), LaN/SmN (~ 1.20), Nb/U (~ 20) and Pb/Nd (~ 0.3), could reflect involvement of the lower crust in the magmatic evolution of the tholeiitic rocks.

Alkali basalts from central Sicily preserve a clear geochemical signature despite the intense alteration. The behaviour of immobile elements such as the low Y/Nb and Zr/Nb and high Th/Yb and Ta/Yb ratios, positive Nb-Ta-Ti anomalies, and the radiogenic Nd isotope ratio (εNd = +3.4 to +3.7) suggests an OIB-like source. The LREE/HREE ratio (LaN/YbN = 7.43-8.76) is higher than in the tholeiitic samples, suggesting a possible role of residual garnet in the magma source, or a lower degree of partial melting, or both. The behaviour of mobile elements, such as the Sr isotopic composition (87Sr/86Sr = 0.706-0.707) and the K depletion, does not contradict this.

On the basis of trace elements and Sr-Nd isotopic composition, the Sicilian Triassic dykes could reflect the early stages of rifting in a continental setting, including initial lithospheric thinning, passive upwelling of hot asthenosphere, and related processes of partial melting involving differently enriched mantle reservoirs.
GARNET COMPOSITION IN RODINGITE OF FRIDO UNIT 
(SOUTHERN APENNINE, ITALY): EVIDENCES FOR METASOMATIC ALTERATION, PRELIMINARY DATA

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The Southern Apennines chain is a fold-and-thrust belt derived from the collision between the African and European plates starting in Upper Oligocene. The ophiolitic sequences occur in the Southern Apennine Chain as remnants of the Liguride accretionary wedge. The Liguride tectonic units derived from the western Tethys ocean which separated the European plate from the African one. The studied ophiolitic rocks emplaced in the Ligurian domain of the Alpine Tethys Ocean during the middle Jurassic. These units outcrop extensively in the southern Apennines in the northeastern slope of the Pollino Ridge. Liguride Units of the Southern Apennine include sequences characterized by HP/LT metamorphic overprint in the Frido Unit. They consist of sedimentary sequences ranging from the Upper Jurassic to the upper Oligocene ages and several bodies of oceanic and continental crust.

The ophiolitic rocks occurring in the Frido Unit consist of serpentinites derived from mantle lherzolite and subordinately harzburgites. Rodingites outcrop as dikes cutting through serpentinites and are a few centimeters thick, grayish-white and show a ductile deformation. Petrography and mineral chemistry of rodingites facilitated the finding of the igneous and metamorphic mineral assemblages related both to the primary magmatic protolith and to the subsequent metamorphic evolution. Rodingites show granoblastic texture. The primary igneous assemblage consists of plagioclase and clinopyroxene; these minerals cannot be preserved in rodingites due to a more accentuated rodingitic alteration. The metamorphic mineral assemblage consists of garnet, prehnite, chlorite, pumpellyite and quartz. Accessory minerals are titanite, epidote, opaque minerals, zircon and apatite. In order to obtain mineral chemistry electron microprobe analyses were performed on the garnet. Brown-yellow garnet crystals show a sub-idiomorphic and xenomorphic habit and/or replace plagioclase. Garnet crystals have coronas and rims of titanite and epidote crystals. Garnet overgrowing on plagioclase is mostly hydrogrossularite-grossularite rich and range between 79.107 and 95.071\textsuperscript{Mo}%, in the structural formula recalculated on the basis 22 oxygens; end member are Prp, Alm, Grs and Spss (pyrope, almandine, grossularite, and spessartine).

Ocean-floor metamorphism occurs with the metasomatic processes of rodingitization typical of dike-cut serpentinite. Rodingitization produces Ca-rich basic rocks during serpentinization. Rodingitization and metasomatic reactions in rodingitic dikes are demonstrated by the replacement of plagioclase by hydrogrossularite.
Mixed H₂O-CO₂ fluids, as H₂O-only fluids do, are thought to play an important role in magma genesis, triggering melting processes by lowering solidus temperature of mantle rocks (e.g., Dasgupta et al., 2007). Compared to H₂O-only and CO₂-only fluid compositions, experiments concerning high-pressure peridotite and mixed fluids are limited. In particular, experimental data on solidus relations of complex peridotite compositions are restricted to date to the two studies of Olafsson & Eggler (1983) and Wallace & Green (1988). However, these studies show many discrepancies, likely due to the different experimental strategies used.

We carried out experiments in the system KNCFMAS + COH at P = 1.8-2.8 GPa, T = 1050-1100°C, fO₂ = NNO, under fluid saturated conditions. A spinel lherzolite –30% olivine + 5% phlogopite (cf. Konzett & Ulmer, 1999) has been used as starting material to model a metasomatized lithospheric mantle. Seeded gels were loaded in a piston-cylinder apparatus using conventional double capsule technique. COH fluids have been generated by addition of 10 wt.% oxalic acid dihydrate and excess graphite. The near-solidus melt at low pressure is silicatic and potassic. At 1.8 GPa, 1075°C melt pools, coexisting with orthopyroxene + augitic clinopyroxene + olivine (Fo0.91) + garnet, are characterized on average by SiO₂ = 58.1 wt.% K₂O = 9.2 wt.% and Na₂O = 1.0 wt.%, being trachyandesitic (shoshonitic) in composition. Similar melts have been produced by Conceição & Green (2004) in CO₂-free, water-saturated K-bearing peridotite at similar P-T conditions (1 GPa, 1050°C). Mass-balance calculations suggest that the amount of partial melting in our experiments at these conditions is about 5.5 wt.%.

The near-solidus melts above 2.1 GPa is magnesio-carbonatitic and display quench-related textures, showing dendritic intergrowth of about 2/3 nearly stoichiometric dolomite and 1/3 K-silicate glass. The melt composition is comparable with published data concerning experimental carbonatites (e.g., Thibault et al., 1992). Carbonatitic melt is in equilibrium with restitic orthopyroxene + garnet + olivine/magnesite. Melting takes place at the expenses of Ca-minerals, in particular amphibole, dolomite and orthopyroxene. Mass-balance calculations suggest that the amount of partial melting is about 15.1 wt.% at 2.6 GPa and 1060°C. The residual water (2.62 wt.%) should dissolve into the melt up to water-saturated conditions, which are unknown at present in this P-T range. In conclusion, phlogopite lherzolite saturated with H₂O and CO₂ starts melting in a T range of 1050-1100°C at P between 1.8 and 2.8 GPa, with a minimum melting temperature located at about 2.3 GPa. The shape of solidus determined in this study is similar to that proposed by Green (1973) for H₂O-saturated peridotite, with a temperature shift of about +50°C due to the lower activity of water in CO₂-bearing systems. The solidus is consistent with Olafsson & Eggler (1983), especially for P > 2.3, while melting temperatures found by Wallace & Green (1988) are about 100°C lower.

The geotherm of lithosphere below a continental rift will intersect the determined solidus at about 2.1 GPa and 1050°C, suggesting that lithospheric mantle could start melting at approximately 60 km depth provided that COH fluids are available.
Sessione tematica H6:
Evoluzione sedimentaria, magmatica, metamorfica e geodinamica della catena Varisca Sud-Europea

Conveners:
Marcello Franceschelli (Università di Cagliari)*
Giacomo Oggiano (Università di Sassari)
UNRAVELLING A PERMIAN VOLCANIC SUCCESSION:
PALEOENVIRONMENTS AND TECTONICS IN
THE VALGANNA AREA (SOUTHERN ALPS)

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In the Southern Alps, at Permian times, post-Variscan extension is commonly associated with widespread plutonic and volcanic activities (Schaltegger & Brack, 2007; Cassinis et al., 2007) We addressed a poorly investigated succession outcropping in the western Southern Alps between Lugano and Maggiore lakes (Valganna area). The Permian volcanic to subvolcanic (Valganna granophyre) sequence is almost tectonically undisturbed. In the area 3 volcanic series (Schaltegger & Brack, 2007; Bakos et al., 1990; Riccardi, 1988) were investigated and our field and petrographic observations suggested different environments of subaqueous lacustrine and subaerial emplacement. Series I (basal series): this extrusive series, directly deposited upon a non-conformity surface over the Scisti dei Laghi basement (Boriani et al., 1990) consists of a few metres-thick volcaniclastic mass-flow followed by lithic-crystal and crystal tuffs interbedded with thin cinerite levels. The M. Piambello rhyolite lava flow ends this series. Series II: it starts with andesite to dacites agglomerates in turn covered by tuff and cinerite levels, the Alpe Tedesco rhyolite flow and a final ignimbrite (P. Ganna ignimbrite), whose geometrical relationships with the youngest Valganna granophyre are unclear. Series III: it starts with the M. Piambello dacite lava flow followed by lithic-crystal and crystal tuffs and a rhyolitic ignimbrite. The whole of volcanic products from the three series show high-K calc-alkaline affinity with similar PM- and REE-normalized patterns, which are characterized by LILE and LREE enrichment relative to HFSE and HREE, respectively. Whereas the andesite to dacite extrusive products show very similar geochemical behaviour, the most outstanding differences are among the acidic volcanic products. The rhyolite tuffs and ignimbrites, as well as the very homogeneous rhyolite lava flow of the Series II, mainly differ from those of the Series I and III in: 1) higher K₂O, Rb, Nb and Y and lower Na₂O, MgO, CaO, TiO₂, Sr and Zr contents; 2) more pronounced negative Ba, Nb, Sr, P, Zr and Ti and positive Th, K, Pb spikes in PM-normalized multielement diagram; 3) higher HREE, but similar LREE, contents that lead to a flatter REE pattern with a more pronounced Eu anomaly. In Valganna, the petrography of the volcanic complex reflects different environments of emplacement. The basal extrusive series (1800-2000 m-thick) was probably emplaced in a shallow lacustrine environment, whereas the Series II could reflect a subaerial apron. The Series III suggest a syntectonic emplacement along an active lineament at the boundary of the paleo-lake (Series I) and its shoulders (Series II). Petrographic and geochemical data reveal an igneous evolution by fractional crystallization within each series together with density selection during the emplacement. The enrichment in LILE and LREE observed from Series I to III could origin in the different abundance of the crustal component or in different source levels in magma genesis. Moreover, the association of high-K-calc-alkaline (Series I and III) with K-rich transitional Series II is consistent with a transtensional setting, probably driven by Permian strike-slip faults at regional scale, as already reported for the Collio and Orobie basins (Cassinis et al., 2007; Cassinis & Perotti, 2007). In progress SHRIMP U-Pb geochronological dating of the key-units will allow to make regional scale correlations with volcanic rocks of similar age and evolution (Schaltegger & Brack, 2007; Cassinis et al., 2007; Cortesogno et al., 1998).

THE TRANSITION FROM LOW-P TO CONTACT METAMORPHISM IN CALABRIA RELATED TO PLUTON GROWTH IN THE INTERMEDIATE CRUST

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Granitoids represent a large proportion of the Hercynian crustal sections exposed in Calabria. In the Sila and Serre massif the granitoid stack has a cumulative thickness of 9 to 13 km and includes tabular intrusions of tonalitic to granitic composition with minor dioritic and gabbroic bodies. Emplacement of the granitoids occurred sometime between 300 and 290±10 Ma during the extensional tectonic stage, following collapse of the Hercynian chain. The heat advected by granitoids was considered responsible both for contact metamorphism in the upper crust and regional low-P metamorphism in the lower to intermediate crust. This was shown by static and dynamical numerical models. A main limitation of the models was the instantaneous emplacement assumed for the magmas.

In the light of the general consensus existing on the idea that large magma chambers can be filled through dykes in a short time (< 100 kyr in Petford et al., 2000), the instantaneous emplacement was considered a permissible simplification. In recent years, the rapid growth of plutons has been questioned, on the basis of radiometric dating at different levels of the magmatic body (e.g., Glazner et al., 2004). Even though the melt flow entering in the magma chamber can be high, feeding may be discontinuous. Consequently, pluton accretion by repeated melt injections can be completed in some million years (Matzel et al., 2006). Another interesting point raised is the way the pluton grows (downward or upward) because this affects the intensity of thermal perturbation above and below the magmatic body (Annen, 2011). On the basis of these arguments we have formulated a new 2D thermal model, to be applied on the Calabria crustal sections, that takes into account the incremental growth of the pluton. We examined the consequences of the end-member processes of pluton accretion and of different growth rates. In case of under-accretion, contact metamorphism in the upper crust occurs before regional low-P metamorphism in the intermediate to lower crust. Model indicates that pluton growth must be completed in a short time (< 200 kyr) to reproduce observed peak temperatures (540-590°C) in the contact aureole. Deformation structures related to pluton growth, overprinted by peak T minerals, must be formed in an even shorter time interval. In case of over-accretion, an opposite sequence of low-P and contact metamorphism is produced and peak temperatures can be generated even when pluton construction lasts for 5 Myr. In comparing data of the Calabria crustal sections with results of under- and over-accretion models, the second option is preferred. Model results suggest also that the smooth transition from regional low-P to contact metamorphism may reflect upward pluton growth and concurrent exhumation by extensional tectonics.

A transpressive geodynamic setting has been recognized since a long time in the Variscan belt of Sardinia (Carosi & Oggiano, 2002; Carosi & Palmeri, 2002). Crustal scale shear zones and folds, with diffuse strain partitioning, have been well documented in the inner zone of the belt (Carosi et al., 2004; Iacopini et al., 2008; Carosi et al., 2009). Only recently a similar geodynamic setting has been proposed for some other branches of the European Variscan belt (Giacomini et al., 2008; Corsini & Rolland, 2009; Guillot & Ménot, 2009). The overall change of the shortening direction in a large sector of the orogenic belt with the occurrence of increasing orogen-parallel displacement, may be regarded as a general mechanism affecting the exhumation of rocks and preventing the overthickened and thermally softened collisional crust from undergoing a diffused gravitational collapse. Shear zones represent efficient ways to exhume deep-seated rocks in collisional orogens (Passchier & Coehlo, 2006), transpressional belts (Goscombe & Gray, 2009; Frassi et al., 2009) and extensional settings. As consequences, assessing the geometry and kinematics of mylonitic belts provide important informations to individuate the mechanisms of exhumation (Xypolias & Koukouvela, 2001; Law et al., 2004; Carosi et al., 2006, 2010; Larson et al., 2009) whereas the timing of shear activity is fundamental to constraint the tectono-metamorphic evolution of the exhumed rocks. Several systems of shear zones have been distinguished in the inner zones of the Variscan chain in Sardinia pointing out opposite sense of shear (Frassi et al., 2009). Structural relations point out that dextral shear zones deform sinistral ones. U-Th-Pb geochronology has been applied on zircons and monazites sampled from both systems of shear zones. The new isotopic data led to constrain at ~ 320 Ma the activity of both systems so that a switch from the sinistral simple-shear- to the dextral pure-shear-dominated regime has to be invoked. The dextral shear belt remained active at upper structural levels before the emplacement of the larger part of the late Variscan batholith.
THERMAL MODELING OF THE SARDINIA VARISCIDES

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This note focuses on the thermal evolution of the Sardinian Variscan crust during the post-collisional stage. One-dimensional thermal modeling has been performed by a Matlab-derived code (geothermMOD1.2), which allows us to simulate the past crustal geotherms for a given model crust with variable distribution of heat-producing elements such as ²³⁸U, ²³²Th and ⁴⁰K. Heat flow is assumed to be controlled only by conduction, hence geotherms have been calculated by solving the second-order partial differential equation \( \frac{d^2T}{dz^2} = -A/z \) (1), where the term \( A \) represents the heat-production rate [W/m³], \( z \) is depth [m] and \( T \) is temperature. The term \( A \) is calculated from the content, within each layers, of ²³⁸U, ²³²Th and ⁴⁰K at the relevant model times.

The past vertical distribution of these elements is inferred from a data sets including about 400 samples acquired directly in the field with a portable NaI(Tl) gamma-ray spectrometer, and about 100 samples measured in laboratory with a HPGe spectrometer. In a first step, the heat-production rate of each layer is calculated at the model age by back-correcting for the radioactive decay.

The corrected \( A \) values and two boundary conditions \( T_0 = \) surface temperature [°C], and \( Q_b = \) basal heat flow [W/m²], were finally used to solve numerically the eq. (1). The evolution of the Variscan crust of north Sardinia has been modeled by two sets of numerical experiments covering the time span 350-280 Ma. In the first group of experiments, which address a fully crustal evolution, \( Q_b \) is assumed to be constant throughout time within each experiment. The value of \( Q_b \) increases linearly with time in the second set of experiments, to simulate an increasing heat flow contribution from the mantle. In all experiments, crustal sections are designed at 320, 310, 300 and 285 Ma with specified thickness, whereas the geometry is based on present-day seismic profile, and Al-in hornblende barometry of dated granitic plutons. The validity of the two models, i.e. the ‘fully crustal’ and the ‘mantle contribution’ ones, is checked out by comparing the experimental geotherms with the available petrological data sets.
The Late Palaeozoic South-Alpine successions can be subdivided into two main and well differentiated tectono-sedimentary Cycles, which are separated by a regional unconformity sealing a gap of as-yet imprecise duration (10 to 20 Ma). In the Southern Alps, which represent the main reference sector of this review and, more generally, in the selected south European or western Mediterranean areas, these cycles mirror two very different “worlds” in terms of tectonics and sedimentation. The Lower Cycle, up to a maximum thickness of more than 2000 m, consists of calc-alkaline, acidic-to-intermediate igneous products and alluvial-to-lacustrine sediments, both infilling fault-bounded intracontinental basins, generally interpreted as strike-slip or pull-apart basins affected by a transcurrent regime. Based on palaeontological evidence (macro-microfloras and tetrapod footprints) and isotopic ages, this Cycle ranges from the Carboniferous (Moscovian) to Early Permian (Kungurian). The Upper Cycle, which is devoid of volcanics, is wider but less thick than the Lower Cycle and dominated by an extensional regime linked to the Variscan crustal thinning. It mainly includes the Mid?-Late Permian Verrucano Lombardo/Val Gardena Sandstone fluvial red clastics (up to about 800 m thick), in part laterally and upwardly replaced, east of Val d’Adige, by gypsum-bearing sabkha sequences and the shallow-marine carbonate of the Bellerophon Formation. According to many authors, this Cycle is regarded as the beginning of the “Alpine Cycle”.

The comparison with some continental successions in southern Europe allows to reconstruct their evolution and set up correlations. A marked stratigraphic gap shows everywhere between the aforementioned Cycles. As in the Southern Alps, it began during the Middle Permian, near the Illawarra Reversal geomagnetic event (~ 265 Ma). In western Europe, however, as in Provence and Sardinia, this gap persists upwardly to Late Permian and Early Triassic or slightly younger times, even though in northeastern Spain (Iberian Ranges, Balearic Islands) it is generally interrupted by late Guadalupian to Lopingian deposits. The major regional angular unconformity between the two Permian cycles was probably caused at least in part by a deformation pulse, which induced faulting, gentle folding, uplift and erosion or non-deposition. This tectonic event, connected to the transformation from a strike-slip to an extensional tectonic regime, and to a change of the relative plate directions, can be related to the so-called “Mid-Permian Episode”.

Therefore, in this geological context, the above Cycles reflect two main geodynamic events, which are respectively characterised by the Late Carboniferous-Early Permian transformation of the Gondwana-Eurasia collisional margin into a diffuse dextral transform margin and the Middle-Late Permian opening of Neotethys, with the onset of a generalised extensional tectonic regime and a progressive westward marine ingressio. In our reconstruction this dextral megashear between Gondwana and Laurasia should be due to the onset of the subduction of the Palaeotethys active oceanic ridge. The dextral shear would be induced and supplied by the nature of the triple junction itself, and is compatible also with the classical Pangaea A configuration.
PETROPHYSICAL PROPERTIES OF VARISCAN MYLONITIC LEUCOGRAINTE
OF MONTE GRIGHINE, WEST-CENTRAL SARDINIA

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Monte Grighini Complex consists of a pile of variscan Nappes and of a suite of granitoid rocks, mostly monzogranite and leucogranite (Musumeci, 1992), that intrudes the tectonic unit of Monte Grighini. Rb/Sr and Ar/Ar radiometric data give, for granitoid rocks, an age of about 305-300 Ma (Carmignani et al., 1987; Laurenzi et al., 1991).

A late variscan shear zone affects the SW side of the complex and produces a wide cataclastic and mylonitic zone, along which leucogranite can be mostly found. In this zone an outcrop, that shows a rapid change in the intensity of mylonitic deformation, has been investigated in detail. The outcrop is affected by a pervasive N162-170° foliation dipping 60-65° W. Petrographic and XRD analysis show the following mineralogical assemblage: quartz, k-felspar, plagioclase (albite), muscovite, biotite, iron oxides and ± tourmaline ± apatite ± zircon ± epidote. Almost all samples are characterized by k-feldspar porphyroclasts in a quartz-phyllosilicate matrix.

On the basis of porphyroclast/matrix ratio protomylonite, mylonite and ultramylonite layers have been identified. In protomylonitic layers k-felspar phenocrysts are fractured and sometimes perthitic. Quartz occurs in microcrystalline lens and bands following the foliation. Phyllosilicate matrix consists of biotite, subordinate muscovite and chlorite. Mylonitic layers are similar to the previous ones but show a decrease in grain-size. Ultramylonitic layer consists of rare k-feldspar relics in a very fine-grained phyllosilicate matrix.

The following physical properties have been determined in 12 series of samples with varying degree of deformation: the open porosity, the total porosity, the real and apparent density, the water imbibition coefficient, and the water saturation index. To calculate the closed and total porosity the real density of ground samples were determined.

The ultrasonic velocity of the studied samples has been determined in three directions: 1) perpendicular to the foliation, 2) parallel to the foliation and to the direction of mineral stretching lineation, 3) parallel to the foliation and perpendicular to the direction of mineral stretching lineation. The overall results indicate that the samples of protomylonite, mylonite and ultramylonite have different physical properties values. The average values of the real density of samples vary from a minimum of 2.66±0.02 g/cm³ in the protomylonitic samples, to a maximum of 2.72±0.01 g/cm³, in the ultramylonitic samples. The mylonitic samples show intermediate values with an average of 2.68±0.01 g/cm³. The open porosity shows a similar trend; it ranges from 4.1±0.2% in the protomylonitic samples, to 6.3±0.9% in the mylonitic samples, to 9.2±0.5% in the ultramylonitic samples. Therefore, there is a positive correlation between the degree of mylonitization and these physical parameters. The ultrasonic velocity values show on one side of the greater porosity of ultramylonites than proto-mylonites and mylonites, on the other side confirm a higher anisotropy degree in the ultramylonitic samples releaved perpendicular to the foliation. Preliminary results seem to suggest a relationship between the petrographic and petrophysical characteristics of the layers.

NEW DATA ON THE GEOLOGICAL HISTORY OF THE ARGENTERA MASSIF AND COMPARISON WITH THE MONT BLANC-AIGUILLES ROUGES AND MAURES-TANNERON MASSIFS

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The “External Crystalline Massifs” of the Western Alps (Aiguilles Rouges, Mont Blanc, Grandes Rousses, Belledonne, Pelvoux, and Argentera) consist of a polymetamorphic Variscan basement, which was only marginally reworked during the Alpine tectonometamorphic cycle. This contribution focuses on the magmatic and Variscan metamorphic history of the Argentera Massif, the southernmost and largest of the External Crystalline Massifs exposed in Italy. Its evolution is compared to that recorded in the Mont Blanc-Aiguilles Rouges Massif, the other External Crystalline Massif extensively exposed in the Italian Alps, and to that recorded in the Maures-Tanneron Massif of Provence, France, the area of Variscan Europe nearest to Argentera.

Some speculations on tectonic models for this evolution are also proposed. The main geological events recorded by these Massifs are similar. They experienced: a) pre-Carboniferous intrusions of both acid and basic magmas; b) a Carboniferous Variscan history consisting of subduction with metamorphic peak at ca. 700°C and 1.5 GPa, continental collision developing amphibolite-facies metamorphism, anatexis, and emplacement of granitoids; 3) Carboniferous exhumation to shallow crustal levels. A few of the events well documented in the Mont Blanc-Aiguilles Rouges and Maures-Tanneron have not yet been characterized in the Argentera Massif. In particular, the Late Proterozoic emplacement of granitoids in a (meta-) sedimentary sequence documented in the Maures and the Late Ordovician granite plutonism documented in the Mont Blanc Massif, still await to be confirmed in the Argentera by geochronological data, though field observations generally support the occurrence of these magmatic events. On the other hand, the age of the high pressure (HP) metamorphic event documented by eclogites and HP granulites found in all the massifs is well constrained so far only in the Gesso-Stura-Vésubie (GSV) Terrane of the Argentera Massif, where Carboniferous ages at ca. 340 Ma were obtained for zircons in the Frisson HP granulites. The LP metamorphism and partial melting in the GSV Terrane are not directly dated, but a Late- to Mid-Carboniferous age for migmatization has been proposed on the basis of a zircon lower intercept age obtained from the Meris eclogite.

These geochronological data link together in a single orogenic cycle the HP and the amphibolite-facies metamorphisms, and suggest that the evolution of the Variscan belt of the Western Alps and Provence may resemble that of present-day collisional settings, such as the Himalayan belt. Similarities between the Variscan and the Himalayan orogenies include the conditions of HP granulite-facies metamorphism, and the rapid (within 20 Ma) succession of HP peak metamorphism, fast exhumation and widespread late anatexis.
An interesting metre-sized metavolcano-sedimentary sequence was discovered a few km south of the Lula village during a geo-petrographical survey within the Variscan chain in NE Sardinia. A detailed petrographic and geochemical study of the collected samples allowed eight different layers from bottom (Layer A) to top (Layer H) in that sequence to be distinguished. Layer A, a few decimetres thick, is rich in 4-5 mm-long albite crystals, showing submillimetric muscovite inclusions and ubiquitous epidote overgrowths, locally concentrated in the crystal cores. A submillimetric matrix made up of quartz, albite to oligoclase grains, chlorite, muscovite, epidote and minor chloritized biotite surrounds the albite phenocrysts. The main foliation is defined by muscovite, chlorite and minor Fe-oxides. Epidote occurs as anhedral 0.2-0.3 mm-sized zoned crystals when scattered in the matrix, and as patches with patchy zoning when replacing albite. Rounded apatite grains also occur. Layer B, 5-8 cm-thick, albite-rich, light-coloured, consists of an aggregate of several micrometric (< 50 microns in size) albite grains enveloping 2-3 mm-sized albite crystals. The foliation is defined in the matrix by biotite-chlorite-Fe-oxide trails. Quartz occurs as submillimetric-thick veins or as clusters of anhedral grains. Apatite and monazite also occur. Layer C, 10 cm-thick, similar to layer A as regards microstructural features, differs from it for higher phyllosilicate content, widespread occurrence of late-crosscutting muscovite, more pronounced foliation, more evident microfolds and quartz-filled veins. Layer D, 20 cm-thick, light-coloured and poorly foliated, shows up to 1.5-2.0 mm-sized albite crystals surrounded by a quartz-albite matrix, with a grain-size < 70-100 microns and albite/quartz ratio ~ 1, including poorly oriented scattered muscovites, clusters of chloritized biotites, apatite and Fe-oxides. Layer E: thin, cm-thick dark metapelitic bed. Layer F, 40 cm-thick, shows almost the same microstructural features exhibited by Layer A. Layer G, 15 cm-thick, medium/coarse grained, contains 5×2 mm-sized albite crystals embedded in a quartz-albite-chlorite-biotite foliated matrix. Unlike layer A, muscovite is rare; neither epidote growth, nor inclusions in albite were observed. Layer H, 40-45 cm-thick, is characterized by up to 0.7-0.8 cm-sized albite porphyroblasts with several inclusions of titanite, epidote, chlorite and apatite. The quartz-albite matrix is striated by elongated muscovite-chlorite-chloritized biotite S2-oriented trails. A relict foliation is revealed by preserved microlithons.

The Lula layers, compared with the Lower Paleozoic paragneisses and Ordovician metavolcanites from Sardinia reveal: 1) a strong enrichment in Na2O and depletion in CaO, K2O, Rb, Ba, that could suggest an albization process of the whole sequence and in particular of the Layer B, whose composition is almost pure albite; 2) major and trace element contents similar to those of the Sarcidano metavolcanites, the nearest ones, and significant differences with the farther Sarrabus-Gerrei metavolcanites; 3) some low SiO2, high Al2O3 and V contents suggesting a possible contribution of a clay component to a probable altered volcanic or volcanoclastic protolith; 4) high contents of FeOtot, MgO, Cr, Co, Ni indicating a significant mafic component in the protolith; 5) a significant depletion in P2O5, LREE, HREE, Th, U that could be explained in two ways: a) they are original features of the igneous protolith; b) they are the product of alteration or sedimentary reworking processes of an igneous protolith. Further research is needed to clarify which is the correct hypothesis.
P-T EVOLUTION OF THE METABASITE WITH ECLOGITE-FACIES RELICS FROM PUNTA DE LI TULCHI (NE SARDINIA, ITALY) AS REVEALED BY THE PETROLOGICAL APPROACH OF PSEUDOSECTIONS

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The Punta de li Tulchi metabasite crops out as a N80/60-oriented decametric lens, hosted in the migmatites of the High Grade Metamorphic Complex in NE Sardinia. The metabasite consists of brownish clinopyroxene + garnet (Cpx+Grt) layers alternated to greenish amphibole + plagioclase (Amp+Pl) layers from a few centimeters up to 50 cm in thickness (Franceschelli et al., 1998). The Cpx+Grt layers mainly consist of millimetric garnet (with inclusions of omphacite) embedded within a fine-grained clinopyroxene + plagioclase symplectite matrix. Orthopyroxene also occurs in these layers, as well as minor amphibole and quartz. Garnet in contact with symplectite is rimmed by amphibole + plagioclase coronas. The Amp+Pl layers consist of millimetric to submillimetric-sized white pods of plagioclase + amphibole + garnet relics set in a amphibole-rich matrix. Less abundant minerals in these layers are quartz, titanite, ilmenite, rare biotite, and chlorite.

Four main metamorphic stages have been recognized basing on microstructural features: (i) a M1 pre-symplectite stage, (ii) a M2 symplectite stage, (iii) a M3 coronitic stage, and (iv) a M4 late retrograde stage. The pre-symplectite (M1) and symplectite (M2) stages have been modeled using the P-T pseudosection approach in the NCKFMASH model system (calculated in the range 550-950°C and 1-25 kbar, at aH2O = 0.5), and using the bulk rock composition of a representative Cpx+Grt layer. Garnet core composition and Na content in omphacite allow to define a M1c stage at T = 610-640°C and P up to 17 kbar corresponding to the field Cpx+Amp+Grt+Rt+Bt+Qtz.

Garnet compositional zoning indicates a progressive increase in both temperature and pressure during garnet growth from the M1c stage up to a M1r stage (T = 620-660°C; P = 19-22 kbar), allowing to reconstruct a prograde segment of the P-T path. The peak pressure was reached in the M1r stage under amphibole-eclogite-facies P-T conditions. As revealed by the composition of the symplectitic minerals, the M1r stage was followed by heating and decompression, resulting in the formation of clinopyroxene + plagioclase symplectite (M2 stage) at T = 750-800°C and P = 9-12 kbar (granulite-facies conditions). The coronitic stage (M3) has been modelled in the NCFMASH model system at aH2O = 1.0 by using the bulk composition of the effectively reacting microdomain, calculated from mineral compositions and stoichiometric coefficients of the corona-forming reaction.

By comparing the measured composition of coronitic minerals with the modeled compositional isopleths, amphibolite-facies P-T conditions (T = 580-640°C, P = 5-7 kbar) have been obtained for this stage. The P-T conditions of the M4 stage can be estimated at about 300-400°C and < 2-3 kbar. The P-T path reconstructed for the Punta de li Tulchi metabasite has significant analogies with that described by Giacomini et al. (2005) for the retrogressed eclogite of Golfo Aranci, NE Sardinia, and with that of the Punta Orvili metabasite from the Metamorphic Complex with Mainly Amphibolite Facies Assemblages described by Cruciani et al. (2011).

Cruciani, G. et al. (2011): Lithos, 121, 135-150.
Recent studies define that the Variscan orogeny should be considered as the result of accretion of peri-Gondwanian terranes rather than a continent-continent collisional belt. The origin of the peri-Gondwanian terranes is linked to a continue evolution and fragmentation of the northern Gondwana margin which started, at least, since the Cambrian with the opening of the Rheic Ocean and the separation of Avalonia. From Devonian times, the northern Gondwana margin has been furtherly affected by separation of continental masses, due to the opening of the Paleotethys, with the formation of a narrow terrane known as Hun superterrane or Galatian ribbon continent.

The closure of the Paleotethys, due to the northward motion of Gondwana, started at ~ 330 Ma and led to the final collision and continental amalgamation between Gondwana, Gondwana derived continents (e.g., Avalonia and Armorica) and Laurussia, with the formation of Pangea, at ~ 300 Ma. In this geodynamic context, the high-grade metamorphic rocks outcropping in the Variscan segment of NE Sardinia experienced an oblique collision under a transpressive tectonic regime during the Early Visean (ca. 340 Ma)-Bashkirian (ca. 320 Ma). Field evidences and finite strain analyses carried out on the HT rocks of NE Sardinia, define that the exhumation of these rocks could have been driven by telescoping processes along a regional “snake” strike-slip shear zone.

Such a shear zone could have induced shear heating processes which led to crustal melting in the order of 3-5%. The restored direction of this shear zone allow us to identify it with the East Variscan Shear Zone (EVSZ). The EVSZ is a NNW-SSE dextral transpressive regional shear zone running from Brunia to the Calabria-Peloritani arc affecting the scattered Variscan Massifs of the Alps as well as the Maures-Tanneron massif, the Corsica-Sardinia massifs and the basement of Northern Apennines. In more recent times, the EVSZ could have represented a pre-existing intra-continental band of weakness on which the following tectonic processes will develop: the Permian-Triassic rifting, the Alpine cycle, the Apenninic cycle and the Miocene-Pliocene opening of the Tyrrenian Sea.
**QUO VADIS, NORTH GONDWANA? EVIDENCE FROM INTEGRATED STUDIES OF LOWER PALEOZOIC SEQUENCES OF THE CARNIC ALPS (AUSTRIA)**

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Significant advances in reconstruction of the geodynamic processes that controlled the dispersal of the North Gondwana margin between Early Ordovician and Carboniferous times are now emerging. Diverse lines of investigation within this regional and temporal context are being applied to the Paleozoic sequences of the Carnic Alps (Austria), in particular to the critical Late Ordovician-early Silurian interval.

Acquisition of paleontological and paleoenvironmental data by study of pelagic faunal exchange, microfacies and climate sensitive sediments of this pivotal middle paleolatitude temperate sector of the Southern Variscan Realm has highlighted critical new evidence based on this non-geochemical method of dating paleocontinent position and opening/closure of seaways.

Faunas suggest plate movement from a moderately cold environment of ca. 50°S latitude (Late Ordovician) to a reef belt of ca. 30°S (Devonian). Eustatic changes are correlated across four paleocontinents (Brett et al., 2009). Sedimentological evidence records the Hirnantian glaciation cold water influx as diamictites within the successions at the Nöblinggraben and Rauchkofel South sections, now precisely constrained biostratigraphically, thus adding further data for timing this event along the North Gondwana Margin. This level is characterized by pyrite and phyllosilicate, (mainly chlorite) -rich arenites and rudites.

The coarser detrital fraction includes subrounded mm to cm sized crystalline clasts, interpreted as dropstones. Their composition of finely banded gneisses characterized by ribbon quartz layers and quartzites, suggests erosion and reworking from a polymetamorphic area. The sulfide rich matrix suggests a cold reducing environment. Mineralogical and petrologic analyses are ongoing. Further evidence for the Hirnantian Stage is based on the recent identification of the 13C Excursion (HICE) in the Cellon Section (Histon et al., 2007). Documentation of igneous activity within this sector of the Southern Alps provides a valuable database for unravelling the related geodynamic history, in particular for the Late Ordovician-early Silurian interval. 97 K-bentonites have been recorded from the Upper Ordovician (Hirnantian) to Lower Devonian (Lochkov) sequences, constrained biostratigraphically within the international standard biozones (Schönlaub et al., 2011).

Volcanism belongs to a tectonically active terrane dominated by calc-alkaline mafic lavas of clear volcanic arc affinities, most samples fall within the andesite and rhyodacite/dacite fields. Upper Ordovician K-bentonites are rare and have few European equivalents. Abundant Llandovery - middle Ludlow levels similar to those in the British Isles, Sweden, Canada and North America may document widespread volcanism related to the closing of the Iapetus Ocean, however, a local origin within northward drifting microplates derived from the Northern margin of Gondwana is considered more likely. Pridolian K-bentonites compare with those from Podolia with a source area in the Rheic Ocean. Characterization by petrography, isotope geochemistry and U/Pb radiometric dating on zircon of these ash levels will yield reliable geotectonic and paleogeographic inferences and internationally important time-lines for chronostratigraphy within both a regional and global context.

TIMING OF HIGH-GRADE SOUTH EUROPEAN VARISCAN EVOLUTION: CONSTRAINTS FROM TRACE ELEMENT PARTITIONING IN GARNET, ZIRCON AND ORTHOPYROXENE ON U-Pb ZIRCON AGES.

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U-Pb zircon ages and chemistries of zircon, garnet and orthopyroxene from different structural sites of a thin section of a granulitic rock from the Serre (Calabria, southern Italy) have been considered in order to reconstruct the evolution of a fragment of south European Variscides. The rock consists of Pl+Grt+Bt+Opx+Qtz+K-feld and accessories as zircon, apatite and opaques. The matrix shows layers containing different abundances of biotite and orthopyroxene. One porphyroblastic garnet (~ 3 cm in diameter) rimmed by a Opx+Pl+Bt+opaques+Zrn+Ap symplectitic corona occurs.

Ten zircon grains are exposed in the thin section: eight in the Bt-rich matrix, one within the corona and one in the rim of the garnet. Zircon shows generally core-rim structures. Frequently, zircon cores appear chaotic, consistently with modification induced by high-grade metamorphism and some are rimmed by unstructurless lobate rims, invading cores, commonly related to interaction with fluids and/or melts. U-Pb analyses have been performed in situ by LA-ICP-MS (IGG-CNR, Pavia). Two core domains of zircons from the matrix give the oldest concordant ages: 357±11 and 334±12Ma; five concordant data ranging from 324±12 to 320±11Ma give a mean concordia age of 323±2Ma. Two younger concordant ages (305±9 and 300±9Ma) are relative to low luminescent inner rims and similar apparent ages have been determined on luminescent zircon rims from matrix, symplectitic corona and garnet rim.

Trace element compositions were collected on specific domains of zircon, garnet and orthopyroxene in different textural sites by LA-ICP-MS. Two trace element profiles relative to porphyroblastic garnet were performed. Garnet is very rich in middle-REE and shows nearly flat profile in the core and fractionated pattern in the rim. The transition zone from core to rim (outer core) is poorer in HREE. Zircon is characterized by a steep pattern with low LREE and high HREE contents both in cores and rims in which, however, the MREE and HREE are lower than in garnet, apart from its outer core region.

The orthopyroxenes show fractionated patterns of MREE and HREE. The apparent DHREE between zircon-garnet and orthopyroxene-garnet pairs have been calculated and compared with literature data considered as suggestive of equilibrium relatively to natural samples and experimental results. The calculated DREEzrn/grt and DREEopx/grt define linear and positive trends for zrn or opx/core and outer core combinations of grt evidencing regular, but variable partitioning and reaching even values higher than unity. So the calculated DREE values seem to be indicative of steps of approaching equilibrium. The combination zrn rim/grt rim, instead, indicates disequilibrium suggesting that the zircon rim formed earlier than garnet rim, which subsequently broke down producing corona. The combination with the outer core of garnet gives higher D than the combination with the inner core suggesting, according to experimental results, lower temperature for the former; this is in agreement with the petrology. The calculated DREEopx/grt approach those suggestive of equilibrium from Er to Lu in the combination opx matrix-grt core. The combination opx corona-grt rim is far from the equilibrium. Probably, orthopyroxene from corona is a residue of the matrix. Accordingly, a well constrained contribution to PTt path relatively to fragments of south European Variscides emerges: the Variscan metamorphism of the lower part of the Serre crust section peaked much earlier than previously assumed (at least ~ 340 Ma ago against 300 Ma) and the multistage Variscan decompression after the metamorphic peak lasted tens millions of years, at least locally. The decompression probably protracted after 300 Ma.
In northern Sardinia, the inner zone of the Southern Variscan belt includes a Medium Grade Metamorphic and a High Grade Metamorphic, mainly migmatitic, Complex, originated in igneous and sedimentary protoliths. The igneous ones were recently recognized of Ordovician ages (Cortesogno et al., 2004; Palmeri et al., 2004; Giacomini et al., 2006, Oggiano et al., 2010). A kilometre-thick mylonitic mélange zone (Posada Asinara line) exhibits ductile deformation and occurs between the HGMC and the other medium to low grade Variscan Nappes (Casini et al., 2010).

Also in the Asinara Island (Oggiano & Di Pisa, 1992), juxtaposed tectono-metamorphic units exhibit an intermediate to high grade granulitic crustal section. In particular, at Punta Scorno, a millimetre to decimetre layered leptino-amphibolic complex (Ca-amphibole+plagioclase+garnet) occurs characterized by cm to meters thick leucocratic (quartz+plagioclase+garnet) layers including sparse amphibole-dominated ultrabasic and metagabbroic boudins with relic coarse-grained hypidiomorphic textures. The peak metamorphic conditions for this association were estimated under granulite (740°C and P > 0.8 GPa) followed by amphibolite facies (500-600°C and P 0.3-0.4 GPa; Di Pisa et al., 1993). The metaigneous bimodal complex is associated with a K-feldspar-phyric orthogneiss presently re-quilibrated under HT/LP high grade metamorphic conditions evidenced by staurolite surrounded by biotite + andalusite coronitic intergrowths and sillimanite + cordierite ± K-feldspar; the tectonic contact between the two lithologies is parallel to their main schistosity. The leucocratic layers of the basic complex and the associated orthogneiss were selected for U-Pb radiometric dating on zircons separates by ELA ICP MS at CNR - IGG Pavia. The preliminary elaboration highlights several populations of U-Pb Concordia ages: in the orthogneiss, an early Paleoproterozoic event at 2006±25 Ma and a second Neoproterozoic between 623±13 and 579±12 Ma. A subsequent Cambro-Ordovician age interval is recorded between 478±11 and 437±11 Ma, followed by a Devonian event 413±11 and 403±7.4 Ma. In the “leptino-amphibolic” complex with granulite relics, each leucocratic layers yielded different ranges of Concordia ages, starting from a Neoproterozoic time interval (stepped between 672±12 and 588±16 Ma) until a Cambrian system closure (514±22 to 506±15 Ma). An Early Ordovician group of Concordia ages spans between 491±13 and 474±12 Ma. Late Ordovician - Early Silurian ages fall in the 461±10 to 435±12 Ma time interval. Some Devonian and Carboniferous age values are also recorded mainly from homogeneous metamorphic cores. Some considerations thus derive: i) the orthogneiss contains evidence of an ancient basement, older than Neoproterozoic which was previously excluded in the north Gonwana margin (von Raumer et al., 2002), in fact the presence of ca. 2 Ga old inherited Pb component in zircon suggests this crustal residence age of the inferred metasedimentary protolith i) the U-Pb system of the orthogneiss opened diachronous with respect to the basic complex iii) within the leptino-amphibolic complex, different age population arise from different felsic layers, likely pointing out that each of them recorded a different timing of events or that they have different protolith ages. This could occur for instance by several steps of partial melting that caused multiple injections of felsic magmas within a deep crust; iv) the orthogneiss and the amphibolite shared a common evolution since the Devonian.

Cortesogno, L. et al. (2004): Ofioliti, 29, 125-144.
ANALOGUE MODELS VS. GEOLOGICAL STRUCTURES:
THE STUDY CASE OF NE SARDINIA (ITALY)

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Recent studies defined that the emplacement of the Variscan HT metamorphic rocks outcropping in NE Sardinia occurred in a transpressional tectonic regime, induced by the oblique collision of Gondwana derived terranes with Laurussia during the Middle-Upper Carboniferous. The possibility to exhume deep crustal rocks by compressional/transpressional kinematics has been tested through an experimental approach based on the production of several analogue models. They consist of three layers, put one on the top of each other: the bottom and the middle layers are made of plasticines with a power-law rheology simulating the behaviour of lower and middle crust; the uppermost layer consists of sand, in order to simulate the brittle behaviour typical of the upper crust. The models have been thus deformed by a thermomechanical apparatus, located at the “Institut für Geowissenschaften Johann Wolfgang Goethe-Universität, Frankfurt am Main”, that induced compression coeval to orthogonal extension, following different finite strain percentages. The temperature and the strain rate conditions have been set in order to generate a viscosity contrast between bottom and middle layers of 2/3 orders of magnitude, reproducing thus the real viscosity contrast deduced for the lower and middle continental crust.

The experiments performed at 20% and 30% of finite strain show processes of cylindrical folding, while at higher finite strain conditions (40% and 50%) the processes of uplift of the lower crust become dominant. In fact, from the observation of cross sections perpendicular to the direction of extension, it is possible to notice that the uplift of the lower crust starts at 40% of finite strain and becomes even more evident at higher strain conditions (50%). The uplift is facilitated by the development of brittle/ductile shear zones which attract the deepest material to shallower levels, (i.e. processes of telescoping), leading in some cases to the formation of laccolith-like structures. The observation of sections parallel to the direction of extension, at the same finite strain conditions, highlights a dome-type geometry, where the long axis of the dome is parallel to the main direction of extension of the system.

The top view of the models shows that the fractures responsible for the telescoping processes described above, are characterized by lateral displacements and reproduce en-echelon structures.

Being aware that the analogue models represent an oversimplified representation of natural cases, it is nevertheless possible to outline some correlations between experimental structures and geological observations:
1) The dome-type geometry obtained with the experimental approach has been already proposed in literature, on the basis of geological-structural data, for the High Grade Metamorphic Complex (HGMC) of Sardinia; 2) The Variscan granite bodies of southern Corsica and NE Sardinia are bounded by sets of shear zones which often show lateral displacements and resemble en-echelon structures; 3) Several geological cross sections of the HGMC show that the contacts between high-grade and middle/low-grade Variscan units are often overturned. The same geometries are observable in numerous cross sections of the analogue models, where the lower crust overrides the middle one during its uplift driven by the development of shear zones; 4) The laccolithic bodies observed in the models are directly observable in the HGMC of Sardinia (i.e. Capo Ferro area), where Variscan syn-tectonic granitoids are emplaced within regional shear zones. The results obtained by the analogue models, compared with the natural geological structures, confirm and strengthen the hypothesis that the HT Variscan rocks of NE Sardinia could have been exhumed by the action of regional shear zones, which developed under a main transpressional tectonic regime.
MELT PRESENT DEFORMATION OF THE
MAFIC LOWER CRUST EXPOSED IN CALABRIA

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In the Serre Massif of Calabria an about 8 km thick sequence of granulite facies rocks constitutes the lower crust of the former Variscan orogen. The base of this lower crustal section is made up of layered garnet-bearing meta-gabbros which are interspersed with lenses of metaperidotites and layers of metapyroxenites and meta-hornblendites (Moresi et al., 1978; Schenk, 1984). Single zircon conventional and spot U-Pb isotopic analyses place the age of the gabbroic protoliths into the Precambrian (Schenk, 1984, 1990; Micheletti et al., 2008).

The main metamorphic overprint under granulite facies conditions of the gabbros has occurred during the Variscan orogeny. Zircon dating constrained the metamorphic peak close to 300 Ma in coincidence with the emplacement of huge masses of granitoid magmas in the middle crust (Schenk, 1984; Caggianelli et al., 2000; Micheletti et al., 2008). Reaction microstructures have induced Schenk (1984) to infer that the lower crust of the Variscan orogen in Calabria was subjected to isothermal decompression immediately after the thermal maximum. He has deduced that the lower crust became decompressed from about 750 to 550 MPa at 800°C and then affected by slow isobaric cooling down to 200°C over the next 250 million years. Acquafredda et al. (2008) have shown that decompression occurred during two different stages and involved a much thicker continental crust than previously assumed. Internally consistent thermodynamic modelling of the pre-decompression mineral assemblage results in 900°C and 1.1 GPa for the metamorphic peak conditions.

We can now show that metagabbros became deformed under melt present conditions. This is evidenced by the occurrence of cm-thin shear zones wherein the partial melt was drained. Shear-zone development occurred in a general deformation regime, with shortening partitioned next to the shear zone resulting in an intense crenulation of the earlier Variscan foliation. Ti-rich pargasitic amphibole layers were involved in this crenulation deformation and recrystallized. Recrystallized amphiboles have the same chemical composition as those tracing the older layering.

Application of the semiquantitative “Ti-in-amphibole” geothermometer of Ernst & Liu (1998) to the recrystallised pargasites results in a deformation temperature of 870°C, whereas application of amphibole-plagioclase thermometry (Holland & Blundy, 1994) results in temperatures of 818 to 857°C (in the pressure range 0.5 to 1 GPa). Minimum pressure conditions of 500 MPa can be assessed using the semiquantitative Al-in-amphibole geobarometer of Ernst & Liu (1998). However, application of the crystal structure modelling geobarometer of Nimis & Ulmer (1998) to clinopyroxene in equilibrium with the plagioclase-rich melt of the shear zones shows that pressures during deformation have been rather close to 1 GPa.

Melt present deformation of the mafic complex was followed by cooling starting from temperature conditions closely identical to that registered by the recrystallized amphiboles. Reaction seams of quartz+phlogopite around Opx suggest that a dehydration reaction of the type phlogopite (Phl) + quartz (Qtz) = orthopyroxene (Opx) + melt has been crossed backwards during cooling. Peterson & Newton (1989) place this reaction above 800°C.

The recognition that plagioclase/Cpx melt-bearing shear zones developed at about 1 GPa pressure and 870°C temperature suggests that incipient melting of the mafic complex of the lower crust may have triggered the extensional tectonics in Calabria.
Sessione tematica I2:
Il contributo della microanalisi nello studio dei sistemi vulcanici

Conveners:
Massimo Pompilio (INGV)
Marco Viccaro (Università di Catania)*
Trace elements distribution in volcanic minerals is influenced by a number of factors including, beside the composition of the magma, also its temperature, pressure, oxygen fugacity and volatile contents. Comparing the trace elements content in crystals of products of different eruptions can allow to understand whether they formed in the same conditions and if they are, therefore, related to the same magmatic system. We applied this principle to the products of historical eruptions occurring almost simultaneously along a N-S tectonic alignment on the island of Lipari, Vulcano and on the Vulcanello peninsula, with the aim to demonstrate that during the last 1000 years, in this sector of the Aeolian arc, eruptions were fed by a common deep magmatic reservoir.

The historical magmas of Lipari and Vulcano range in composition from shoshonites (Vulcanello, 1100-1600 AD) to rhyolites (Rocche Rosse; Lipari, 1230±40 AD; Commenda and Palizzi; Vulcano, 1200 AD; products of 1888-90 eruption on La Fossa ). Mafic enclaves of latitic composition are present in the obsidian rhyolitic lava flows of Rocche Rosse and Commenda, or are emitted as lavas (Palizzi) and/or pyroclastics (Vulcanello). In order to compare minerals in equilibrium with the same melt composition we focused our study on these intermediate products. Many similarities exist between the different latites in terms of petrography and whole rock chemistry. Clinopyroxene (Wo43-46En39-44Fs13-15, Mg# = 0.72-0.76) is always the most abundant phase, followed by plagioclase (An25-60Or12-9), sanidine (An0-3.5Or50-70) and olivine (Fo50-75). A detailed LA-ICP-MS microanalytical study on all the mineral phases showed that the pyroxenes of the different latites have very similar trace elements and REE patterns, with an Eu negative anomaly of about 0.65. Also plagioclase and K-feldspar show almost superimposed trace elements and REE patterns. Due to their small size it was possible to analyze olivine crystals only in Vulcanello and Rocche Rosse latites; their FME contents are also very similar. The strong geochemical similarities of the latites suggest a common origin, i.e. the same volcanic system or the same magma. On the basis of geochemical models drawn using major, trace and isotopic data, a possible common parental magma has been recognized in the shoshonitic basalt found in the olivine melt inclusion within La Fossa cone 1888-1890 products (Gioncada et al., 1998). The present work supports the hypothesis of Davì et al. (2009 and 2010) suggesting a common deep feeding system for both islands in historical time. Mafic melts of the deep system can directly reach the surface (e.g. at Vulcanello) and/or periodically refilling shallower magma batches with latitic to rhyolitic composition, enabling the rhyolitic eruption. Hazard evaluation in the southern sector of the Aeolian islands should consider Lipari and Vulcano as a unique magmatic system.

CHEMICAL VARIATION DURING MAGMA ERUPTION AT MT. BIDKHAN(IRAN)

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Mt. Bidkhan’s volcanic rocks (South-East Iran) cover a compositional spectrum from andesite to dacite. A plot of K₂O + Na₂O vs. SiO₂ suggests a medium to high calcalkaline for volcanic products. The geochemical trends of the Bidkhan volcanics are depicted through the use of the harker diagrams. Many of compositional arrays of Bidkhan samples are linear (e.g. Fe, Ca, Y) which support amagmatic differentiation in parental magmas. Some element arrays, however, are scattered (e.g. Ba, Sr, P) or curvilinear (e.g. Al, Na). These suggest that processes such as crystallization, and assimilation also probably operate in the magma chamber. In addition, some features such as high amounts of Th/Nb and Zr/Nb ratios in Bidkhan samples, suggest crustal contamination has been played an important role in the evolution of Bidkhan parental magmas. Field observations and whole rock chemistry for Bidkhan rocks suggest that the last melts that have differentiated and erupted from shallow magma chambers had been intermediate (probably andesitic) melts and have been repeatedly invaded by newly intermediate batches of magmas during differentiation. Then we have to search the traces of magma mixing in mineral chemistry, especially plagioclase crystals in the Bidkhan rocks. Bidkan’s plagioclases can be divided in 4 category: 1) Normal zoned plagioclases, In this type, An mol% varies from 53 in core to 10 in the rim; 2) Reversely zoned plagioclase crystals that make up a significant percentage of the Bidkhan plagioclases and occur in all of the rock types, with a compositional range from 30 An mol% in core to 55 in rim; 3) Normal oscillatory zoned plagioclases that also occur in all of the rock types; their An mol% fluctuates from core to rim, The ∆An in oscillations are relatively small (~ 5 An mol% ), that suggest newly melts were nearly similar in composition; 4) Reverse oscillatory zoned plagioclases, in this group of plagioclase crystals, An mol% content fluctuates and increases from their core to rim overall. Investigation of chemistry data in Bidkhan reveals that there are some plagioclase crystals with calcic cores (An 75 mol%) in andesites. These features must be established due to magma mixing.

This situation that has stated by Toothil (2007) means a combination of fractionation and magma mixing, where crystals growth in a relatively shallow magma chamber has periodically been interrupted by injection of other melts, with nearly similar composition of some many plagioclase phenocrysts. All these data suggest that, in Bidkhan, before and during eruption, some phenomena like fractional crystalization (F.C), assimilation and crystal fractionation (A.F.C), crustal contamination and magma mixing processes have a great role to construction of Bidkhan’s volcanic products.
Noble gas compositions (He, Ne, Ar) and isotopic ratios (He, Ar) in olivine- and clinopyroxene-hosted fluid inclusions were measured for the (i) present-activity basalts, i.e. Low Porphyritic (hereafter LP) pumices and High Porphyritic (hereafter HP) scorias, and (ii) ultramafic nodules within the ~2 ka old San Bartolo basaltic andesite lavas. The ultramafic nodules (mostly wehrlites) are igneous cumulates consisting of clinopyroxene and olivine crystals with abundant fluid and melt inclusions. Textures and mineral chemistry of the wehrlites suggest that they are the products of early crystallization of primary basaltic magmas at mantle conditions. In addition, ultramafic cumulate and LP pumice crystals show similar major oxide composition (olivine and clinopyroxene) and trace element patterns (clinopyroxene). The gas content in mafic crystals decreases from ultramafic nodules to LP pumice and finally to HP scoria. This is probably due to the decreasing pressure (and depth) of fluid entrapment. In agreement with previous knowledge, the HP crystals are severely degassed and, as a result, the measurement of their $^{3}\text{He}/^{4}\text{He}$ ratio was unsuccessful. The $^{3}\text{He}/^{4}\text{He}$ of LP pumices and San Bartolo ultramafic nodules converge to a range of 4.2-4.7 Ra that we interpret as the magmatic value of the least degassed actual feeding system of Stromboli. This also allows the helium isotopes of the thermal waters of the Stromboli basal aquifer to be considered a mix between mantle-derived and atmospheric fluids. Therefore, the $^{3}\text{He}/^{4}\text{He}$ values measured in the Stromboli rocks represent the upper limit that should be expected in thermal fluids during long-term monitoring in case of events such as lava effusions and/or paroxysms.
LARGE-VOLUME EFFUSIVE ERUPTIONS AND CALDERA COLLAPSES AS THE RESULT OF UNCOMMON MAGMA STORAGE CONDITIONS AT MT. ETNA VOLCANO (SOUTHERN ITALY)

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The emission of plagioclase megacryst-bearing lavas, locally known as “cicirara”, is rare throughout the volcanic record of Mt. Etna and generally related to unusual volcanological dynamics. Highly porphyritic lavas were emitted either during the final phases of the Ellittico volcano (14-16 ka) in association with a caldera collapse or during long-lasting and large-volume, effusive events of the XVII Century. This eruptive period culminated with the catastrophic 1669 AD eruption, which was followed by the formation of a caldera at Piano del Lago (ca. 2500 m a.s.l.), as reported by detailed historic chronicles.

We tried to decipher the magma chamber processes and the structural features of the plumbing system that led to the formation of large plagioclase crystals (up to 1.5 cm). Selected plagioclase megacrysts, belonging to the final phase of the Ellittico and to the XVII Century, were investigated through high-resolution BSE images and core-to-rim compositional profiles for An% and FeO wt.%. A similar approach recently provided key information on the feeding system and ascent dynamics at Mt. Etna for mildly porphyritic lavas of the historic and recent eruptive record (Viccaro et al., 2010). Larger crystals (> 7 mm) showed patchy zoning at the core followed by oscillatory-zoned envelopes. Crystals with size 1-7 mm display coarse sieve-textures at the core followed by oscillatory-zoning towards the rim. The most frequent texture is oscillatory-zoning, which is recorded by crystals of the dimensional class < 7 mm. Three types of oscillations, characterized by different wavelength and frequency of An content, were observed. Oscillatory zoning can be interrupted towards the rim by other textures such as stripes of melt or fluid inclusions or strongly sieve-textured envelopes. Patchy zoning provides important indications on the styles of magma ascent between the plagioclase nucleation threshold and the volatile saturation depth (~ 6 km beneath the summit craters), suggesting limited ascent in the deep levels of the plumbing system. At shallower, water-undersaturated levels ascent might be faster, as testified by crystals smaller in size affected by coarse sieve-textures. Conversely, oscillatory zoning and the other textures give information on the magma evolutionary processes during storage at shallow, water-saturated levels (above 6 km of depth). Stripes of melt or fluid inclusions and strongly sieve-textures towards the rim are an indication that other physical and chemical perturbations occur at shallow levels. Stripes of melt inclusions can be associated with steps of magma ascent coupled with volatile loss, whereas layers of fluid inclusions may be related to episodes of volatile influx into the residing system. Finally, strongly sieve-textured envelopes with An increase and constant FeO (found exclusively in lavas of the XVII Century) may be related to mixing with magmas similar in composition but more volatile-rich. The manifestation of “cicirara” lavas in some specific periods of the volcanic record is evidence that the plumbing system structure underwent a progressive coalescence of the complex network of dykes and sills as a response to increasing magma supply rate from depth, which finally led to a large reservoir at shallower depth. Huge amounts of magma withdrawal during long-lasting, purely effusive eruptions from this reservoir may be linked to episodes of summit instability that caused major caldera collapses at Mt. Etna in the past.

Although sulfur is a minor element in magmas it plays key roles in processes of magma evolution, volcanic degassing and eruption. As a dissolved species in magmas, sulfur mainly exists as sulfide ($S^{2-}$) under reducing conditions, and sulfate ($S^{6+}$) under oxidizing conditions. Probing sulfur in magma is challenging because more than 90% of the sulfur initially dissolved is released at the time of eruption. Silicate melt inclusions trapped within early crystallized olivines provide a means of preserving melt compositions prior to significant modification of the magma such as assimilation, crystallization and degassing. Melt inclusions can provide reliable estimates of melt oxidation state at the time of inclusion entrapment. Oxidation state in melt inclusions has been assessed by electron microprobe (EMP) measurements of sulfur speciation, determining the relative proportions of $S^{2-}$ and $S^{6+}$, on the basis of the sulfur Kα X-ray peak shift method. This technique provides relatively rapid analysis of small samples (~ 30 μm) and is therefore ideal for application to melt inclusions.

A selection (30 to 40) of olivine-hosted melt inclusions and relative matrix glasses from 2001-2006 Mt. Etna eruptions, embedded in epoxy resin, were considered for this investigation. The selected samples have been previously characterised as for texture, major, minor and volatiles (including S). All the studied inclusions are hosted by forsteritic olivine (Fo 78-82) and sulfur concentrations widely range from approximately 400 to 8000 ppm. Pyrite, Troilite, Sphalerite, Cinabro, Barite and Celestine mineral grains were used as reference materials to define the peak position for SKα for a wide range of different $S^{6+}/S_{tot}$ ratios and defining the peak position for pure sulfide and sulfate. With the aim of better constraining the oxygen fugacity in our MIs we also measured, by EMP, iron speciation (Fe$^{2+}$/Fe$^{3+}$) by using the iron Lα/Lβ intensity ratios.

Aim of this study is to characterise the variations of sulfur speciation in melt inclusions as a result of natural magmatic processes. Based on sulfur X-ray wavelength measurements, calculated oxygen fugacities for etnean basaltic melt range from –0.4 to +2.5 log units (ΔNNO), with the highest calculated oxygen fugacity from the 2006 eruptive products. $S^{6+}/S_{tot}$ ratio in melt inclusions generally well correlate with that of relative matrix glasses, although we observed a wider range in the former. Large ranges in measured sulfur speciation in naturally quenched melt inclusions may be related to degassing of the melt synchronous with entrapment in the olivine host crystals during closed-system ascent of etnean basaltic magma.

We normally observed that dissolved water and sulfur contents in melt inclusions simultaneously decrease during melt degassing, and according to that melt inclusions with higher $S^{6+}/S_{tot}$ (more oxidized) appear to correspond to high water concentrations.

A notable exception was observed in some melt inclusions of 2002 eruption showing a very different behaviour, mainly characterised by large differences in S content at almost constant K$_2$O, and displaying an inverse relation between H$_2$O and S. The former condition is compatible with a rapid decompression accompanied by a limited crystallization processes, that causes rapid degassing with irrelevant chemical evolution of the melt. An attempt to explain the opposite variation of H$_2$O and S occurring in some primary etnean melt inclusions was made taking into account the involvement of an immiscible sulphide melt phase which has been observed and documented in some etnean melt inclusions.
Mount Etna, the largest volcano in Europe, displays the peculiar condition of lying on continental crust and close to the subduction-related Aeolian volcanic arc, while its products show typical affinities with Ocean-Island Basalts (OIB). The finding of subduction-related geochemical tracers in the volcanic products of the last thousand years, along with an increased explosivity of eruptions, led to develop a model for Etnean magmas that states that the mantle source is progressively undergoing metasomatic influx by slab-derived fluids released from the Ionian slab (Tonarini et al., 2001).

We present the results of a geochemical study of olivine-hosted melt inclusions (MIs) from 2001-2006 Mt. Etna basaltic lavas. Two different suites of MIs were observed. They represent different magma batches that variously evolved inside the feeding system before their entrapment in host olivines. Type-1 MIs share their trace element signatures with bulk-lavas and closely approach OIB-like magmas whereas type-2 reveal “ghost plagioclase signatures”, namely lower concentrations in strongly incompatible elements and positive Sr, Ba and Eu anomalies. Noticeably, both melt types occur in 2006 MIs, which, more importantly, include composite inclusions consisting of plagioclase surrounded by type-1 melt.

Trace-element critical ratios, namely Ce/Nb, Ba/La and K/La, which are not or poorly affected by process of global differentiation, provide evidence that sources of type-1 MIs are highly heterogeneous in composition, with signatures that are intermediate between those of HIMU/FOZO-like and EM-like sources. Differently from type-1, type-2 MIs testify for en-route processes that are peculiar for eccentric eruptions. These latter are strongly controlled by tectonics or flank instability, which occasionally promote the upraise of undegassed and more primitive magma that may interact with variable volumes of crystal mush and plagioclase-rich cumulates before reaching the surface. Previously formed plagioclase crystals are thus trapped in olivine, possibly along with minor reacted melt, and then forced to react and melt due to the high magma temperature, as suggested by Danyushevsky et al. (2003 and 2004) to explain the “ghost plagioclase signatures” in MORB olivine-hosted MIs.

It is also emphasised that the occurrence of melt inclusions with distinct geochemical signatures, rather than different melt types and sources, may reflect important en-route processes that are occasionally recorded only on a micro-scale and cannot be identified from chemical investigations of bulk-lavas.
SOURCE METASOMATISM BENEATH STROMBOLI: A STUDY OF TRACE ELEMENTS AND Pb-B-Li ISOTOPIES IN OLIVINE-HOSTED MELT INCLUSIONS

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Several studies provide evidence that magma sources beneath the Aeolian arc volcanoes were contaminated by variable amounts of metasomatic agents released from the subducting slab. It has been proposed that the composition of the mantle wedge beneath Stromboli is strongly influenced by the addition of a recycled sedimentary component, and that two distinct enrichment events triggered by slab-released aqueous fluids and supercritical liquids were responsible for its source metasomatism (Tommasini et al., 2007).

We carried out an elemental and isotopic (Pb, B and Li) characterization of olivine-hosted melt inclusions (MIs) to explore the sources of Stromboli magmas and to assess nature and relative contributions of slab components and metasomatic agents involved in the source metasomatism. The studied MIs have primitive calc-alkaline to high-K calc-alkaline basaltic compositions; they are trapped within early-formed highly forsteritic (Fo83-91) olivine phenocrysts, which were collected from lava (San Bartolo lava) and pumices erupted in historical times. The studied melts cover a compositional range far wider than that exhibited by the whole-rocks and differ in key trace element ratios. San Bartolo melts are characterized by lower incompatible trace element abundances, higher LILE/HFSE, LILE/REE, U/Nb, Ba/Th, U/Th and Pb/Ce, and lower La/Yb ratios relative to the pumice-hosted MIs and pumiceous melts erupted during paroxysmal events. The MIs Pb isotope composition is highly heterogeneous and extends from EM2 (Enriched Mantle)-like compositions (San Bartolo sample) to lower \(^{207}\text{Pb}/^{206}\text{Pb}\) and \(^{208}\text{Pb}/^{206}\text{Pb}\) values that are similar to those observed in lavas from the central and western Aeolian volcanoes and point to a FOZO-like fingerprint. The MIs B isotope compositions for San Bartolo and pumice samples are slightly heavier (\(\delta^{11}\text{B} \sim -2.0\%\)) and significantly lighter (-8.6 ÷ -13.7‰) than whole-rock compositions, respectively. Their Li isotope signature of olivine-hosted MIs from pumices is more heterogeneous and significantly lighter than bulk-rock samples.

These features testify small-scale heterogeneities in the source regions of magmas feeding the present-day and > 2 ka Stromboli activity. Isotopic melt compositions are consistent with a two-stage mantle enrichment process during which supercritical liquids and aqueous fluids partially overlapped on the same mantle domain. Variable amounts of Th-rich supercritical fluids mainly released from the altered basaltic oceanic crust are required to explain the composition of both olivine-hosted MIs from pumices and the high \(^{208}\text{Pb}/^{206}\text{Pb}\) ratios of San Bartolo melts. However, the distinct geochemical and isotopic fingerprint of San Bartolo melts can be modeled only assuming a later metasomatic event driven by U-, B-, Ba- and Pb-rich aqueous fluids. These latter were probably expelled at relatively shallow depths from both sediments and basaltic crust (~ 30 and 70%, respectively) and promoted higher degrees of melting. In contrast, a later flux of aqueous fluids is not necessary to model the geochemical signatures of olivine-hosted MIs from pumices. Rather, their light Li and B isotope compositions indicate that they formed from mantle sources modified by supercritical liquids escaped from dehydrated metabasalts and metasediments constituting the deep portion of the slab. An overall important contribution from laterally heterogeneous subducted sediments characterized by high Th and U contents and variable Th/U ratios was most likely responsible for the large variations observed in Pb isotope ratios.

PLAGIOCLASE TEXTURES AND COMPOSITIONS TO UNRAVEL THE FEEDING SYSTEM DYNAMICS AT AVACHINSKY VOLCANO (KAMCHATKA, RUSSIA)

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Aim of the work is the identification of the feeding system processes and styles of magma ascent before the 1991 eruption at Avachinsky through whole rock and textural/compositional data of plagioclase crystals obtained by high-resolution BSE images and core-to-rim profiles. The 1991 volcanics at Avachinsky are porphyritic basaltic andesites and andesites with low-K (tholeiitic) affinity. Major oxides are within the compositional range of other Kamchatka products of similar evolutionary degree. Trace elements define two trends: some samples show a progressive evolution from basaltic andesite to andesite that can be ascribed to crystal fractionation, whereas other products are not in accordance with a differentiation process driven by crystals removal. A two-steps fractionation modeling for both major and trace elements was performed to justify the basaltic andesite and the andesite compositions. Results of the first step show that basaltic andesites are consistent with fractionation from a poorly-evolved basaltic andesite of 27 wt.% ~ An₈₀ plagioclase, 12 wt.% augitic clinopyroxene, 4 wt.% orthopyroxene and 6% opaque oxide (P = 150 MPa; T between 1150°C and 1000°C; initial H₂O = 2.0 wt.%; fO₂ at the QFM+1 buffer). The second fractionation modeling justifies the andesite starting from the less evolved basaltic andesite of the 1991 eruption dataset. Results show that the andesite can derive from the basaltic andesite by fractionation of 24 wt.% An₇₅ plagioclase, 7 wt.% augitic clinopyroxene, 4 wt.% orthopyroxene and 3 wt.% opaque oxides (P = 50 MPa; T between 1150°C and 1000°C; initial H₂O = 2.6 wt.%; fO₂ at the QFM+1 buffer). Trace element geochemistry suggests the occurrence of other differentiation processes beyond the two-steps fractionation. The coupled increase of Zr - Ba/Sr - Rb/Sr for some samples indicates that some assimilation may have occurred during the evolution from basaltic andesite to andesite. Other basaltic andesites keep Ba/Sr and Rb/Sr rather constant at increasing Zr, ruling out the contribution of a crustal component. Thus, a hypothesis of new magma recharge was verified through the integrated textural and compositional study of plagioclase crystals. Several texture types were found: 1) small and large-scale oscillation patterns; 2) disequilibrium textures at the crystal core (patchy zoning, coarse sieve-textures, dissolved cores); 3) disequilibrium textures at the crystal rim (strongly sieve-textures); 4) growth textures consisting of melt inclusion alignments at the rim. Disequilibrium textures found at the cores testify episodes of destabilization at variable decompression rates under water-undersaturated conditions, which suggests different pathways of magma ascent at depth. At shallower, water saturated conditions, plagioclase textures and compositional profiles suggest that crystallization continues in reservoirs not affected by important chemical and physical perturbations (oscillatory zoning develops). Strongly sieve-textured rims are evidence for the occurrence of a mixing process prior the 1991 eruption: the behaviour of An and FeO suggests that the recharging magma was geochemically-distinct at rather comparable evolutionary degree and with higher temperature and volatile contents than the residing one. Assuming a certain degree of undercooling, the timescales derived to develop this envelope indicate less than 4 months. The occurrence of only two types of textures that cut the oscillatory zoning (strongly developed sieve-textures or thin alignments of melt inclusions) evidences that crystals underwent common histories at shallow levels, favouring the hypothesis of the existence of a large magma reservoir at < 5 km of depth, more than several separated batches. The presence in a hand-size sample of these two types of textures also implies that crystals mix mechanically at very shallow levels, supporting the existence of a small magma reservoir at < 1.5 km of depth.
Sessione tematica I3:
Processi di genesi, intrusione, risalita ed eruzione di magmi:
un approccio multidisciplinare

Conveners:
Raffaello Cioni (Università di Cagliari)*
Massimo Coltorti (Università di Ferrara)
Francesco Mazzarini (INGV, Pisa)
THE CAMPANIAN IGNIMBRITE CATACLYSMIC ERUPTION THAT SEGREGATED AND DISCHARGED A HUGE AMOUNT OF VOLATILES AND GENERATED EXTREMELY DILUTED PYROCLASTIC DENSITY CURRENTS

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The late Pleistocene trachytic Campanian Ignimbrite (CI; 300 km³ DRE) covers the Campanian Plain near Naples, and is found behind ridges more than 1,000 m high at 80 km from source, the Campi Flegrei caldera (CFc). Distal ignimbrite deposits reveal downhill and/or downvalley flow directions prior to deposition, whereas in the absence of significant topography, deposition came from a flow moving in a roughly radial direction. These features point to very dilute currents, that together with the huge amount of discharged magmatic material, suggest a magma reservoir highly enriched in volatiles, rather than fluid entrainment from hydrothermal bodies or seawater.

Petrologic and geochemical modelling of erupted products and their chemical and textural zoning, together with MI-based studies of gas-melt saturation, corroborate this view and show that the CI huge volume differentiated and mixed at shallow depth (6-3 km). With respect to compositionally similar but also smaller CFc eruptions (e.g. Agnano-Monte Spina, A-MS), the large amount of volatiles discharged by IC was likely due to fractional crystallization and longer residence times of volatiles sourced by the subducting Appenninic slab. This yielded high-water contents (up to 6-7 wt.%), as well as high void fractions (~ 70-80% for IC, ~ 45% for A-MS) and also produced an overpressurized CO₂-dominated gas cap (about 150 km³), uniformly distributed at the top of the magma chamber. The onset of the eruption tapped this cap, with consequent depressurization and fast volume decrease that facilitated or even drove the caldera collapse, and allowed the water-rich magma to be discharged during the pyroclastic current phase. The gas saturation-based estimates of the tapped foamy magma are compatible with the extent of magma chamber roof collapse, strong expansion revealed by textural data and transport and deposition mechanisms, reflecting depressurization and magma inflation within the collapsed and laterally confined caldera.
Mt. Etna is located in a quite complex tectonic context and large sectors of the eastern and south-eastern flanks of the edifice move downward at very different rates. During last years, the flank slip has been somehow related to the magmatic intrusions refilling the shallow and deep portion of the volcano plumbing system, suggesting a feed-back between flank dislocation and magma emplacement within the volcano.

The petrologic studies performed during last decades at Mt. Etna, evidenced that the plumbing system of the volcano has a quite complex geometry, variable in space and time and consisting of storage zones at different depth, where magma ascending to the surface experiences complex processes such as mainly fractional crystallization and mixing. In this framework it’s quite interesting to further investigate if a possible cause-effect relationship exists between the displacement of the volcano East flank and the pre-eruptive magmatic processes in the plumbing system. We went into this matter with a petrologic study of the products erupted in the decade 1995-2005. In particular we analyzed the petrography, mineral chemistry, geochemistry, Sr and Nd isotopes emitted by the four summit craters of Mt. Etna (South-East, North-East, Bocca Nuova and Voragine) from 1995 to 2001 and integrated them with petrologic data already available in literature for the investigated decade.

This approach allowed us to better constrain the temporal evolution of the main magmatic processes occurring in the plumbing system of Mt. Etna (mainly mixing between compositionally distinct magmas and fractional crystallization) and to make inferences on the geometry (shape and depth) of the shallow (> 5 km b.s.l.) storage zone. In the studied decade, the comparison between petrologic data and deformaive patterns evidences that, from 1995 to July 2001, the aforementioned pre-eruptive magmatic processes did not significantly influence the displacement of the flank, which maintained slow and quite-regular downward movement throughout these years. Differently, the onset of the 2001 flank eruption leads to an accelerated displacement of the movement, up to 2005. Well-known petrologic published data evidence that during the 2001 activity (and 2002-03 too) a primitive, volatile-rich, sub-aphyric basalt upraised directly from a deeper (8-10 km b.s.l.) reservoir to the surface. In conclusion, at least for the investigated period, the pre-eruptive magmatic processes in the shallow portion (< 5 km b.s.l.) of Mt. Etna plumbing system, do not seem to directly affect the movement of the volcano eastern flank. Conversely, a magma intrusion which forcefully opens a new path from a deeper zone (8-10 km b.s.l.) of the plumbing system, causes a dramatic increase of deformaive pattern, which strongly accelerate the slide of the volcano eastern flank, as it occurred during both 2001 and 2002-03 eruptions.
A NEW INTERPRETATION OF PHLEGRAEAN FIELDS CALDERA USING ANALOGUE MODELS

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Recently, to better understand structures and deformations of volcanoes new data became available by the use of analogue models that reproduced natural events in laboratory, simplifying them reducing the number of variables, and allowing to characterize the main phases of the processes by a well defined scale ratio between the events and their reproductions in laboratory. We used an analogue model by gelatine as a material analogue to the crust, in order to identify a new mechanism explaining the origin of the Phlegrean Fields Caldera, a volcanic structure that extends over the city of Naples and its western surroundings and formed during a distensive tectonic phase associated with the opening of the Tyrrhenian Basin and eastward migration of Apennine Chain.

The volcanic field is constituted of two calderas and of several monogenic cones. The oldest caldera is related to the Campanian Ignimbrite eruption that occurred about 39 ka BP, and the youngest caldera formed 15 ka BP with the Neapolitan Yellow Tuff eruption. An accurate analysis of the volcanic history of the Phlegrean Fields area and of the data available from the literature brought out doubts on two issues: 1) source of Phlegrean volcanism; 2) actual location of the limits of the Campanian Ignimbrite (CI) Caldera.

Our research began with previous interpretations that at the origin of the Neapolitan volcanism there is a mantle upwelling occurring about 2 Ma BP, associated with tensile tectonics generated by the opening of Tyrrhenian Basin.

In order to simulate a rising plume in the Neapolitan area we built two analogue models, set by volcanological, geophysical and geochemical constraints. The models were built using a layer of gelatine in order to obtain a spatial distribution of fractures in the material, source pressure values, scaled elastic parameters, a 3D model constrained by geological data. The difference between the models was the type of source: in the first model, a silicon balloon was placed at the bottom of the gelatine layer and was slowly inflated to simulate a rising plume; in the second model, animal fat was injected in the gelatine through a conduit in order to constrain it during the upward migration.

The effect of the experiment by the silicon balloon was the tumescence of the surface of gelatine layer with the formation of fractures just like a triple junction, followed by detumescence when the source pressure decreases.

For the second model, experiments were realized by varying the overburden thickness, hence the source depth. The effects were different: by greater source depth, a fat sill expanded in the analogue crust triggering the formation of a horizontal fracture, from sill to the surface, and it was followed by a triple junction. In the second case, by a shallower source, the fat sill only triggered the formation of a triple junction. The analogue models allowed to obtain the pressure of the magmatic source necessary for the overburden uplift and the formation of triple junction, in the Phlegrean Fields, and were used to determine the plume diameter. Therefore, the evolution time of deformation phenomenon in the analogue model allowed to scale the time of pre-Campanian Ignimbrite Caldera volcanism: the formation of CI Caldera was preceded from a fracture along which volcanic activity would develop initially and then migrate to the Gulf of Pozzuoli favoring a director E-W corresponding to the fault scarps of half graben basement of Campanian Plain; during this process of activity migration, a triple junction grows slowly giving rise to the Campanian Ignimbrite eruption and the subsequent collapse; the time between the first activity along fracture and the formation of the CI Caldera is about 25 ka scaled by the analogue model; a further triple junction was generated as a result of a new rising magma inside the CI caldera giving rise to the formation of Neapolitan Yellow Tuff caldera about 15 ka BP.
CALCITE-BEARING FOIDITIC LAVA FLOWS FROM COLLI ALBANI VOLCANIC DISTRICT

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The Colli Albani (hereafter CA) ultrapotassic volcanic district (near the city of Rome, Central Italy) belongs to the Roman Province whose magmatism is thought to result from the combined effects of crystal fractionation and crustal assimilation on a parental magma derived from a metasomatized mantle source. The CA district represents one of the most peculiar volcanic districts on the Earth because of its liquid line of descent characterized by differentiated, low silica (45 wt.%), K-foiditic magmas. Field, geochemical, and experimental studies have demonstrated that such a differentiation trend, starting from trachybasaltic parental magma, is mainly due to magma-carbonate interaction (Gaeta et al., 2009 and references therein). Despite many studies have investigated petrological and geochemical features of the Colli Albani magmas, several questions remain unanswered. One of these concerns the occurrence of calcite crystals in the groundmass of some lava flows. In general all CA lava flows are made up of leucite and clinopyroxene phenocrysts; some deposits (corresponding to less evolved products) also contain forsteritic olivine. The groundmass is generally made up of leucite, clinopyroxene, and Ti-magnetite; more evolved products may also contain amphibole or, and these are the object of our study, calcite, usually associated with nepheline.

The textural study of calcite-bearing lava flows, by means of Field Emission SEM, revealed that calcite usually occurs as interstitial phase, intergrows with nepheline and, in some cases, contains inclusions of oxide (e.g. hematite) or fluorite. Calcite is also present: i) as spherical “ocelli” with tangentially arranged crystals of clinopyroxene; ii) interstitial at clinopyroxene rim and leucite; and iii) rarely, around coronitic texture of leucite produced at the expense of K-feldspar xenocrysts. All these textural features indicate that calcite occurring in the lava flows groundmass crystallize above the solidus temperature. The high activity of calcium in the lava flow groundmass is also supported by the mineral chemistry of silicate phases. For example, olivine crystals in groundmass are enriched in FeO and CaO (up to 4 wt.%) and a positive correlation between CaO in olivine and melt differentiation (i.e. Mg#) is observed. Carbon and oxygen isotope values, as well as trace elements abundance, have been determined on calcite and phenocrysts occurring in the CA lava flows. Oxygen isotope values (25-26‰ SMOW) result higher than that of phenocrysts (6-8‰ SMOW) and, interestingly, coupled with very low carbon isotope values (-14.4 – -15.7‰ PDB). Trace elements abundance in calcite is lower than abundances measured in both clinopyroxene phenocrysts and bulk rocks (LREE100 chondrite).

Textural and mineral chemistry data indicate, unambiguously, that calcite in the CA lava flows has crystallized from a carbonate-bearing melt in a magmatic environment (Freda et al., 2011). Although carbon isotope values could suggest a mantle origin for the carbonate-bearing melt, oxygen isotopic composition and trace element abundance suggest a different origin.

We propose that calcites in CA lava flows form as result of a mingling process between Ca-rich melts, originating in skarn environment and/or during sin-eruptive carbonate assimilation, and potassic magmas.

Mount Etna activity is characterized by different eruptive styles, from effusive to highly explosive, involving both central and lateral feeding systems, not accompanied by significant variation in lava compositions. The most important parameter in determining the eruptive styles is therefore the dynamic of magma within the feeding systems. Plagioclase is the most common phenocrysts in all terms of the etnean magmatic suite (~ 50% in volume). Its stability field is dependent on chemico-physical variations of the melt and it can be used as a tool to highlight the dynamics of magma uprising. Textural and compositional study of plagioclases has thus performed on the products emitted during the 2001-2006 eruptive period, and compared with theoretical models that constrained its stability field and with the eruptive mechanisms put forward by various authors.

During 2001-2006 eruptions plagioclase with an average length of about 1mm present i) clear crystals (about 800 µm in size), rich in An (An90-85) with oscillatory zonation pattern or ii) phenocrysts with clean or dusty cores lower in An content (An85-75) with complex dissolution textures (4-500 µm): when simple dissolution occurs cores are rounded and clear, while if partial dissolution occurs cores are dusty due to numerous glassy inclusions (coarsely sieved cores) (Tsuchiyama, 1985). In the latter case both cores are followed by a lower An overgrowth ranging in size from 100 to 400 microns. Finally two types of rims (max 100 µm) can be also recognized: i) partially dissolved dusty rims, with An-rich composition and ii) a more albitic rims characterized by alignments of melt inclusions along crystallographic planes. MELTS calculations have been performed to constrain the crystallization conditions, starting from the most primitive magma (2004/2005 eruption) under different pressure (2500-0 bars) and water contents (3.5-0 wt.%). Based on whole-rock composition the program estimates the liquidus temperature, which were decreased by step of 20°C down to 1030°C. Volatile saturation depths were estimated using VolatileCalc and water content in Etnean lavas by the plagioclase-liquid hygrometer/thermometer of Lange et al. (2009). Independent determinations of oxygen fugacity ($fO_2$) of the system have been calculated using the method of France et al. (2010), indicating a range of values varying from QFM = 0.3 to QFM = 1.8. These simulation indicate that An-poor (An75-85) plagioclases crystallized at about P = 2500 bars and 1 wt.% H₂O, while An-rich (An85) plagioclases is stable only at P = 800 bars and 2.5 wt.% H₂O. Thus clear An-rich (> An85) crystals can be obtained only at very shallow pressure (< 1000 bars) with water content of about 2.5-3.3 wt.%. Clean or dusty dissolved cores An85-75 in composition cannot be in equilibrium with high water content at depth greater than 3 km. Dissolution processes suggest disequilibrium conditions within the deep magma reservoir which can be related to an input of new undegassed magma or decompression during magma ascent which rise the water pressure. The more albitic overgrowth probably develops at shallower level where the magma can rest, followed by water oversaturation and degassing. The outermost narrow rims can be explained by i) input of new basic magma or ii) rapid growth due to degassing just prior to the eruption. Textural and compositional study reveals a dependence of plagioclase liquidus on water content dissolved in the melt. Furthermore, the textures at the crystal rims suggest different trigger mechanism of the eruption: an active one, induced by magma mixing and a passive one, promoted by decompression due to fracture opening, probably associated to regional tectonics.

PETROLOGICAL AND GEOCHEMICAL STUDY OF PRODUCTS AND LAVAS EMITTED DURING THE BILATERAL 2002-2003 ERUPTION EVENT AT MOUNT ETNA

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The 2002-2003 eruptive event of Mount Etna lasted from 26th October 2002 to 28th January 2003 and was characterized by the contemporaneous activity at the NERS (North East Rift System) and SRS (South Rift system).

A detailed and stratigraphically controlled sampling was developed along the SRS between 2,900 and 1,700 meters a.s.l. Whole rock major and trace elements analyses were carried out and results compared with those obtained from the NERS (Ferlito et al., 2009). Eight main eruptive stages were distinguished on the basis of Catania-INGV daily Reports. The first stage, T1, correspond to the beginning of volcanic activity at SRS on 26th October 2002, although samples referable to this period are no longer accessible. From T2 to T5 the activity was concentrated along the NERS with the opening of three main fracture segments and the contemporaneous emission of several lava flows that reached the touristic centre of Piano Provenzana. The last three stages, from T5 to T8, developed on the southern flank. On the base of petrographic (P.I.) and geochemical features (mainly K₂O, Rb, Nb), three different magmas have been recognised: (1) High-K Porphyritic (HKP) group with high-potassium contents (K₂O > 2 wt.% and P.I. ranging between 20 and 32%); (2) High-K oligophyric (HKO) group with high-potassium content (K₂O > 2 wt.% and P.I. ranging between 10 and 18%); (3) Low-K oligophyric (LKO) group with low potassium content (K₂O < 2 wt.%) and P.I. between 10 and 17%. Low-K lavas are only present at the NERS. HKP lavas emitted at T5 on the southern flank of the volcano are similar to those found on the lowest segment of the NERS, although the former are less differentiated. Quarzarenitic xenoliths are present in lavas from both sides of the volcano.

Major and trace elements mass balance and Rayleigh fractionation models were developed on representative NERS and SRS samples. The modeling indicates that NERS T5 lavas can be fractionated from those outpoured at SRS, suggesting a common fractionation trend. Textural and petrological studies of plagioclases enclosed in these lavas also suggest that chemical-physical conditions at depth were similar, while at shallow levels lavas evolve independently.

These new geochemical and mineralogical data, together with published seismotectonic data, support the idea that the main magma feeding the eruption was common on both sides of the volcano even though magma ascent probably occurred through the South Rift fractures and was intercepted from the NE Rift system only at relatively shallow depth. New magma inputs were recognized at SRS where eruption lasted until the end of January. On the other hand at NERS eruption, which was most probably passively triggered by tectonic activity, lasted only for few days.

Basaltic volcanic fields, formed by several volcanic constructs, are common features in the main Ethiopian Rift. Their age spans from 3 Ma to Holocene and are distributed along belts in the rift floor and clustered along magmatic belts close to the western rift margin.

The strict relation between vent and dike allows analysing the vent spatial distribution in relation with tectonic features and crust layering. Observed vent distribution suggest a strong control in vent location by crust layering and by tectonic features. Moreover, vent distribution is defined by power-laws (fractal distribution).

These distributions are defined by upper and lower cut-off lengths, where the upper one shows scaling relationship with the thickness of the crust beneath the volcanic field. This point suggest that vent distribution could be used as a proxy in defining the distance between the reservoirs and the sink, that in the case of basaltic magmas often represent the crust thickness.
A NEW RECONSTRUCTION OF THE VAL CALANNA VOLCANIC SUCCESSION (MT. ETNA, ITALY): INFERENCES ON A NEWLY DISCOVERED, SMALL-SIZE ERUPTIVE CENTER

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Since the beginning of its activity about 500 ka ago, Mt. Etna has been characterized by the growth and destruction of several eruptive centers. Our knowledge on the most ancient of them derives from the study of the steep and friable walls of Valle del Bove, carved on the eastern flank of the volcano edifice. The understanding of long-term variation in terms of volcanological and geochemical evolution of basaltic magmas at Mt. Etna can lead to a more global view of the volcanic system. Within this frame, a multidisciplinary study on ancient eruptive centers can also offer new insights for interpreting the current volcanic activity, providing general models of magma evolution and eruptive behavior. An integrated study embracing geology, petrography and geochemistry was undertaken on the Val Calanna area, located at the south-eastern end of the Valle del Bove. The volcanic succession of Val Calanna is of interest for the study of the Mt. Etna evolution, as the remains of several eruptive centers attributed to the first stages of the alkaline activity outcrop on its flanks. The new geological survey of the Val Calanna area, along with petrographic and geochemical data, highlighted some differences in the volcanic succession with respect to that previously reported in literature.

Our study confirms that the most ancient volcano-stratigraphic Unit of the VdB crops out at Mt. Calanna, recently interpreted as a dyke swarm. The Mt. Calanna Unit is overlain by the 80-m-thick lava succession of the Salto della Giumenta Unit, one of the Ancient Alkaline Centers, which at its top is mantled by pyroclastic flow and epiclastic deposits. Above this, volcanics of the Mt. Zoccolaro Unit constitute the frame of the present-day homonymous ridge with a 200-m-thick succession of basaltic lava flows characterized by amphibole megacrysts and showing features similar to those of the Trifoglietto phase (80-60 ka). The eastern portion of the Mt. Zoccolaro edifice is overlain by the volcanic succession of a newly recognized, small-sized, eruptive center: the Fior di Cosimo (FdC).

The FdC Unit is constituted of a sequence of alternating lavas and pyroclastic deposits which dip radially away from an inferred vent hypothetically located in the middle of Val Calanna. The relationship between major oxides of FdC lavas and their stratigraphic position shows an increasing degree of differentiation through time, from basalts to benmoreites. Simulations of crystal fractionation through MELTS revealed that the most evolved FdC lavas can be derived by subtraction of 54% of solid phases (An96-82 plagioclase, augitic clinopyroxene, Fo68-72 olivine, Ti-magnetite and traces of apatite) from a basaltic composition. The proposed model for the FdC magmatic evolution is therefore the intrusion of a slightly differentiated magma at shallow crustal levels. Magma supply should have then ceased forming a reservoir that allowed differentiation by crystal fractionation, gradually leading to an increase of the volatile pressure of the system. This favored amphibole crystallization, as observed in the last-emitted products. The available data suggest that FdC can be attributed to a pre-Ellittico eruptive phase.

THE 2010 ERUPTION OF EYJAFJALLAJÖKULL VOLCANO, ICELAND: CONTRIBUTIONS FROM CHEMICAL AND Sr-ISOTOPIC MICROANALYTICAL DATA ON TEPHRA

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During the 39 days of summit activity at the Eyjafjallajökull volcano (14 April - 22 May 2010) a nearly continuous injection of tephra in the atmosphere with a large production of ash caused disruption to the aviation over Europe. The activity consisted of an initial intraglacial phase (14-19 April) of Vulcanian-type explosions, followed by intermediate phase (19 April - 3 May) of weak magmatic explosions and lava emission; a final renewed phase of pulsatory explosions occurred between 3 May - 22 May. The eruption emplaced about 0.1 cubic km (DRE) of benmoreite tephra with 10-20% of fine ash (< 10 micrometers) (Thordarson et al., 2011, G.R.A., 13, EGU2011-12046). The summit activity was preceded (20 March - 12 April) by a mildly Na-alkaline basaltic fissure eruption on the East flank (Fimmvörðuháls) of the Eyjafjallajökull volcano, where up to 150-m-high lava fountains, emplaced 0.025 cubic km of lava (Thordarson et al., 2011, G.R.A., 13, EGU2011-12147).

We sampled a pristine fallout sequence packed in the snow 5 km East from the vent, representing the opening, the 14-15 April and the 17 April activity, respectively. A sample of falling particles was also collected 5.5 km from the vent on 6 May. Lapilli and lava of the Fimmvörðuháls basaltic fountains were also collected. Samples were processed for grainsize analyses; juvenile clasts were hand-picked in the range 0.7-1 mm and selected clasts were analyzed and characterized with SEM imaging. Matrix glasses of the chosen tephra clasts have silica ranging between 58-64 wt.%, FeO between 7-10 wt.% and K2O between 2-3 wt.%. Compositions are extremely homogeneous within single clasts but slight variations can also occur between different clasts of the same sample. Major and trace elements and isotope data on whole-rock samples were also performed. Tephra samples show small compositional variations (SiO2: 58-64 wt.%, MgO: 1.5-3.0 wt.%, FeO: 8-10 wt.% and K2O: 1.6-2 wt.%). Although a good correlation between trace elements and silica exists, the trends of incompatible elements cannot be simply explained with fractional crystallization of the present mineral phases (olivine, clinopyroxene, plagioclase, magnetite and apatite). Matrix glasses of variably-vesiculated clasts, showing different composition and crystallinity, were also micro-milled and analysed for Sr isotope ratios by TIMS at the University of Florence. We found a range in 87Sr/86Sr values that nearly encompass that of Iceland magmas at the Eyjafjallajökull latitude (Sigmarsson et al., 2008, Jökull, 58), with the exception of some higher values which seem to be correlated with the phase of eruption and/or with magma evolution. No correlation has been found between 87Sr/86Sr and vesicularity or microlite content of the groundmass. Magma mixing and/or mingling between a new basaltic melt and a residing evolved magma is proposed to be occurred before the explosive eruption, with end-members that changed in composition with time (Sigmarsson, 2011, G.R.A., 13, EGU2011-12589). Our data help to shed light on this hypothesis and on the eruption dynamics, although they also highlight a more complex plumbing system.
Scalera (2007, 2008) using the data available in 2006 in the Smithsonian Institution Catalogue of volcanic eruptions revealed evidence that South-American Wadati-Benioff zone earthquakes with $M > 8.4$ are associated to enhanced rates of volcanic eruptions. The occurrence of the Chilean Maule earthquake of 27 February 2010 ($M = 8.8$) has been the occasion to rework all the data adopting a non-compression framework of mountain building. This framework suppose a common secular process involving the complete South American Pacific margin linked to TPW. Indeed, in the expanding Earth schema both PM and TPW are explained by assuming an emplacement of mass in the Southern Hemisphere on the Nazca region. The TPW path through geological time is then naturally linked to the slow displacement of the region of maximum planetary expansion.

Passing from the older Andean volcano-seismic correlation events to the 2010 one, it is clear the trend - as soon as the data have become more precisely located on the time axis - of an enhanced rate of eruptions before the main seismic event.

The 1868 event – In this case data were collected only by visual witness, listening inhabitant of localities nearest the volcanic apparatuses or people passing for a direct inspection. The date of the eruptions may be confused with the observation date, displacing the event many months ahead and possibly one or more years ahead. The peak of eruptions after the quake, can be then an artifact.

The 1906 event – This event is a pair of great earthquakes (Ecuador, January 31; $M = 8.8$; Chile, August 16; $M = 8.4$) that occurred in the same year separated by very long distance. Only the southern district appears to have a peak of eruptions correlated to the earthquakes. The maximum is one year after the seismic event but the growing of the eruptions’ amount starts in the same year of the quake. Then the real distribution on the time axis must be different and considering the reasons explained above in the preceding 1868 case, some of the real onsets could be occurred many months before and also one year before.

The 1960 event – The earthquake occurred (1960, Chile, $M = 9.5$) in the times of more modern scientific instrumentations and surveying facilities (quick transportations, airplanes, helicopters). This time the maximum eruption rate is in the same year and the growing of the rate starts before the quake occurrence.

The 2010 event – This time all the onset date of the eruptive events are known thanks to modern surveillance methods. The rate of eruptions occurred in the northern and southern volcanic district increased from one-two erup/year to five in 2009 and we expect that an enhanced rate will be revealed until the end of 2010. The northern volcanic district was active in 2007-2009, while the central district did not contribute to the constitution of the volcano-seismic correlation event. There is then a precursory behavior of the northern and southern volcanic activity in this case.

Moreover, a possible synchronicity should be considered. If on the same plot both the secular polar motion (from 1846 to 2009) and the time of occurrence of the volcano-seismic events of correlations are represented, it is possible to see: i) Only three volcano-seismic events, 1906, 1960 and 2010, can be correlated to the series of PM data 1846-2009. ii) The PM data preceding 1900 are not homogeneous with the 1900-2009 ones. iii) The events of 1960 and 2010 occur about 12 years after a five-years window of ‘stasis’ of the secular PM (a very low velocity, witnessed by the extreme proximity of the annual averaged points in the plot). Albeit the data are not against the same mutual pattern between the event of 1906 and the PM data of the last decade of the XIX Century, the non-homogeneity of data do not allow a positive conclusion. iv) To ascertain the reality of this synchronism with the Markowitz oscillation of PM, a greater amount of volcano-seismic events is needed.
The Sesia magmatic system allows direct study of the links between silicic plutonism and volcanism in the upper crust and the coeval interaction of mafic intrusions with the deep crust. In this talk we focus on the chemical stratigraphy of the pre-intrusion crust, which can be inferred from the compositions of crustal-contaminated mafic plutonic rocks, restitic crustal material incorporated by the complex, and granitic rocks crystallized from anatectic melts.

These data sources independently indicate that the crust was compositionally stratified prior to the intrusion of the Mafic Complex, with mica and K-feldspar abundance decreasing with depth and increasing metamorphic grade of the restites. Reconsideration of published zircon age data suggest that the igneous evolution initiated with sporadic pulses at around 295 Ma, when mafic sills intruded deep granulites which provided a minor amount of depleted crustal contaminant. At increasing rates of the intrusion, between 292 and 286 Ma, mafic magmas invaded a significantly more fertile crustal level, consisting of amphibolite-facies paragneisses, so generating hybrid rocks with distinct chemistry. At this point, advanced anatexis produced a large amount of silicic hybrid melts that fed the incremental growth of upper-crustal plutons and volcanic activity, while the disaggregated restite was largely assimilated once ingested by the growing Mafic Complex.

This “igneous climax” was coincident with an increasing rate of intrusion, when the upper Mafic Complex began growing according to the “gabbro glacier” model and, at about the same time, volcanic activity initiated. In conclusion, the fertility of “under/intra-plated” crust plays a crucial role in governing the generation of large volumes of continental silicic magmas.
LONG-TERM VS. SHORT-TERM GEOCHEMICAL CHANGES OF MT. ETNA LAVAS: THE PUZZLING EFFECT OF A VARIEGATED MANTLE

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Mt. Etna volcano fascinated the scientific community during the last decades due to its unusual geodynamic location and geochemical signature of the erupted lavas. Although the edifice is placed above the front of a compressive regional tectonic setting, volcanic products have a marked intraplate signature. The volcano has shown a complex geochemical variability during the half-million years of life, with sub-alkaline products erupted during the early stage of volcanism up to < 220 ka ago, then followed by a Na-alkaline stage. The alkaline stage displays long-term geochemical variations, as a result of evolutionary processes acting at various levels of the feeding system. The Etnean lavas also exhibit short-term changes in some periods. For example, an increase in some LILEs and volatiles together with marked changes of the Sr-Nd-Pb-Hf isotope ratios are observed since the 1971 (Viccaro & Cristofolini, 2008; Viccaro et al., 2011). Mt. Etna can surely be considered as one among the most studied volcanoes on Earth, although the features of the source are still matter of discussion. The absence of mantle material (xenoliths), which is efficiently fractionated in the deep levels of the feeding system, makes more intricate the picture. Thus, indirect information can be only attained from magma compositions. The behavior of incompatible trace elements for mantle-equilibrated magma compositions of the Ellittico (60-15 ka) and Recent Mongibello (15 ka-present), and of their enrichment ratio show that the Etnean magmas are produced by a variable, low degrees of partial melting. The enrichment ratio also reveals that magmas can be generated from a classic garnet peridotite variably enriched by metasomatic mineral phases (amphibole-phlogopite). The Zr/Nb vs. Ce/Y and Ba/Th vs. Lu/Hf diagrams highlight the enriched signature of the Etnean mantle. The Zr/Nb vs. Ce/Y diagram evidences the progressive contribution of metasomatic phases with time. The Ba/Th vs. Lu/Hf diagram shows the short-term coupled increase of the contribution by metasomatic agents and partial melting degree during the last 400 years of volcanic activity. In terms of mantle components, the integration of Sr-Nd-Pb-Hf isotopic ratios suggested that FOZO is the dominant component in the Etnean source (Viccaro et al., 2011). However, the FOZO component is not able to fully account for the isotopic changes from the Ellittico to Recent Mongibello magmas. Indeed, the isotopic compositions of the Ellittico and Recent Mongibello volcanic products can be explained by addition of an EM1-type component (up to 10%) to a dominant FOZO. The integrated analysis of Sm/Hf and Th/Hf ratios, together with Hf isotope ratios, gives evidence that the enriched component may be metasomatizing silicate melts. Long-term vs. short-term compositional changes at Mt. Etna are here related to partial melting of a recycled, altered oceanic lithosphere, infiltrated by metasomatizing silicate melts. Variable amounts of the enriched component participating to partial melting are able to affect its degree and the geochemical signature of the produced magmas.

Sessione tematica J2:
Il patrimonio mineralogico italiano

Conveners:
Cristian Biagioni (Università di Pisa)*
Marco Ciriotti (Associazione Micromineralogica Italiana)
Mn-rich tourmalines, structurally and chemically characterized by Bosi et al. (2005), occur in a druse of aplitic dike from Grotta d’Oggi (Elba Island), associated with quartz, K-feldspar, plagioclase, elbaite, and schorl. Among these Mn-rich tourmalines, one sample (Tsl2g) could be considered as a new species in agreement with the recommendations of Henry et al. (2011). In fact, the ordered empirical formula of this sample, approximated as $\frac{x}{3}(Na_{0.67}\square_{0.33})^y(Mn^{2+}_{1.34}Al_{1.14}Li_{0.52})^zAl_9(Si_6O_{18})(BO_3)_3^v(OH)_3^w(F_{0.41}OH_{0.39}O_{0.20})$, is consistent with a $^zAl$-dominant tourmaline belonging to the alkali-subgroup 1: Na-dominant at the X position and OH+F > O$^{2-}$ at the W position of the general formula $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$.

As the content of Mn$^{2+}$ is larger than that of 2Li$^+$ at the Y position (1.34 and 1.08 apfu, respectively) and because no tourmalines have yet been documented as $^yMn^{2+}$-dominant, this tourmaline could be classified as a new species. As the OH and F contents at W are statistically equal, 0.39±0.16 and 0.41±0.02 apfu (respectively), the correct name can be assigned on the basis of inverse correlation between F and Mn$^{2+}$. As such a correlation indicates that the F content decreases with increasing Mn$^{2+}$, the excess of O$^{2-}$ at the W position can be related to the substitution $^{v}Al^{3+} + ^wO^{2-} \leftrightarrow ^yMn^{2+} + ^wOH^{-}$ rather than to $^{v}Al^{3+} + ^wO^{2-} \leftrightarrow ^yMn^{2+} + ^wF^{-}$. Through the former substitution, $^wO^{2-}$ is replaced by $^wOH^{-}$ (as well as $^{v}Al^{3+}$ by $^{y}Mn^{2+}$) giving a composition $\frac{x}{3}(Na_{0.7}\square_{0.3})^{y}(Mn^{2+}_{1.5}Al_{0.8}Li_{0.5})^{z}Al_9(Si_6O_{18})(BO_3)_3^v(OH)_3^w(OH_{0.6}F_{0.4})$ that falls in the hydroxyl subgroup with $^wOH > ^wF$.

Minor constituents can be related to the substitutions $^vNa^{+} + ^yMn^{2+} \leftrightarrow ^v\square + ^yAl^{3+}$, $2^vMn^{2+} + ^wOH^{-} \leftrightarrow ^y(Al^{3+} + Li^{+}) + ^wF$ and $2^yMn^{2+} \leftrightarrow ^y(Al^{3+} + Li^{+})$, which would lead to the end-member composition NaMn$_3$Al$_9(Si_6O_{18})(BO_3)_3(OH)_3$OH.

Wakefieldite-(Y) was first reported in quartz cavities from a zoned granite pegmatite of the Evans-Lou quarry [near Lac Saint-Pierre (Wakefield Lake), Val-des-Monts, Québec, Canada] as canary-yellow to tan pulverulent masses intimately associated with hellandite-(Y), quartz, kainosite-(Y), montmorillonite, thorogummite, Y-bearing fluorapatite, fine grained xenotime-(Y), and some unidentified compounds (Miles et al., 1971). The definition was based on X-ray powder diffraction (XRPD) and spectrographic chemical data obtained from a mixture of the new mineral with quartz, “hellandite”, kainosite-(Y), and montmorillonite. Following the identification in the XRPD pattern by comparison with synthetic YVO₄, the authors assigned yttrium (Y) dominancy to the chemical composition of the new species. This assignment was not obvious because in the studied mixture hellandite-(Y) and kainosite-(Y) were Y-bearing species too. Other three world finds of wakefieldite-(Y) are known, but all of them are verified by microprobe SEM-EDS tests only.

Wakefieldite minerals and dreyerite represent the vanadate members of a group of minerals with zircon-type structure that includes also arsenates [chernovite-(Y)], borates (behierite and schiavinatoite), chromates (chromatite), phosphates [pretulite, xenotime-(Y), and xenotime-(Yb)] and silicates (coffinite, hafnon, stetindite, thorite, thorogummite, and zircon).

Wakefieldite-(Y), with approximate composition (Y₀.₄₅Nd₀.₁₅Ce₀.₁₅Ca₀.₁₅Th₀.₁₅)(V₀.₉₂As₀.₀₈)O₄, is now reported as small group of vitreous reddish-brown microcrystals (up to 0.15 mm in size); the garnet-like crystals with tetragonal bipyramid faces were implanted on quartz-calcite matrix and associated with tilasite (or, possibly, svabite), hematite, and montmorillonite, from an abandoned Fe- and Mn-ores mine located at Borgata Oberti, Montaldo di Mondovì, Cuneo, Piedmont, Italy. The mine was operated since 1855 for about one century extracting Fe- and Mn-ores (Kolitsch et al., 2011). Due to the paucity and tiny dimensions of the available material, only semi-quantitative energy-dispersive electron-microprobe analysis could be carried out on unpolished crystals. The semi-quantitative data unambiguously indicate Y > Nd ≈ Ce ≈ Ca ≈ Th and V by far higher than As; minor quantities of La and Gd were detected. X-ray single-crystal diffraction data for wakefieldite-(Y) were collected on an Oxford Gemini R Ultra diffractometer equipped with a CCD area detector (50 kV, 40 mA; graphite-monochromated Mo Ka radiation). The zircon-type crystal structure (space group I₄₁/amd; a = 7.2591 Å, c = 6.4255 Å) has been refined (R = 0.017 for 175 independent reflections) using X-ray diffraction data collected on a crystal from this locality. That confirms the validity of the species which previously had been only roughly defined using an impure pulverulent sample from Wakefield Lake (Québec, Canada). The substantial (30%) joint replacement of Ca²⁺ and Th⁴⁺ for Y³⁺ in the present wakefieldite-(Y) expands the cell volume of pure YVO₄ and could anticipate the existence of minerals with zircon-type structure and A²⁺A⁴⁺T⁵⁺O₄ composition.

A NEW MINERAL WITH A PYROCHLOR-RELATED STRUCTURE FROM EUGANEI HILLS, PADOVA (ITALY)

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The mineral was found by Mr. B. Fassina at Monte delle Basse, Euganei Hills, Galzignano Terme, Padova (Veneto, Italy) in millimetric secondary vugs of a sanidine-bearing rock. These sanidinites are xenoliths hosted by calc-silicate rocks metamorphosed by the intrusion of syenite-gabbros. Calc-silicate rocks are formed by wollastonite, gehlenite, gyrolite, hibschite, kilchoanite, pectolite, rankinite, and sanidine. The new mineral forms fan-shaped groups of platy crystals, a few microns in thickness, brown-orange in color, and up to one millimeter in length. Minerals associated are colorless to grey titanite and dark yellow to dark brown hibschite garnet.

Electron microprobe analyses yield the empirical formula

(Ba₁₋₀.₉₃Ca₁₋₀.₂₀Sr₀.₅₃Na₀.₂₅Fe²⁺₀.₁₀)Σ₄.₀₁(Nb₂.₈₇Ti₂.₀₅Ta₀.₀₇Zr₀.₀₁V⁵⁺₀.₀₁)Σ₅.₀₁SiO₁₇[(P₀.₁₃Si₀.₁₂S₀.₀₇)O₀.₆₄(OH)₀.₆₄]F₀.₀₉(OH)₀.₂₇[O₋₀.₃₆,
on the basis of (1₈₊₂ₓ)(O,F) pfu with x = [P+S+(Si-1)] < 0.₅ apfu.

Single-crystal X-ray studies show that the mineral is orthorhombic, space group Fmmm, with a = 7.₄₁₀₅(₄), b = 2₀.₆₇₆₅(₁₁), c = 2₁.₄₄₇₁(₁₁) Å, V = 3₁₈₉.₅(₅) Å³ and Z = ₈. The structure was solved using Superflip. Weighted full-matrix least-squares refinement on F² was performed using SHELX 97. The structure consists of a framework of Nb(Ti)-octahedra and BaO₇(2+) polyhedra sharing apexes or edges, and isolated Si tetrahedra sharing apexes with Nb(Ti)-octahedra and BaO₇(2+) polyhedral. There are three Nb(Ti)-octahedra, two of them are Nb dominant and one is Ti dominant. Chains of CaO₈ octahedra extend along [1₀₀] and are surrounded by Nb-octahedra. There are channels formed by six Nb(Ti)-octahedra and two tetrahedra, or four BaO₈ polyhedra, alternating along [1₀₀]. The channels are partially occupied by [PO₄(OH)]₂ in two mutually excluding positions, alternating with fully occupied Ca(Na)O₇ polyhedral pairs. Each P atom at the P sites of the [PO₄(OH)]₂-groups is coordinated with two (OH) groups and two different pairs of oxygen atoms, which are mutually exclusive, depending on the P site occupancy. Therefore, in terms of formula normalization, if the P site is vacant it means that there are 17 oxygen atoms per asymmetric unit plus one (OH) group, i.e. 1₈ anions. An occupation of the P site of x requires 2x additional oxygen atoms present. Thus, the total amount of anions is (1₈₊₂x), being x the occupation of the P site [i.e., P + S + (Si-1)]. x cannot be > 0.₅, and therefore the maximum quantity of anions is 1₉ pfu.

The observed structure is related to the pyrochlore structure with the addition of a slab of Si₃O₉ [PO₄(OH)]₂[O₋₀.₅] every 0.₅ b translation parallel to [1₁₀] of pyrochlore. Other pyrochlore-related structures have been described, although they have alternate one [K-nénadkévichite (Na,K)(Nb,Ti)₃Si₂O₇] (O,OH)₂ 1.₆ H₂O], two [fersmanite (Ca₅₋₀.₄Na₂₋₀.₇Sr₀.₀₈Fe₀.ₐ₁(Nb₀.₈₁Ti₂.₉₉)Si₂O₇)₂O₈F₃], or three [Na-komarovite Na₅₋₀.₅Ca₀.₈La₀.₂Ti₀.₅Nb₅₋₀.₅Si₄O₂₆F₂ H₂O] octahedra-thick (1₀₀)-pyrochlore slabs with (SiO₄) groups showing different degrees of polymerization (four-membered rings being the most frequent unit). This new structure thus represents a novel type of pyrochlore-related structure, which includes further anionic groups other than (SiO₄).
THE OCCURRENCE OF LAFOSAITE AT VESUVIUS

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As a part of a joint project concerning the study of fumarole minerals of the Italian volcanoes, carried out in collaboration with the Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano, a systematic investigation of old fumarole mineral samples was undertaken. The presence of natural thallium chloride lafossaite, first described at La Fossa crater, Vulcano Island by Roberts et al. (2006), was detected on two small samples from “Atrio del Cavallo” dated 1906 and obtained together with other fumarole material from an old collection belonging to the “Istituto Geomineralogico Italiano”, a mineral-dealer society active in the ‘20s of the past century.

In our samples lafossaite forms small aggregates of colorless cubic crystals, up to 0.05 mmm, associated with realgar, dimorphite in small orange-yellow crystals, anhydrite, and an unknown thallium mineral containing S, Cl, K, As. Differently from that of Vulcano, lafossaite from Vesuvius contains only small amounts of bromine. The unit-cell parameters obtained by least squares method from X-ray powder diffraction are also in good agreement with those of pure TlCl.

NEW MINERAL SPECIES FROM VULCANO, AEOLIAN ISLANDS, SICILY, ITALY

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Since 2006 Vulcano Island was the object of a joint project concerning the study of fumarole minerals of Italian volcanoes, carried out in collaboration with Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano.

At present, the mineral species found at Vulcano are over 100; the island is the type locality for 23 species, 17 of which were discovered by us, and it is the unique occurrence for 20 of them. Besides the already IMA-approved “official” species, there are at least 38 potentially new minerals currently under examination. By far the main occurrence for these minerals are the fumaroles located at La Fossa crater which provide especially halides (fluorides, chlorides) and sulfides/sulfosalts, together with abundant native sulphur and boric acid; there are however other localities, which are especially rich in sulfates, a few of them very rare and interesting. Another interesting locality is the “Grotta dell’Allume”, a partially collapsed cavity whose walls are completely encrusted by sulfates of different colour.

In spite of the lowering of temperature of the fumaroles with respect to 1990, our research in 2006 provided remarkable specimens of very interesting and new mineral species. The most important of these are the thallium lead chloride hephaistosite, TlPb2Cl5, and three rare fluorides such as demartinite, K2SiF6, knasibfite, K3Na4[SiF6]3[BF4], and thermessaite, K2[AlF3][SO4]. As a result of further trips to the island, considerable additions to the list of new minerals were made. These include a new series of sulfohalides: demicheleite-(Cl), demicheleite-(Br) and demicheleite-(I), BiSX (X = Cl, Br, I), the lead-ammonium chloride brontesite, (NH4)3PbCl5, as well as other interesting chlorides such as panichiite, (NH4)2SnCl6, and steropesite, Tl3BiCl6, and the sulphates aiolosite, Na2(Na2Bi)(SO4)3Cl, adranosite, NaAl2(NH4)4(SO4)4Cl(OH)2, and pyracmonite, (NH4)3Fe(SO4)3. Additional species recently approved by IMA are cossaite, (Mg0.5)Al6(SO4)6(HSO4)F6·36H2O, aluminocoquimbite, AlFe(SO4)3·9H2O, clinometaborite, HBO2 and adranosite-(Fe), NaFe2(NH4)4(SO4)4Cl(OH)2.
ELECTRON MICROSCOPY INVESTIGATION OF A FLOWER-LIKE MINERALIZATION ON Bi-SULFOSALTS FROM ALFENZA (CRODO): A NEW Bi HYDRATED SULFATE?

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A flower-like mineralization of white, micrometer-sized crystallites, occurs on Bi sulfosalts from the Alfenza Mine (Crodo). Each single crystal is hardly resolvable using a standard optical stereomicroscope. At the scanning electron microscope (SEM), the crystallites show perfect, pseudo-hexagonal, randomly oriented platelets forming a hemispheric aggregate up to several tens of microns in radius. The EDS spectra show distinct S, Bi, O peaks, pointing to a Bi sulfate (or Bi hydrated sulfate). As far as we know, only two natural phases, cannonite, [Bi₂O(OH)SO₄], and riomarinaite, [Bi(OH)SO₄·H₂O], have been reported with a composition that qualitatively match the observed one. However, available physical properties for these minerals (habit, color, cleavage…) do not match with those observed in our case.

In order to solve the puzzle, few mineral aggregates were peaked up with a knife tip, dispersed in ethanol, ultrasonicated, and pipetted on a holey-carbon Cu grid for TEM analyses. Preliminary results show a Pmnm projected symmetry down the pole of the pseudo-hexagonal platelets consistent with a monoclinic or orthorhombic system, 2D cell parameters $a = 17.2(4)$ Å and $b = 15.9(3)$ Å, ($\gamma = 90^\circ$), and systematic absences consistent with a 2₁ screw along the $b$-axis.

A comparison of the observed electron diffractions with those simulated for (synthetic) cannonite and riomarinaite reveals substantial differences, excluding these two phases as possible and opening to the possibility for a new mineral. Deeper investigations are in progress.
SrV₃O₇·4H₂O, A NEW MINERAL FROM MOLINELLO MINE, VAL GRAVEGLIA, EASTERN LIGURIA, ITALY

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The sample containing the new mineral SrV₃O₇·4H₂O was collected at the Molinello mine, Val Graveglia, Eastern Liguria, Northern Apennines, Italy. In the Val Graveglia mines, Mn ores occur as braunite-bearing layered massive lenses, and boudins near the stratigraphic base of the cherts of the “Diaspri di M. Alpe” Formation, overlying ophiolitic basement (Cabella et al., 1998). Mineralizations are characterized by a braunite + quartz association equilibrated under prehnite-pumpellyite facies conditions (Cortesogno et al., 1979; Lucchetti et al., 1990) during the tectono-metamorphic evolution which affected both ophiolites and cherts. Hydrothermal fluid circulation along later extensional fractures, at decreasing metamorphic conditions, induced the concentration of dispersed elements such as As, Ba, Cu, Sr, and V and the precipitation of great variety of uncommon minerals. The new mineral SrV₃O₇·4H₂O was found in association with rhodonite, pyroxmangite, quartz and braunite.

Electron microprobe analyses carried out on the same crystal used for the structural investigation led to the following empirical chemical formula: (Sr0.97Ca0.02Na0.01)V₃.00O₇·4H₂O. H₂O was calculated by stoichiometry from the results of the crystal-structure analysis and its presence was confirmed by Raman spectroscopy.

SrV₃O₇·4H₂O is monoclinic, space group P2₁/m, with a = 5.313(3), b = 10.495(3), c = 8.568(4) Å, β = 91.14(5)°, V = 477.7(4) Å³, and Z = 2. Its crystal structure [R = 0.0209 for 1148 reflections with Fo > 4σ(Fo)] consists of layers of VO₅ pyramids (with vanadium in the tetravalent state) pointing up and down alternately, with Sr between the layers (in nine-fold coordination). The mean bond distance for the VO₅ pyramids (range 1.871-1.906 Å) is in excellent agreement with those observed for synthetic AV₃O₇ (A = Ca, Sr) V⁴⁺-oxovanadates (Prinz et al., 2007). Despite the fact that the hydrogen atoms were not located in the difference Fourier maps, bond valence calculations clearly indicate that three oxygen atoms belong to water molecules which assure linking between the layers. The similarities of the crystal structure of SrV₃O₇·4H₂O with that of the anhydrous mineral cavoite, CaV₃O₇ (Basso et al., 2002), will be discussed.


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Monoclinic churchites (formerly “weinschekite”) are members of the gypsum supergroup, which includes the phosphates brushite, Ca(PO$_3$OH)·2H$_2$O, and churchite-(Y), Y(PO$_4$)·2H$_2$O, the sulfate gypsum, Ca(SO$_4$)·2H$_2$O, and the arsenate pharmacolite, Ca(As$^5+$O$_3$OH)·2H$_2$O. A mineral, which is included in the IMA list of the valid species as Rn (renamed) was described by Podporina et al. (1983) and considered the Nd-dominant member of the churchites. Instead, the chemical data in the above paper clearly demonstrate that the natural phase (“n. 2 Nd-churchite from Kazakhstan”) is only a Nd-bearing variety of churchite-(Y). So the first, and at today the only, described occurrence of churchite-(Nd) is not correct and the validity of the species (based on the paper by Podporina et al., 1983) must be reconsidered and discredited.

All the members of the gypsum supergroup has an isotopic layer structure, the layers being parallel to (010) face. The two sheets of sulfate ions are intimately bound together by calcium ions so as to form a strong double sheet. These double sheets are separated by sheets of water molecules. Each calcium ion is eight-fold coordinated by six O atoms, belonging to sulfate groups, and by two water molecules. The arrangement of the square-antiprismatic CaO$_8$ groups and the sulfate tetrahedra consists of centrosymmetric pairs of chains along [101]. The tetrahedral sulfate group is not regular.

Due to the paucity and the micrometric size of the elongated needle crystal aggregates, a diffraction for the new find of the natural Nd(PO$_4$)·2H$_2$O, from Costa Balzi Rossi (Magliolo, Savona, Liguria, Italy) was not possible. The two specimens in which churchite-(Nd) occurs, always on xenotime-(Y) crystals, were used, the first for chemical analysis (semi-quantitative energy-dispersive electron-microprobe analysis on unpolished crystals) and the second for a Raman spectroscopy.

The analytical results demonstrate the Nd-dominance on all REE and also on Ca and Sc. The stoichiometric formula (O = 4) is: $(Nd_{0.31}La_{0.11}Sm_{0.10}Pr_{0.07}Ca_{0.05}Y_{0.05}M_{0.31})_2(PO_4)·2H_2O$ (where $M$ is the sum of all other REEs and Sc, Al and Fe for which the values are between 0.04 and 0.01 apfu).

The comparison with the Raman spectrum of churchite-(Y) (Frost et al., 2010) would seem to be confirmed as Nd-dominant churchite. A similar comparison is provided with the synthetic Nd(PO$_4$)·2H$_2$O.

Costa Balzi Rossi is a recently discovered well known locality in which the following REE minerals were found: aeschinite-(Y), allanite-(Ce), bastnäsite-(Ce), churchite-(Y), fergusonite-(Y), monazite-(Ce), paranite-(Y), thortveitite and xenotime-(Y) (Balestra et al., 2011).

If the IMA CNMNC will recognize the invalidity of the Kazakhstan occurrence, Costa Balzi Rossi should be the type-locality of the actually first natural churchite-(Nd).
THE HISTORY OF THE DISCREDITED MOHSITE

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Mohsite is a discredited mineral, and is now recognized as a member \( i.e. \) crichtonite of the sénaitecrichtonite series, but the history of its description and identification is of notable interest for the mineralogy of the Susa Valley. The authors had the opportunity to examine and investigate the samples of “mohsite” described by Colomba, an Italian eminent mineralogist, in 1902. These samples were lost during years and found again some years ago, after more than a century, in the historical mineralogical collection of the Turin University, now in the Piedmont Council Museum of Natural Science of Turin. These new analysis proves that the mohsite of Colomba has a high Sr content, and should thus be identified as crichtonite.

Mohsite was first reported by Lévy in 1827, on material probably from the Dauphiné Region, in France. The chemical composition was unknown, and the description was mainly morphological. The original samples of Lévy was never traced again. In 1901 Lacroix found some other samples in the Haute Alpes, again in the Dauphiné. This material was not chemically analyzed because of its very small amount but, being these samples morphologically similar, they became neotype.

In 1902 Colomba found similar material from near the Dora Riparia, Oulx, Italian Alps, some ten km from the previous locality but in the Italian sector of the mountain chain. Some qualitative analysis performed at that time showed that the samples contained titanium and iron, as well as small quantities of Ca and Mg, and for this reasons Colomba identified these small black crystals as mohsite.

Kelly et al. (1979) obtained a sample of Lacroix’s specimen from the Museum National d’Histoire Naturelle of Paris, and they found that the main cation was Sr; consequently, they identified the samples as crichtonite, and in the same time discredited the name “mohsite” due to temporal priority of the name “crichtonite” (De Bournon, 1813).

The authors, as a consequence of the rediscover of the Colomba’s samples, used these 1902’s specimens for SEM-EDS and micro-XRF analysis, and found that the small crystals were made of a complex oxide of titanium, iron, and vanadium, with Sr as the main bivalent cation, followed by Y and small amount of U and Yb. The formula of this oxide as mean of many analysis could be written, as \((\text{Sr}_{0.9} \text{Y}_{0.7} \text{U}_{0.2} \text{Yb}_{0.1})(\text{Ti}_{13.7} \text{Fe}_{7.3} \text{V}_{0.3}) \text{O}_{38}\) on the basis of 38 oxygens. This formula is close matching with the one of crichtonite \((\text{Sr}, \text{Y}, \text{U}, \text{Yb})(\text{Ti}, \text{Fe}, \text{V})_{21} \text{O}_{38}\), the Sr-bearing term of the group (the other important terms being sénait if Pb is the main large cation, davidite for REE, landauite for Na, and loveringite for Ca).

Thus, the mohsite of Colomba is actually a sample of crichtonite, and probably Colomba may have misidentified Ca with Sr in the old analysis, or these analysis were performed on dirt samples with interference from others minerals.
THE MT. MAZZOLU QUARRY: A NEW MINERALOGICAL LOCALITY

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Sardinia, due to its “geo-diversity”, is rich of mineralogical localities. The minerals are mostly related to hydrothermal and/or pneumatolitic processes which mainly affect the low-grade metamorphic basement and the tertiary volcanites. The minerals associated with the granites of the Corsica-Sardinia Batholith are less known for their scarce economic relevance. However, the Batholith hosts a large variety of rare minerals related to the pegmatitic stage. Recently, detailed works allowed to discover new mineralogical sites with rare minerals (Gamboni & Gamboni, 2006). This note focuses on the Mt. Mazzolu quarry, a location where several species of minerals, including some rare varieties, occur because related to the chemistry and to the emplacement level of the intrusion.

Among the plutons until now identified, the Arzachena intrusion is the largest. It crops out in the north eastern sector of Sardinia and has a roughly ellipsoid shape, elongated NW - SE. Recent works (Casini et al. 2008; Oggiano et al., 2005) allowed to identify the bulk geometry of the pluton, as well as its internal architecture. The apical zone was identified around the Mt. Mazzolu area, where the magmatic flow markers describe some circular trajectories matching the inferred shape of the pluton shell. This area is characterized by widespread pegmatitic pockets, aplitic dikes, wall-rock xenoliths, and biotite schlieren. The relatively low confining pressure and the occurrence of structural traps allowed the formation of pegmatitic pockets where centimetric quartz, K-feldspar, plagioclase, and “biotite” crystals occur. Accessory minerals are: allanite-(Ce), babinstonite, bavenite, calcite, chabazite-Ca, clinozoisite-epidote series, epidote, fluorapatite, fluorite, “garnet” (almandine-spessartine), goethite (resulting from the weathering of pyrite), graphite, heulandite-Ca, laumontite, magnetite, molybdenite, monazite-(Ce), muscovite, opal, prehnite, “pumpellyite”, pyrite, rutile, stilbite-Ca, titanite, and zircon. Kaolinite, montmorillonite and some minerals of the chlorite group results as alteration products.

The apical zone of the Arzachena intrusion, due to the widespread occurrence of pegmatites, is a new noticeable site for the occurrence of rare minerals of naturalistic and scientific relevance.


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The Istituto Nazionale di Geofisica e Vulcanologia, sezione di Napoli - Osservatorio Vesuviano began actions for the acquisition (by donation) of the mineral collection of Mariano Carati, Neapolitan collector of Somma-Vesuvius minerals. The collection, set up in about forty years, consists of both personal findings and acquisitions of parts of existing collections, such as the important one (60 samples) of Antonio Parascandola, who was professor of mineralogy at the faculties of Science and Agriculture at the University of Naples, and the one (27 samples) of Roberto Palumbo, a well known Roman collector, as well as of specimens got by exchange with other collectors.

The collection consists of 444 mineral specimens of great scientific value, four medallions of lava, two lava samples incorporating a coin, two cases containing thin sections of minerals, one of which belonged to Eugenio Scacchi, professor of mineralogy at the University of Naples and son of the famous Arcangelo, “the father of mineralogy of Vesuvius”, and another belonged to Ferruccio Zambonini, mineralogist known throughout the world and great scholar of Vesuvius mineralogy, and other rarities from the world of mineralogy. Samples of minerals found by Carati were collected in a period between 1970 and 1994, mostly in quarries and ravines of the volcano Vesuvius.

The collection includes about 130 of the 230 mineral species currently known at the Somma-Vesuvius. Extremely rare species are represented: aphthitalite, avogadrite, bassanite, cotunnite, hematite, euchlorine, haiüyne, lazurite-“lapis lazuli”, litidionite, magnesioferrite, malladrite, millerite, rimneite, vesuvianite, and others.

Many of the minerals of the Carati collection are not present in the section “Vesuvius minerals” of the prestigious Museum of Mineralogy of the University of Naples; for this reason, with this acquisition, the museum of the Vesuvius Observatory aims to become a valuable complement of the major Neapolitan museum, in the field of mineralogy.

Examples of such minerals are: åkermanite, albite, artroeite, chabazite-K, chrysocolla, ettringite, fluoborite, fluoro-potassicrichterite, geikielite, gismondine-Ca, hibschite, magnesite, marialite, montesommaite, natrolite, norbergite, pargasite, piypite, quadridavyne, thaumasite, thorite, tremolite, zirconolite.

The Museum of Vesuvius Observatory will display the collection in a permanent exhibition, in specifically made cabinets, using criteria inspired by educational and scientific needs of the museum itself, which has an audience mainly composed of middle and high school students.
NEW FUMAROLE MINERALS AT VULCANO: LUCABINDIITE

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Lucabindiite is a new As(III)-oxygen phase, with ideal formula \((\text{K},\text{NH}_4)\text{As}_4\text{O}_6(\text{Cl},\text{Br})\). It was found among medium-temperature fumarole encrustations \((T = 170^\circ\text{C})\) collected in 1998 during a sampling field at the “La Fossa” crater of Vulcano island, Aeolian archipelago, Italy. Individual single crystals of lucabindiite are very rare. Generally it appears in aggregates of minute, hexagonal, and platy crystals of micrometer-size (up to \(70\times70\times3\,\mu\text{m}\)) directly deposited on the surface of the pyroclastic breccia. In places, the lucabindiite aggregates appears covered by a vitreous reddish crust containing mainly sulfur and arsenic. Associated minerals are arsenolite, salammoniac and realgar.

The new phase from La Fossa crater volcano is colorless to white, transparent, non-fluorescent, has a vitreous lustre and a white streak. The calculated density is 3.679 g/cm\(^3\). Chemical analyses were obtained by SEM-EDS methods. The ammonium content was deduced from the K content, taking into account the \((\text{K},\text{NH}_4)\text{As}_4\text{O}_6(\text{Cl},\text{Br})\) stoichiometry \((\text{K} + \text{NH}_4 = 1\,\text{apfu})\). The presence of ammonium was confirmed by FTIR spectroscopy. Analytical data (in wt.%) are the following: K\(_2\text{O}\) 3.67-6.70 (average 5.14, \(\sigma\ 0.70\)), As\(_2\text{O}_3\) 80.52-88.84 (average 84.62, \(\sigma\ 2.90\)), Cl 1.90-5.81 (average 3.63, \(\sigma\ 1.41\)), Br 3.70-10.31 (average 6.92, \(\sigma\ 2.24\)), F 0.27-1.21 (average 0.77, \(\sigma\ 0.27\)), (NH\(_4\))\(_2\text{O}\) 1.72-3.13 (average 2.51, \(\sigma\ 0.35\)), O = F, Cl, Br -1.84, total 101.75. The empirical chemical formula, calculated on the basis of 5 anions per formula unit, is \([\text{K}_{0.51}(\text{NH}_4)_{0.45}\text{As}_{3.99}\text{O}_{5.93}(\text{Cl}_{0.48}\text{Br}_{0.40}\text{F}_{0.19})_{0.17}]\). The simplified formula is \((\text{K},\text{NH}_4)\text{As}_4\text{O}_6(\text{Cl},\text{Br})\); the end-member formula is KAs\(_4\text{O}_6\text{Cl}\), which requires: K\(_2\text{O}\) 10.02, As\(_2\text{O}_3\) 84.15, Cl 7.54, O = Cl\(_2\) -1.71, total 100.00 wt.\%.

Single crystal X-ray studies showed hexagonal symmetry, space group \(P6/\overline{mmm}\), with the following unit-cell parameters: \(a = 5.2386(7)\,\text{Å}, c = 9.014(2)\,\text{Å}, V = 214.23(7)\,\text{Å}^3, Z = 1\). The strongest reflections in the calculated X-ray powder-diffraction data \([d\,\text{in Å}, (I\,\text{relative to 100})]\) are: 5.20, (100); 2.62 (66.57); 4.51, (51.64); 4.54 (30.49); 1.98 (28.01); 1.485, (20.99); 1.60 (20.28); 2.26 (18.89).

The structure of lucabindiite is topologically identical to that of the synthetic compounds MAs\(_4\text{O}_6\text{X}\) \((M = K, \text{NH}_4; X = \text{Cl, Br, I})\) described by Pertlik (1988). It consists of neutral As\(_5\text{O}_3\) sheets arranged parallel to (001). Each As\(_5\text{O}_3\) sheet is formed by As\(_2\text{O}_3\) pyramids \((\text{As-O} = 1.796(5)\,\text{Å})\) connected by shared oxygen atoms. The As atoms of two neighbouring sheets point at each other and the sheets are separated by interlayer \(M = \text{K, NH}_4\) and \(X = \text{Cl, Br, F}\) atoms. The \(M\) and \(X\) atoms show hexagonal prismatic coordination with twelve oxygen atoms and twelve arsenic atoms, respectively. Refinement of the occupancy of the \(M\) site gave K\(_{0.52(4)}\text{NH}_4_{0.48}\), in good agreement with the chemical data. Occupancy of the site \(X\) was assigned as 0.5 Cl, 0.3 Br and 0.2 F on the basis of the results of chemical analyses.

The name is in honour of Luca Bindi (1971), head of the Division of Mineralogy of the Natural History Museum of the University of Florence. Both the mineral and the mineral name have been approved by the IMA-CNMMNC commission (IMA 2011-010).

NEW FUMAROLE MINERALS AT VULCANO: ADRANOSITE-(Fe)

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Adranosite-(Fe), (NH₄)₄NaFe³⁺₂(SO₄)₄Cl(OH)₂, is the Fe³⁺-analogue of adranosite and corresponds to (NH₄,K)₄Fe₂(OH)₂(SO₄)₄NaCl, an anthropogenic product recovered from a burning coal dump at the Anna mine near Aachen, Germany (http://www.mindat.org/min-38898.html). Both the mineral and the mineral name have been approved by the IMA-CNMNC commission (IMA 2011-006).

The history of the discovery of adranosite-(Fe) is curious: it was independently and simultaneously identified by the two different research groups of the University of Bari and Milano in fumarole products collected at La Fossa crater of Vulcano ( Aeolian Islands, Italy) in different years and around different high-temperature fumaroles. It’s a long time that the two research groups are intensively studying rare or new fumarole minerals from Vulcano so, after exchange of information, the researchers were happy to join the results and to work together at the characterization of the new phase.

The group of the University of Milano found adranosite-(Fe), in association with thermessaite, pseudocotunnite, and bismuthinite, on a sample collected in 2007 from fumarole F11; the group from Bari University found the new mineral, associated with barberiite, salammoniac, anhydrite, sassolite, and sulphur, in a sample collected in 1996 from the intracrater fumarolized area (IC area, T = 250°C). Besides the mineralogical association, the two occurrences mainly differ for the size of the crystals: up to 0.3 mm in the 2007 sample, micrometer-sized in the 1996 material. Due to the too small size of crystals deposited in 1996, a complete determination of the physical properties could be possible only in the 2007 sample, which was consequently considered and described as the holotype material. The occurrence of adranosite-(Fe) in both the fumarole deposits of 1996 and 2007 is related to the reaction of fumarole vapours with rocks crossed by the fluids rising to the surface.

Adranosite-(Fe) occurs around La Fossa crater fumaroles as a spray of pale-yellow, elongated, prismatic crystals covering the pyroclastic breccia. The mineral is tetragonal, space group: I₄₁/acd with a 18.261(2), c 11.562(1) Å, V 3855.5(7) Å³ and Z = 8. The strongest six reflections in the X-ray powder-diffraction pattern are: [d_{obs} in Å(I/I₀(hkl))] 9.134(100)(020), 4.569(83)(040), 3.047(79)(152), 6.462(36)(220), 3.232(29)(251) and 2.156(7)(660). The average result of chemical analyses (wt.%) is: Na₂O 5.01, Fe₂O₃ 15.77, Al₂O₃ 5.11, K₂O 0.82, (NH₄)₂O 15.76, SO₄ 50.96, Cl 3.71, H₂O 2.75, -O=Cl -0.84, for a total of 99.05. The measured density is 2.18(1) g/cm³, calculated density is 2.195 g/cm³. The mineral is uniaxial (−) with ω = 1.58(1), ε = 1.57(1) (λ = 589 nm). Using single-crystal diffraction data, the structure was refined to a final R = 0.0415 for 670 observed reflections [I > 2σ(I)]. Building blocks of the structure are FeO₆ octahedra [Fe-O in the range 1.929(1)-2.034(1) Å] and SO₄ tetrahedra, which are linked together to form spiraling chains parallel to [001], and NaO₅Cl₂ octahedra [Na-O 2.327(1), Na-Cl 2.891(1) Å], linked together by sharing the Cl corners. The ammonium ions occupy the voids in the resulting framework and interact with the Cl ions via hydrogen bonds.
Pb$_2$(CO$_3$)(S$_2$O$_3$), THE FIRST MINERAL WITH COEXISTING CARBONATE AND THIOSULFATE GROUPS FROM TRENTINI MINE, VICENZA, ITALY

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The sample containing the new mineral here described was found in the Trentini mine, Mount Naro, Torrebelvicino, Vicenza, Italy. The mine is in the Vicentine Alps metal-bearing district, exploited for lead, zinc, and silver from ancient times. From a genetic point of view, the mineralization is linked to Mid-Triassic calc-alkaline magmatism. Hydrothermal fluids related to volcanism deposited sulfides, barite, and Fe- and Mn-bearing minerals mainly at the boundary between Ladinian volcanites and carbonates of the Mount Spitz. Oxidation and hydrothermal alteration minerals are very common (Maini et al., 2000) and are represented by sulfates, carbonates and arsenates of Zn, Pb and Cu. The new mineral described here was found in association with galena, quartz, and anglesite.

Electron microprobe analyses carried out on the same crystal used for the structural investigation led to the following empirical chemical formula Pb$_{2.09}$C$_{1.05}$S$_{1.82}$O$_6$ (based on 6 O apfu), ideally Pb$_2$(CO$_3$)(S$_2$O$_3$). The presence of both carbonate and thiosulfate groups was confirmed by Raman spectroscopy.

The crystal structure of Pb$_2$(CO$_3$)(S$_2$O$_3$) consists of rods of Pb-polyhedra that extend along the [010] direction. Among such rods there are, alternatively, CO$_3^{2-}$ and the S$_2$O$_3^{2-}$ groups. The latter point alternatively left and right, considering the apex occupied by sulfur as the atom giving the direction. Pb atoms are nine-coordinated with 7 oxygen atoms (Pb-O 2.41-3.18 Å) and 2 sulfur atoms (3.22-3.31 Å). In the thiosulfate group, the central sulfur is linked to three O atoms at a mean distance of 1.48 Å and to a sulfur atom at 2.03 Å, the four anions forming a very distorted tetrahedron. Carbon makes two C-O bonds at 1.25 Å and one at 1.32 Å. Bond valence sums are 1.96 (Pb), 5.60 (S$_1$), 4.13 (C), 2.02 (O1), 2.06 (O2), 1.87 (O3), 2.11 (O4), and 1.66 (S$_2$).

To our knowledge, the new mineral here described is the third thiosulfate-bearing mineral known to occur in Nature [after sidpietersite (Roberts et al., 1999) and steverustite (Cooper et al., 2009)]. There are other two minerals which are reported to contain the thiosulfate group, bazhenovite, CaS$_5$·CaS$_2$O$_3$·6H$_2$O·20H$_2$O (Chesnokov et al., 1987), and viaeneite, (Fe,Pb)$_4$S$_8$O (Kucha et al., 1996). For bazhenovite, Bindi et al. (2005), studying the type-sample, did not detect the presence of the thiosulfate group either by structural analysis or spectroscopic investigations. Viaeneite was only poorly characterized because of the scarce amount of material available and its very low quality.

Natural Pb$_2$(CO$_3$)(S$_2$O$_3$) was found in a matrix consisting of a mixture of fine-grained minerals with a strong predominance of galena. Together with Pb$_2$(CO$_3$)(S$_2$O$_3$) it is possible also to find anglesite. Pb$_2$(CO$_3$)(S$_2$O$_3$) is considered to be secondary after galena. We suggest that thiosulfate formation occurred during an intermediate stage of oxidation as the assemblage moved toward complete oxidation and subsequent formation of sulfate (anglesite) with decomposition of galena.

A significant mineral collection was assembled by Camillo Gualteroni (1861-1908), a gentleman of means who lived in Ornica, a small town on the mountains of the Bergamo area in Northern Italy. Most of Gualteroni’s acquisitions were made between 1890 and 1900. In that year, Gualteroni married and soon had children, so his mineral activity was greatly reduced, although the collection was carefully preserved.

Gualteroni tried to obtain a sample of all the species known at the time. His collection, which today would be considered a species collection, included more than 2,000 mineral specimens; each of them was placed in a pasteboard tray with a concise external label and a neatly handwritten label with full details inside the tray. Original dealers’ labels were also saved in the tray under the specimen along with Gualteroni’s own labels.

The collection was preserved in the original state in the residence of the Gualteroni family for almost 120 years, and was completed with its catalogue and original letters from most of the European dealers and Italian collectors of that time. Various other significant mineralogical items (Gualteroni’s books, instruments, crystal models, etc.) were also kept with the collection.

The entire mineral collection, including the original cabinets, has been purchased by the Museum of Natural History of Milan from the Gualteroni family. The specimens and their labels are now being restored and studied.

The Gualteroni holdings provide a very unusual insight in the activity of a collector of that time - a real time capsule worthy of being preserved for the future generations.
From a geological point of view, the High Vicentino, i.e. the area comprising the adjacent valleys of Agno, Leogra and Posina, known as the “Recoarese”, belongs to the southernmost part of the Southern Alps (Sudalpino) and differs from all the neighboring areas due to the occurrence of the so-called “Crystalline Basement”. About 230 million years ago, in mid-upper Ladinic (Triassic), a widespread volcanism took place in this area and led to the emplacement of acid lavas, forming the rocks now outcropping in the hills that surround the Mercanti Valley (Torrebelvicino, Vicenza). This volcanic activity is at the origin of the genesis of a series of metalliferous deposits of pyrite and base metal sulfides.

The Senate of the Republic of Venice was particularly interested in searching for noble metals like gold and silver for the supply of its mint; under its rule, in the early XV Century, Venice handed the territory of Schio, exercised a careful control over the mining activities in the Vicenza area, increasing the investigations and funding cultivations. The periods of most intense mining operations covered the years ranging from 1450 to 1515. In the Sixteenth Century, with the clash between the Emperor Maximilian and the Venetian Republic (War of Cambrai, 1509-1518), began the crisis of Venetian mining with the result that one by one all the mines were deliberately closed, hidden, or abandoned. During this period, the most important mines were opened in the mountains surrounding the Mercanti Valley; they were named Sant’Alvise, Santissimo Nome di Dio, San Martino, San Marco, Sant’Isidoro, San Giacomo, Madonna del Rosario, Beata Maria Vergine, etc. A lot of different minerals can be found in these localities. For example, Monte Trisa is the type locality of cerussite and montetrisaite and studies are under way on possible new species.

In the early ’500, two technological innovations were implemented for the first time in the world: i) in 1507 the use of amalgam to separate the silver from other minerals; ii) in 1572 the use of gunpowder to break the rock in the tunnels.

Vannoccio Biringuccio from Siena, who lived for more than two years in Veneto, wrote that in the mining district of Schio a new system to separate the silver was in use: “the amalgamation”.

The merit of this innovative technique is due to two Veronese men, Ioannes Antonius De Mauris and Thomaso de Cusano, who, on January 19th, 1507, wrote to the Consiglio dei Dieci a plea for a twenty-five years deprivation in some mines of the Schio mining district, petition granted on January 30th, 1507. According to literature, the amalgamation was first introduced in Europe around 1613 in Freiberg (Saxony, Germany) by Martin Weigold; this is the prevailing version, but according to others its use began in 1627 in Schemnitz, present-day Banská Štiavnica in Slovakia.

The documentation at the Archivio di Stato of Venice confirms undoubtedly that in December 1572, in the Schio mining district, in the mines owned by Giovanni Battista Martinengo, the use of gunpowder in the tunnel to break the rocks was current. Unfortunately, these two important innovations, for some unknown reason, are not reported in the major publications.
MINERALOGICAL HERITAGE AND ENHANCEMENT OF THE ABANDONED MINING SITES IN SARDINIA

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In recent decades, the birth of Geoparks focused the need to protect and enhance the abandoned mining heritage. In the experience of the Authors, the knowledge of the mineral species in the abandoned mining sites, in terms of study and scientific disclosure, can provide a great contribution to their enhancement. In scientific and popular ambit good results were obtained in the past twenty years, which led to the definition of new mineral species and the publication of valuable monographs. This justifies the possibility of a regulated access to the collection and study of minerals in the abandoned mining areas, even to amateur mineralogists. The present study compares the increase of knowledge of the mineralogical species from some “classic” sites with others until recently nearly forgotten, precisely thanks to the collaboration between professional and amateur mineralogists.
The 1944 eruption of Vesuvius began on March 18th and ended on the 29th of the same month. It was the last eruption of Vesuvius and marked the transition from an open conduit to a closed conduit state.

The eruption took place during wartime so that nobody was interested to sample fumarolic minerals before and after the eruption. The only mineralogical work was made by Parascandola (1951), but most interesting were his comments on the temperature of the fumaroles and his observations about fumarolic minerals in the period between 1947 and 1960. Parascandola indicated the presence of about ten mineral species found on the fumaroles.

As a part of a joint project concerning the study of fumarole minerals of the Italian volcanoes, carried out in collaboration with the Università degli Studi di Milano - Dipartimento di Chimica Strutturale e Stereochemica Inorganica, a systematic investigation of old fumarole mineral samples was undertaken. Two old fumarolic sites, unfortunately almost completely destroyed by man and landslides has been identified and sampled. In these sites several Vesuvius-rare and Vesuvius-new mineral species were found, many of which were not mentioned by Parascandola, probably because of the inadequacy of the analytical instruments of the time or/and because some of these minerals could have formed later. The first site is a fumarole that was active in 1944 and has currently a temperature of 70-80°C; the second one is a fumarole with a temperature of about 100°C and the occurrence of H₂S, located at the bottom of the crater.

Ammineite, CuCl₂(NH₃)₂, is one of the most interesting minerals found; this species was recently described for the first time in a guano deposit, in contact with plutonic rocks at Pabellón de Pica in Chile by Bojar et al. (2011), therefore the finding at the fumaroles of Vesuvius represents not only the second occurrence of this species in the world, but also the first in a totally different environment. The mineral occurs in bluish crusts associated with altered tenorite, opal and artroeite.

Matlockite, PbFCl, was identified as colorless platy crystals up to 1 mm, together with artroeite, tenorite and calciocaravaitaipaite. Other species of great interest, new for Vesuvius, are gearksutite, hemimorphite and caledonite.

On post-eruption fumaroles the following minerals have been found: alun-(K), ammineite, anglesite, antlerite, artroeite, baryte, calciocaravaipaite, calcite, caledonite, cerussite, challacolloite, cotunnite, chrysocolla, cumengeite, erythrosiderite, fluorite, gearksutite, gypsum, halite, halotrichite, hematite, hydrozincite, linarite, matlockite, metavolinite, mimetite, opal, pickeringite, salammoniac, sassolite, sulphur, sylvite, tenorite and, on the scoriae, siderazot.

MINERALS FROM CAMPANIA BEYOND VESUVIUS: CAMPI FLEGREI, ROCCAMONFINA, GYPSUM-SULPHUROUS AND SEDIMENTARY FORMATIONS

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After the completion of the monography “I Minerali del Somma-Vesuvio” (Russo & Punzo, 2004), edited by the Associazione Micro-mineralogica Italiana (AMI), the authors are finishing a new book which deals with the mineralogy of the whole Campania area, excluding Vesuvius, again for the AMI.

The mentioned areas are many and many of them are of remarkable scientific interest, though always overshadowed by one of the most famous volcanoes in the world: the Somma-Vesuvius. For example, Campi Flegrei are type locality for misenite from the Grotta dello Zolfo, for marialite from Pianura, for nacholite from Stufe di Nerone, and for alum-(K), dimorphite, and voltaite from Solfatara di Pozzuoli. Other interesting areas are those of Fiano, close to Salerno, for fluoborite (ex nocerite), Roccamonfina for leucite, etc.

The new book is modern work, whose release is scheduled for 2013, suitable to both professionals, and collectors, and learned readers.

CAMPOTRERA OPHIOLITE (REGGIO EMILIA, NORTHERN ITALY):
A NATURAL PRESERVE FOR GEOLOGY AND MINERALOGY

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The Natural Preserve of Campotrera, in the Enza river valley (Reggio Emilia province, Northern Apennine), was established in 1999 and its management was entrusted to Canossa municipality, where the preserve is present. This Natural Preserve includes a huge ophiolitic outcrop, composed by pillow-lavas basalts and subordinately by polygenic and ophiolitic breccias. Campotrera ophiolitic block, together with nearby Rossena and Rossenella ones, represents an ophiolite (Campotrera ophiolite) belonging to the External Ligurian Units, composed by ophiolitic slide-blocks embedded in a sedimentary melange that marks the base of flysch-like sequences of Cretaceous-Eocene age. These basalts underwent a low-grade metamorphism (oceanic metamorphism), represented by prehnite-pumpellyite to greenschist facies assemblages. The main chemical effect of this transformation is silica liberation and calcium mobilization. In ophiolitic basalts, plagioclase is transformed 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, up to 30 centimetres in thickness, are hosted in basalt-pillows and breccias, and here several minerals occur: datolite, calcite, prehnite and to a lesser extent natrolite, analcime, barite, hematite, magnetite. Sometimes these minerals can occur as euhedral crystals. Indeed, Campotrera is one of the most famous places in Italy for the beauty and the size of some of its minerals, especially centimetric red datolite crystals. Since 2000, the SRSN has been cooperating with Canossa municipality in order to reconstruct the quarrying history of these ophiolitic bodies (Borghi & Scacchetti, 2002) and to investigate their mineralogy. For this purpose, the SRSN established a collaboration with the University of Parma (Department of Physics and Department of Earth Sciences) and with the Department of Applied Geological Sciences and Geophysics of Leoben (Austria). At the beginning of this collaboration, according to the Canossa municipality provisions, we sampled and then identified by micro-Raman spectroscopy the major number of mineralogical phases (Bartoli et al., 2003). Afterward, several rock samples from Campotrera ophiolite were analyzed by electron microprobe and a fluid inclusion study (Zaccarini et al., 2008) along with a crystal chemistry characterization (Rinaldi et al., 2010) were carried out on datolite crystals. Micro-Raman spectroscopy enabled the discovery of new minerals in the ophiolite, such as magnetite, pumpellyite, and hematite. The latter is present as solid micro-inclusions in datolite and analcime crystals. Thin sections obtained from a single datolite vein show a symmetrical structure with coarse grained datolite in the vein core, characterized by mosaic texture, triple junctions, and palisade-like aggregates of minute datolite crystals typically elongated normally to the contact with the wall rock. Two-phase (L+V) fluid inclusions were observed, texturally identifiable as primary and secondary. Microthermometry analyses suggested a NaCl-H₂O system for all inclusions. The calculated salinity is in the range of 10-16 wt.% NaCl equivalents. Paragenetic considerations and mode of occurrence of datolite from these ophiolitic basalts indicate that the mineral precipitated from hydrothermal fluids circulating through the ophiolitic rocks during some post-magmatic stage. The chemical analyses show no significant site substitution. The single-crystal structure refinements confirm the structural model of datolite previously reported (with \( a \sim 4.83, b \sim 7.61, c \sim 9.63 \) Å, and \( \beta \sim 90.15^\circ \), space group \( P21/c \)).

Sessione tematica J3:
Idrogeno nei minerali nominalmente anidri o idrati: un elemento chiave nei processi crostali e nel mantello terrestre

Conveners:
Bernardo Cesare (Università di Padova)*
Giuseppe Cruciani (Università di Ferrara)
Giancarlo Della Ventura (Università Roma Tre)
Fabrizio Nestola (Università di Padova)
Hydrogen can be a major, a minor or a trace constituent of a large variety of minerals. It is usually bonded to oxygen to give H₂O, OH⁻, or more rarely H₃O⁺, H₃O₂⁻ units, but also NH₄⁺ or organic compounds. It can be a structural component in stoichiometric hydrates, hydroxides, and in many silicate minerals, or can be non-stoichiometrically present as a major extraframework component in microporous minerals (e.g. zeolites). Hydrogen also occur as a minor constituent in structural defects of nominally anhydrous minerals (NAMs) (Keppler & Smyth, 2006). H exerts a strong influence on the chemical and physical properties of minerals; hence it has a controlling effect on many high-temperature geological processes (e.g. magma genesis, kinetic of phase transformations, etc.), as well as low-temperature alteration processes. Unfortunately, H is a rather elusive element, specially when it occurs in very low amounts, as in NAMs. Conventional micro-analytical techniques (EMPA) and X-ray diffraction are generally unsuitable to characterize this element; secondary ion mass spectrometry (SIMS) and neutron diffraction are not easily accessible and requires complex, time-consuming, analytical procedures. A possible alternative is offered by spectroscopy: Raman, Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR). FTIR is particularly suitable for hydrogen, since the O-H (C-H and N-H) bond absorbs the infrared radiation very efficiently. The relatively low cost, ease of use and ease of sample preparation makes the FTIR technique an extremely powerful tool for the study of H-bearing minerals (Libowitzky & Beran, 2004). Using FTIR spectroscopy we can: a) quantify hydrogen, b) study its distribution (Della Ventura et al., 2004), c) distinguish its speciation, d) define the structural orientation of the O-H dipole, e) study phase transitions associated with H loss, and f) study thermal processes (Bonaccorsi et al., 2006). We present here the recent developments of the FTIR activities at Roma Tre and describe the new facilities which are currently available in our laboratories (high temperature stages, Focal Plane Array detectors). We will use, as examples, the most recent results obtained by our group, including studies on beryl, cordierite, feldspathoids, phosphates and hydrocarbons-bearing materials.

DEHYDRATION AND REHYDRATION OF BIOTITE DURING ANATEXIS: CONSTRAINTS FROM MICROSTRUCTURALLY-AIDED SIMS ANALYSIS OF HYDROGEN

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The SIMS-based study of Ti-H relationships in biotite during the prograde and retrograde phases of HT metamorphism and anatexis (Cesare et al., 2008) has been expanded with the addition of three new case studies, that help providing a coherent scenario for metapelitic rocks. Two of the three sample suites are enclaves or xenocrysts in lavas, which have been demonstrated to be the ideal setting for the preservation of the primary composition of biotite from high-grade anatectic metapelites (Cesare et al., 2003).

In a Spl-Crd enclave from El Hoyazo, Spain (Alvarez-Valero et al., 2005) biotite shows TiO₂ contents ranging from 2.5 to 7.5 wt.%. The Ti contents are microstructurally controlled: small biotite inclusions in the core of garnets have the lowest contents, whereas the coarser grained crystals toward the garnet rims have the highest. Biotite in the matrix outside garnet shows intermediate Ti contents. Like in the samples of Grt-Bt-Sil enclaves from the same lavas, the measured H contents are negatively correlated with Ti along a trend that provides further support to the Ti-oxy exchange. Furthermore, the decrease of H₂O contents from 4 to 2.5 wt.% show the progressive dehydroxylation of biotite associated to the growth of garnet which records the development of partial melting of the rock with increasing temperature.

Biotite inclusions have been studied also in garnet and cordierite xenocrysts and in enclaves of the Crd-bearing lavas from Lipari ( Aeolian arc, Italy; Di Martino et al., 2011). Here the range of Ti contents (3 to 11 wt.% TiO₂) includes the highest reported values in the literature, whereas analysed H contents include the lowest (from 1.9 down to 0.2 wt.% H₂O). These data extend the occurrence of a Ti-oxy exchange to Ti contents not previously investigated. In addition, they suggest that the (OH + F + Cl) content of extremely Ti-rich biotites may decrease to almost zero.

The third case study is represented by the metapsammitic granulites (leptynites) of the Kerala Khondalite Belt (India), in which Cesare et al. (2008) suggested the occurrence of retrograde hydroxylation and fluorination during the slow cooling of these regional anatectic rocks. SIMS profiles at high spatial resolution (1.8 μm spot size, 2-4 μm scan step) combined with EMP traverses demonstrate that H, Ti, Fe, Mg, and F diffusion profiles are preserved in the outermost 50 μm of biotite in contact with garnet. These patterns indicate an increase of H, F and XMg, and the simultaneous decrease of Ti, in accordance with an inverse Ti-XMg relationship and the Fe-F avoidance. The new data integrate and confirm previous findings or inferences, showing that:

- Ti-oxy is the dominant exchange mechanism over the entire TiO₂ range so far investigated in biotite from metapelitic rocks;
- during prograde heating and continuous melting biotite is progressively dehydroxylated mainly through Ti uptake, until it may eventually become OH-free;
- in most granulites and migmatics the halogen and hydrogen contents of micas are probably increased by retrograde diffusion, and biotite may preserve evidence of such reequilibration in thin (a few tens of μm) rims at the contact with garnet.

WATER IN ZEOLITES: RELATIONSHIPS BETWEEN THERMAL STABILITY AND ENERGETICS

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The relation between heat and water in zeolites has attracted great interest since their discovery as ‘boiling stone’ minerals, being able to dehydrate reversibly. The contribution of water to zeolite thermodynamic properties has been matter of debate. In fact, it is generally assumed that zeolites are thermodynamically metastable phases. On the other hand, its has been suggested that hydrated aluminosilicate zeolites can have true stability fields near room temperature because the exothermic enthalpy of hydration more then compensates for the metastability of the anhydrous framework. Nevertheless, due to the large differences in the enthalpy values determined by different techniques, no consensus exists about the magnitude of the total energetic stabilization imparted by H2O. In any case, zeolite thermodynamic stability is limited to T < 400-500 K by the large positive entropy of dehydration. As far as the effect of water on the thermal behavior and stability of zeolites it is known that zeolite structures subjected to dehydration by heating give rise to several intriguing phenomena from crystallographic, chemical, and physical viewpoints. Understanding the zeolite thermal stability from both the kinetic and thermodynamic standpoints is of particular importance in order to model, optimize, and design zeolite-type materials with promising performances in many fields (industry, environment, energy). As a first attempt to quantify and predict the zeolite behavior upon heating, it was recently introduced a stability index (S.I.) ranging from 1 to 5 as a function of increasing thermal stability (Cruciani, 2006). This index displays systematic correlations with chemical composition of both the zeolite framework and extraframework (EF) cations.

The present study aims to improve the quantitative relationships established between the zeolite thermal stability index and the zeolite chemical and structural features, and to explore the possible correlations existing with the thermodynamic data taken from the literature.

The critical review of experimental data, in particular those from in situ X-ray diffraction studies, for thermally induced transformations in zeolites has been extended starting from previous work (Cruciani, 2006). As discussed in the latter paper, several intrinsic chemical and structural factors have been suggested to control the thermal behavior of zeolites, affecting the dehydration and collapse/breakdown temperatures: i) the framework Si/Al ratio; ii) the (weighted) ionic potential (Z/r) and size of EF cations; iii) the coordination of bare cations after H2O expulsion; iv) the framework topology. In addition, the temperature at which dehydration and structural collapse/breakdown occur can be affected by several extrinsic factors. In fact, the structural modifications occurring in the same zeolite framework can be different when heated in ‘near-’ or ‘far-equilibrium’ conditions.

The present study enforces the previously found generalizations (Cruciani, 2006): zeolites with Si/(Si+Al) 0.6 (Si/Al 1.3) or/and Z/r 0.187 always have S.I. < 3 (poor thermal stability), while zeolites with Si/(Si+Al) 0.8 (Si/Al 4) or/and Z/r 0.072 are very stable (S.I. 3). The largest group of zeolites do not show definite trends as simple functions of Si/Al and Z/r. However, the definition of a ‘combined factor’ which accounts for both the latter two variables plus a parameter newly introduced to quantify the ring/channel size and geometry in different zeolite topologies, greatly improves its relationship with the S.I. and allows to recognize a correlation, never reported before, with zeolite thermodynamic data.

Naturally leucite crystallizes in the cubic phase, with space group $Ia\overline{3}d$ (Peacor, 1968). On cooling below $T = 625^\circ$C it undergoes a phase transition to a tetragonal $I4/a$ form (Mazzi et al., 1976); there are indications, however, that an additional tetragonal phase is stable over a narrow temperature interval (Lange et al., 1986). Palmer et al. (1997) have shown that the displacive phase transition to tetragonal symmetry is due to twisting of tetragonal prisms of corner-linked (Al,Si)O$_4$ tetrahedra about [001] and a collapse of the [111] structural channels with concomitant volume reduction. Although nominally anhydrous (NAM), leucite typically contains significant amounts of water; this feature was reported for samples from Roccamonfina (Balassone et al., 2006) and the Alban Hills volcano (Della Ventura et al., 2008). Della Ventura et al. (2008) have shown in addition that H$_2$O may be significantly zoned, thus providing a potential tool to monitor the evolution of the magmatic conditions with time.

More recently, Martucci et al. (2011) studied the dehydration of synthetic B-substituted leucite (KBSi$_2$O$_6$) by synchrotron powder diffraction and concluded that the structural modifications accompanying the tetragonal-cubic transition is associated with the migration of H$_2$O molecules through the [111] channels.

We relate here a single-crystal high-T in situ FTIR study of a set of natural inclusion-free leucite phenocrystals occurring within lava flows, pyroclastic rocks or ejecta in the Roman Comagmatic Province. The spectra show broad absorptions in the 4000-3000 cm$^{-1}$ region consisting of overlapping components around 3604, 3500 and 3250 cm$^{-1}$. Interestingly, two different types of spectra are observed in the H$_2$O stretching region, indicating that water molecules may be trapped in leucite in two different environments (hereafter “type I” and “type II”).

These different H$_2$O types are systematically associated with samples from different volcanic areas, thus suggesting a possible role of the petrological conditions (pressure, temperature) of crystallization on the H$_2$O entrapment in leucite. FTIR-FPA images show significant H$_2$O zoning across the samples; crystals with homogeneously-distributed water were selected for the dehydration experiments, done using a Linkam T600 heating stage fitted under a NicPlan FTIR microscope at University Roma Tre.

The evolution of the water loss as a function of $T$ was monitored by measuring the principal H$_2$O water absorption. The data indicate a continuous water loss with a break in the trend; in “type I” leucite the slope change occurs at $\sim 500^\circ$C, and dehydration is complete at $T > 600^\circ$C, probably close to the transition temperature. In “type II” leucite, the slope change occurs at $\sim 350-400^\circ$C, and dehydration is complete at $\sim 500^\circ$C. This behaviour is compared with isostructural materials like analcime or pollucite.
WATER IN BERYL: A CONTRIBUTION FROM THEORETICAL CALCULATIONS
AT THE AB INITIO LEVEL, AUGMENTED BY AN
EMPIRICAL DISPERSION TERM

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Dispersion forces can be modeled by none of the ab initio Hamiltonians currently available, either at the purely DFT level (no matter if LDA or GGA), or at the hybrid HF/DFT one. The reason is related to the fact that DFT functionals are specifically designed to deal with short range electron correlation effects (dynamic correlation), whereas long range effects (static correlation), which encompass dispersion energy, are not taken into account (Cremer, 2001). It is possible to augment the ab initio Hamiltonian by a London type empirical term, which is parametrised in such a way to properly deal with dispersion energies (Grimme, 2006). The approach has been applied to the case of beryl, to model the behaviour of water inside its structural channels. Calculations confirmed previous findings which located the water molecule at the 2a Wyckoff position (Space Group P6/mcc), with a type I orientation having the H–H axis parallel to [001] (see for instance Kolesov & Geiger, 2000). The calculated hydration energy (-20 Kcal/mol) is in reasonable agreement with experimental measurements (-13 Kcal/mol; Barton, 1986). The activation energy for the diffusion of the molecule through the structural channels has also been calculated, and it amounts to 38 Kcal/mol: a result which is not far from the experimental datum of 32 Kcal/mol (Fukuda et al., 2009). The approach can thus reliably be used to model the position of the water molecule in minerals, and the involved hydration energy, even in cases of weak bindings of dispersive type.

THE QUANTITATIVE ANALYSIS OF H$_2$O AND CO$_2$ IN CORDIERITE USING SINGLE CRYSTAL POLARIZED-LIGHT FTIR MICROSCOPY

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Cordierite is a unique case of a microporous mineral stable under geological conditions spanning from the amphibolite facies to UHT metamorphism to crustal anatexis (Harley et al., 2002; Bertoldi et al., 2004). Because of its structural channels, it is able to trap H$_2$O and CO$_2$ (Armbruster & Bloss, 1980), and for this reason the analysis of the volatile constituents of cordierite may help constraining the geological conditions and the composition of coexisting fluids during its formation (Vry et al., 1990; Harley et al., 2002). It follows that the quantitative evaluation of the channel constituents is crucial in petrologic studies. We address here this point by studying, using a multidisciplinary approach, a set of cordierite samples from different occurrence and with different H$_2$O / CO$_2$ content. The aim of the study was a calibration of reliable absorption coefficients to be used for the quantitative microanalysis of H$_2$O and CO$_2$ in cordierite based on single-crystal polarized-light FTIR spectroscopy. The specimens were fully characterized by a combination of techniques including optical microscopy, single-crystal X-ray diffraction, EMP (electron micro probe), SIMS (secondary ion mass spectrometry), and FTIR spectroscopy. All cordierites are orthorhombic Ccmm; the 2V$_\alpha$ optic axis angle is linearly related to the CO$_2$ content. According to the EMP data, the Si:Al ratio is always close to 5:4; X$_{Mg}$ ranges from 76.31 to 96.63 and additional octahedral constituents occur in very weak amounts. Extraframework K and Ca are negligible, while Na may reach values as high as 0.84 apfu. SIM spectrometry shows H$_2$O up to 1.52 and CO$_2$ up to 1.11 wt.%. Optically transparent single-crystals were oriented using a spindle-stage and examined under polarized light. On the basis of the literature data and the polarizing behaviour, the observed bands were assigned to water molecules in two different orientations and to CO$_2$ molecules in the structural channels. The spectra also show the presence of $^{13}$C and $^{18}$O, and weak amounts of CO in the samples. FTIR imaging done using the novel FPA detector system clearly shows that at a m-scale the distribution of H and C in this mineral may be significantly inhomogeneous, and this must be taken into account when collecting analytical data for petrological purposes. This feature is probably less important for carbon molecules than it is for H$_2$O, whose distribution within the crystal can be strongly affected by the geological history of the mineral after its formation.
Ti-garnets commonly occur as accessory phases in silicocarbonatite and carbonatitic rocks. They are believed to be tracers of magma evolution (Lupini et al., 1992; Brod et al., 2003) and the speciation of Fe and Ti is of relevant petrological interest (Malitesta et al., 1995; Scordari et al., 1995). In Ti-garnets, hydrogen may be incorporated via the hydrogarnet substitution, where a SiO$_4$ unit may locally be replaced by a H$_4$O$_4$ tetrahedron. However, more complex mechanisms have also been proposed (Kühberger et al., 1989). In the present work, a crystal chemical study was undertaken on a suite of Ti-bearing garnets of different origin (igneous and metamorphic). The garnet samples underwent multiple technique investigation, which consisted in the combination of chemical (EPMA, SIMS), structural (SCXRD) and spectroscopic (Mössbauer) techniques.

In particular, SIMS has been used to analyse hydrogen (quantified conventionally as H$_2$O, wt.%), fluorine and lithium. Salient chemical analytical data (wt.%) are: CaO (31.34 - 33.23), FeO$_{tot}$ (18.01 - 20.53), Al$_2$O$_3$ (0.86 - 2.46), TiO$_2$ (5.57 - 17.10), ZrO$_2$ (0.01 - 2.87), SiO$_2$ (25.70 - 32.89). SIMS investigation yielded: H$_2$O 0.091(7) - 0.46(4) wt.%; Li 11.3(1.6) ppm; F 42(8) - 483(28) ppm. Mössbauer analysis provided spectra with different complexity, which could be fitted with a number of components variable from one (VIFe$_{3+}$ (Y)) to five (VIFe$_{2+}$ (X), VIFe$_{3+}$ (Y), IVFe$_{2+}$ (Z), VIFe$_{3+}$ (Y), IVFe$_{3+}$ (Z)). However, the IVFe$_{2+}$ (Z) component has been reinterpreted by some authors (Chakhmouradian & McCammon, 1989) as due to VIFe$_{2+}$ (Y) → IVFe$_{3+}$ (Z) electron hopping. From X-ray data, such garnets were expected to have tetrahedral substitutions and a hydrogarnet component. FTIR preliminary spectra in the OH$^-$ stretching region evidenced that the samples were characterized by various degrees of hydration.

The comparison with data obtained by X-ray site scattering refinement and Mössbauer spectroscopy allowed to ascertain that the combination of VI$^{4+}$Ti$^{4+}$M$^{3+}$, VIFe$_{3+}$IVSi$_{3-}$ (schorlomite substitution) and VI$^{2+}$M$^{2+}$IV$^{2+}$Ti$^{4+}$IVFe$_{3+}$ (moturite substitution), with M$^{3+}$ = Fe$^{3+}$, Al$^{3+}$, and M$^{2+}$ = Fe$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, can explain most of the chemical variation of tetrahedral and octahedral sites.

In our samples the hydrogen is incorporated uniquely via the hydrogarnet substitution. In all cases excellent agreement was found between charge balance and SIMS determined OH$^-$ groups per formula units (g.p.f.u.). Specifically, in igneous garnets samples the OH$^-$ content ranges from 0.08 to 0.20 g.p.f.u. Out of the two metamorphic garnets considered, one has low OH$^-$ content (0.05 g.p.f.u.), while the other has the highest OH-content of the suite (0.26 g.p.f.u.). Fluorine was considered as OH$^-$ substituent following the recent literature (Chakhmouradian & Cooper, 2008).


Sessione tematica J4:
Minerali e materiali cristallini di sintesi: caratterizzazione, trasformazioni, proprietà e potenzialità di utilizzo.
Sessione in onore di Sergio Lucchesi

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RAMAN INVESTIGATION ON MgAl$_2$O$_4$ - MgCr$_2$O$_4$ AND MgAl$_2$O$_4$ – CoAl$_2$O$_4$ SPINEL SERIES

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Raman spectroscopy, like other spectroscopies, provides a mean to investigate the local environment in different crystallographic sites. This is useful when the local structure in solid solution has to be investigated. In the case of spinels, it was observed by changes in UV-VIS-NIR absorption spectroscopy of Cr (Halenius et al., 2010) that only partial relaxation occurs at the Cr site in solid solutions along the join MgAl$_2$O$_4$-MgCr$_2$O$_4$. It is expected that such feature should be apparent also from Raman spectra, and likely found in several spinel solid solutions involving transition elements. We have therefore undertaken Raman analysis of twelve synthetic spinels of the series MgAl$_2$O$_4$-MgCr$_2$O$_4$ and ten of the series MgAl$_2$O$_4$-CoAl$_2$O$_4$. The spinels were previously analyzed by electron microprobe. Raman spectra were collected with a Jobin Yvon LabRam micro-spectrometer using two different laser wavelengths. A 632.8 nm He-Ne laser was used for the samples with high Cr content, while in the samples containing Co and in those with the lower Cr content the spectra were recorded with a 473.1 nm wavelength from a solid state laser, to avoid the fluorescence. The spectral resolution was about 2 cm$^{-1}$ at 473.1 nm and 1.5 cm$^{-1}$ at 632.8 nm. The laser power on the sample was selected by inserting a neutral density filter to avoid heating effects (2-5 mW).

Along the MgAl$_2$O$_4$-MgCr$_2$O$_4$ series a marked change in intensity and position of the Raman peaks is observed. A peak at 410 cm$^{-1}$ is evident in the Al richest portion of the series and disappears at about the 50% of the series (corresponding to Cr 1.00 atoms per formula unit, apfu): according to the existing literature, it is ascribed to Al ion bending (Cynn et al., 1992). A peak at 685 cm$^{-1}$ dominates the Cr richest portion of the series and increases its wavenumber with a step by 15 cm$^{-1}$ up to 730 cm$^{-1}$ for Cr decreasing and sample composition approaching Cr 0.70 apfu (that is, corresponding to Al:Cr ratio of 2:1). Furthermore, another signal at about 650 cm$^{-1}$ appears in intermediate compositions only. The observed sudden change in the peak at 650-730 cm$^{-1}$ is likely related to a change in the O site local environment, represented by one tetrahedron and three octahedra. Given that the tetrahedron is (almost completely) centered by Mg, the observed Raman spectra modifications must be ascribed to the progressive substitution of Al by Cr in the octahedra.

Along the MgAl$_2$O$_4$-CoAl$_2$O$_4$ two distinct profiles of Raman spectra may be observed. Up to intermediate compositions the spectra show the peaks at 410 cm$^{-1}$, 670 cm$^{-1}$ and 770 cm$^{-1}$, typical of the spinel s.s. (Cynn et al., 1992), whereas in the Co-richest region all spectra have a Raman band at ca. 530 cm$^{-1}$ which is attributed to the Co-O stretching vibration (Kock & De Waal, 2007). This trend is due to both compositional change (Co$^{2+}$ → Mg substitution) and cation distribution. Indeed Co$^{2+}$ strongly prefers the tetrahedral coordination with respect to Mg and only starts to disorder into the octahedrally-coordinated sites after 50% of the series.

Nb and Ta are geochemically related elements which typically give rise to isomorphous series of oxides as accessory minerals in granitic pegmatites (e.g. columbites, pyrochlores, fergusonites, etc). However, in spite of the natural occurrence of orthorhombic alumontite (AlTaO₄), its Nb counterpart is only known as a synthetic product. AlNbO₄ crystallizes with monoclinic symmetry (e.g. C2/m) and was early described with a strict ordering of Nb and Al, respectively over M1 and M2, the two non-equivalent octahedral sites in the structure (Pedersen, 1962). This model was revised by successive refinements showing that a partial disorder occurs in AlNbO₄ with a ~ 20% inversion degree (Efremov et al., 1981; Greis et al., 1996). CrNbO₄ is a disordered MM'O₄ compound, crystallizing with the rutile structure (e.g. P42mmnm) while FeNbO₄ crystallizes with wolframite (e.g. P2/c), orthorhombic -PbO₂-type, rutile, or AlNbO₄-type structure as the temperature increases.

This brief review shows that, even at room conditions, the chemical nature of the metal cations M³⁺ strongly affects the crystal structure of MM'O₄-type oxides. In order to better understand the substitution mechanisms, the cationic ordering, the structural stability, and the phase transition processes for (M³⁺)(Nb⁵⁺)O₄ compounds, six samples along the (Al₁₋ₓCrₓ)NbO₄ join (x: 0.0-0.5) were synthesized by the solid-state reaction process and investigated by means of a X-ray powder diffraction (XRPD) and electron absorption spectroscopy (EAS) combined approach. Monophasic up to x(Cr) = 0.125 apfu (AlNbO₄-type structure), the samples along the join become biphasic (the former plus the CrNbO₄-type structure) for x(Cr) > 0.125 apfu, indicating the impossibility to have a complete solid solution between (Al,Cr)NbO₄ oxides. The lattice parameters increasing with the Al-Cr substitution defines a structural expansion limit (x(Cr) > 0.24 apfu) that is ascribed to the maximum chromium content that the structure can accept. The samples up to x(Cr) = 0.25 also exhibit the typical optical spectra of Cr³⁺ in 6-fold coordination, involving d-d electronic transitions. Ascertained that the proposed octahedral ordering models were corrected (Efremov et al., 1981; Greis et al., 1996), through different refinement strategies, the global instability index, GII (Salinas-Sanchez et al., 1992), was calculated over the un-doped structure by varying the Al/Nb ratio in the two metal sites. Unpredictably, even the minimal values of GII obtained are very close to the limit of 0.20 v.u. that implies strained structures. With a crystal field strength that decreases moving from x(Cr) = 0.06 to 0.50 apfu, and both the Racah parameters and the nephelauxetic trends nearly constants, no significant change in the degree of covalency and polarization of the Cr-O bond are found. The 10Dq decreasing suggests an elongation of the local Cr-O distance for Cr³⁺ increasing at site M2 and to a minor extent at site M1, fitting well the structural data on the long-range mean bond distances. The degree of structural relaxation around Cr³⁺ was also assessed by means of the relaxation coefficient, until the structure will maintain the same symmetry. The AlNbO₄ lattice has a limited propensity to relax (0) and the AlNbO₄ structure follows the Vegard’s law. In contrast with the well known Al-Cr joins in garnets, spinels, perovskites and corundum, the AlNbO₄ structure is strongly constrained by other factors, like cation ordering and electrostatic charge balance. Indeed, the M2 site hosting Al³⁺ is underbonded and Cr³⁺ can be accommodated at this site without significant strain for that the lattice does not need to relax around the bigger ion.

HIGH-PRESSURE PHASE TRANSITIONS IN ALKALINE-EARTH FELDSPARS

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While the structural and thermodynamic behaviour of the phase transitions induced by temperature in feldspars was subject to several investigations and is now well described, their high-pressure behaviour has been investigated only in more recent times. At room conditions, in alkaline-earth feldspars, a triclinic $P\bar{T}$ symmetry is observed with Ca as M cation, whereas the symmetry becomes monoclinic $I2/c$ when the larger Ba or Sr cations replace Ca, as in celsian (BaAl$_2$Si$_2$O$_8$, Cls) and Sr-feldspar (SrAl$_2$Si$_2$O$_8$, SrF).

High-pressure investigations on anorthite (CaAl$_2$Si$_2$O$_8$, An) were performed by Angel (1988), that observed a reversible first-order phase transition from $P\bar{T}$ to $I\bar{T}$ between 2.6 and 3 GPa. Along the An-SrF join, with increasing pressure, the An$_{20}$SrF$_{80}$ feldspar shows a displacive first-order $I\bar{T}$-$I2/c$ phase transition at about 4.3 GPa, analogous to the displacive second-order $I\bar{T}$-$I2/c$ transition observed with increasing temperature at room pressure for the same feldspar. Both high-pressure and high temperature $I2/c$ monoclinic structures are characterized by an increase of the coordination number of the Ca/Sr cations, which can be ascribed to an increase of the $r_c/r_o$ ratio, where $r_c$ is the ionic radius of the non-tetrahedral cations and $r_o$ is the ionic radius of oxygen. In particular, the triclinic-monoclinic $I\bar{T}$-$I2/c$ high-pressure transition can be justified by the higher compressibility of the oxygen atoms with respect to the non-tetrahedral cations, causing the increase of the $r_c/r_o$ ratio. At about 7.3 GPa, the An$_{20}$SrF$_{80}$ feldspar shows a further first-order transformation from monoclinic $I2/c$ to monoclinic $P2_1/c$ (Nestola et al., 2004; Benna et al., 2007). In pure Sr-feldspar, Pandolfo et al. (2011) observed the same $I2/c$-$P2_1/c$ phase transition at about 6.6 GPa. In the present work the results obtained in celsian, by single-crystal in situ high-pressure X-ray diffraction up to 6.5 GPa, show the same $I2/c$-$P2_1/c$ transition between 5.5 and 5.9 GPa. The results highlight the significant reduction of the transition pressures in comparison to An$_{20}$SrF$_{80}$ and SrF$_{100}$ feldspars. This allows to correlate the decrease in the transition pressures with the increase of the average ionic radius in alkaline-earth feldspars along the An-SrF and SrF-Cls joins. Considering the well known morphotropic phase transitions occurring at room condition with changing composition, the results obtained on celsian allow to draw, along the Ca-Sr and Sr-Ba-feldspars joins, the stability fields of the observed phases between 0 e 7.5 GPa.

A COMPARISON OF THE STRUCTURAL AND MICROSTRUCTURAL FEATURES DETERMINED FROM RIETVELD REFINEMENTS AND PAIR DISTRIBUTION FUNCTION ANALYSES OF IRON OXIDE NANOPARTICLES

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Rietveld method is by now the conventional crystallographic method for structural analysis. However, in the past few years total scattering technique has become increasingly important for crystalline materials that show reduced long-range periodicity. Data are evaluated by the Pair Distribution Function technique, that allows analyzing simultaneously Bragg and diffuse scattering, revealing short and intermediate range order of the material. This function is defined in real space, in terms of atomic coordinates. The aim of this work is to compare the results from Rietveld and Pair Distribution Function analyses applied to powder diffraction data on iron oxide nanoparticles.

Diffraction data were obtained from the ADXD (Angular Dispersive X-Ray Diffraction) method, using a parallel beam Bruker AXS D8 Advance diffractometer operating in transmission mode $\theta$ - $\theta$ geometry, and from a non conventional EDXD (Energy Dispersive X-Ray diffraction) diffractometer characterized by a $\theta$ - 0 vertical geometry. ADXD data were analyzed by the Rietveld method while EDXD data were evaluated by the PDF method using PDFITGui (Farrow et al., 2007) software. Samples are maghemite nanoparticles of different nominal size (10 nm, 7 nm, 5 nm, 3.5 nm). They were synthesized by condensation in aqueous medium by controlling temperature, $p\text{H}$ and system composition ($\text{Fe}^{3+}/\text{Fe}^{2+} + \text{Fe}^{3+}$). Both techniques (Rietveld and Pair Distribution Function analyses) apply least-squares full profile refinements: the first operating in reciprocal space and the second in direct space. Cell parameter, atomic displacement parameters, $x$ coordinate of the oxygen site, and size of nanoparticles were common parameters refined with both approaches. A big problem to be faced of with ADXD data was the very large absorption. Two different series of refinements were performed using GSAS & EXPGUI (Larson & Von Dreele, 2004; Toby, 2001) and TOPAS v. 4.2 (Bruker AXS, 2009) programs. TOPAS implements the Fundamental Parameters Approach FPA (Cheary & Coelho, 1992), a convolution approach in which the peak-shape is synthesized from a priori known features of the diffractometer and the microstructural features of the specimen. This approach is believed to provide more accurate microstructural parameters than a conventional Rietveld refinement. In the case of the Rietveld refinements, individual isotropic displacement parameters were refined with the full ionization model (Ballirano, 2003) for the oxygen atom.

The PDF technique allowed the refinement of the individual anisotropic displacement parameters that were found systematically larger than those from the Rietveld analyses possibly because of correlations among parameters. Only FPA provided a meaningful analysis of the microstrain. As expected, strain decreases with the increase of the particles diameter due to the reduction of the specific surface. The cell parameter $a$ obtained from Rietveld refinement (ca. 8.353 Å) was very similar for all analyzed samples: it was slightly smaller than that reported for other nanocrystalline maghemite (Di Marco et al., 2009; 2006), and greater than that of microcrystalline sample (Greaves, 1983; Shmakov et al., 1995). The $x$ coordinates of the oxygen site obtained from the Rietveld refinements (ca. 0.254) didn’t show any significant difference from reference data as well as those from PDF analyses. Therefore both conventional and FPA Rietveld and PDF approaches can provide reliable information on the atomic displacement parameters and on the $x$ coordinate of the oxygen site. Moreover, nanoparticles size has been reliably estimated only by PDF and FPA Rietveld analyses.
TOWARDS HIGHLY-ORIENTED NANOSTRUCTURED THIN FILMS OF NATURAL AND SYNTHETIC MINERALS: NEW CHANCES FOR NANOTECHNOLOGY

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In recent years, many efforts have been made on the synthesis of new self-assembled materials, and on scientific understanding of the formation mechanism from building molecules. With the aim to develop new functional materials, layered inorganic compounds recently attracted considerable interests for the preparation of nanoscale organic/inorganic hybrids. A large class of minerals presents inherently nanostructured morphologies. Within this group, we cite, to name a few, chrysotile, crocidolite, and montmorillonite, being examples of crystalline aggregates of nanotubes, nanorods, and nanosheets, respectively. On this basis, synthetic “geo-inspired” materials are being developed, with the aim to enhance their possibility to be employed as nanomaterials in technological applications. On the other hand, the surface of such minerals is rich of chemical groups which can bind covalently or electrostatically organic compounds capable to confer technological functionalities to the ultimate hybrid system. In order for a transition from bare mineral to functional material to be achieved, the development of processes for the deposition of highly-oriented thin film phases of such mineral nanoparticles are mandatory. Indeed, their marked anisotropic morphology influences also their physical properties, which may vary to a great extent depending on the probed direction. Here, we show the results of a scanning probe and electron microscopy, X-ray diffraction, and IR optical analysis of nanostructured thin films of natural and synthetic minerals obtained by liquid phase deposition of colloidal solutions. By assisting the deposition process with a static magnetic field, we demonstrate the possibility to induce a preferential orientation of the deposited nanoparticles, thanks to the anisotropy of their diamagnetic or paramagnetic susceptibilities. This effect is also studied in minerals deliberately doped with paramagnetic species such as Fe(II) and Fe(III) ions. Hybrid inorganic-organic colloids are synthesized by reacting chrysotile nanotubes with ionic derivatives of metal-phthalocyanines, organic molecules which display semiconducting character in the solid state. The structure, morphology and optical properties of the magnetically driven ordered deposits of hybrid nanoparticles are analyzed and compared with those of the bare minerals. Some conclusive remarks for their technological application and perspectives are drawn.
PROBING THE DYNAMICS OF MATTER BY TIME-RESOLVED DIFFRACTION WITH SYNCHROTRON RADIATION: STATE-OF-THE-ART AND TRENDS

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The intense, tunable and highly collimated synchrotron X-ray sources have opened the possibility to investigate the dynamics of condensed matter under perturbed states (e.g. chemical gradients, magnetic or electrical fields, etc.) or at non-ambient conditions (increasing temperature or pressure). In particular, time-resolved X-ray scattering experiments performed at in situ conditions are increasingly attracting the interest of crystallographers, chemists, physicists, Earth and material scientists. The paramount importance of recording transient and non-quenchable states of perturbed matter in order to obtain a deep understanding of its properties is documented by a selection of recent studies performed by in situ time-resolved diffraction in order to follow processes in a continuous way at different time-scales (from hours, to minutes, to seconds, to picoseconds).

Among those, the study of the structural modifications upon heating of zeolites and zeolite-like microporous materials in far-from-equilibrium conditions has allowed to shed light on water confinement and diffusion processes, and to discover phenomena like the ‘trap door’ and ‘molecular gate’ effects which are exploited in ton-scale industrial applications. Similarly the ‘breathing effect’, recognized by time-resolved diffraction experiments in the new class of metal-organic frameworks, makes these materials very promising for hydrogen and carbon dioxide storage/capture.

The structural tracking of molecular reactions or electronically excited states in solution, with time-scale of pico-seconds, has been achieved in a number of systems by the pump-probe time-resolved X-ray scattering experiments performed at synchrotron light sources. All the above studies show that there is still plenty of justification to design and build synchrotron radiation beamlines dedicated to multimodal time-resolved experiments. These stations will fruitfully complement the forthcoming free-electron laser based instruments.
HIGH-PRESSURE STRUCTURAL CONFIGURATIONS OF CELSIAN

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Single-crystal in situ high-pressure X-ray diffraction was performed at P = 0.0001, 2.1, 4.2, 5.5, 5.9 and 6.5 GPa on celsian (Ba0.97K0.03Al1.95Si2.04O8) from Jakobsberg, Sweden. The evolution of the unit-cell parameters as a function of pressure shows a discontinuity at pressure between 5.5 and 5.9 GPa (mainly in angle and b parameter) and highlights a displacive first-order transformation. The data collections between 0 an 5.5 GPa show only a-type and b-type reflections (a: h + k = even, l = even; b: h + k = odd, l = odd) confirming the I2/c space group of celsian. The I2/c structures show only minor modifications mainly involving a shortening of the average < M-O > distances. The data collections at 5.9 and at 6.5 GPa show the presence of also c-type and d-type reflections (c: h + k = even, l = odd; d: h + k = odd, l = even) indicating a primitive lattice. As in the high-pressure P21/c configurations of the feldspars of composition Ca0.2Sr0.8Al2Si2O8 (An 20SrF80) and SrAl2Si2O8 (SrF100) (Benna et al. 2007; Pandolfo et al. 2011), in celsian the scheme of intensity of the different reflections is: a > d > b c. Only reflections h0l, 00l and 0k0 with l and k even were observed, confirming the P21/c space group. At pressure between 5.5 and 5.9 GPa, the I2/c-P21/c phase transition involves a reduction of the symmetry with the loss of the two-fold axes and of one-half of the centers of symmetry. In the P lattice the numbers of independent atomic sites is doubled and pairs of atoms related by the pseudo-body centering (a + b + c)/2 vector are present. The most significant changes in the P21/c configuration are: the deformation in the Ba polyhedra and the variation in the T-O-T angles. In particular, the T2(00)-OC(0i)-T1(0i) angle decrease to 112.24° at P = 6.5 GPa. The very small value of this angle in celsian at P = 6.5 GPa is related to the large changes in the OC oxygens in the M(0)-polyhedron.

CATION DISTRIBUTION AND OPTICAL PROPERTIES OF MgAl$_2$O$_4$-CoAl$_2$O$_4$ FLUX-GROWN SINGLE CRYSTALS

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Co-spinels are important compounds for many different uses as ceramic pigments, catalysts, and gemstones. Studies of cation distribution in these spinels are of considerable interest for a better understanding of relationships between structure and physical properties (such as colour). Spinel single crystals having different compositions along the MgAl$_2$O$_4$-CoAl$_2$O$_4$ series were synthesized by flux growth method with Na$_2$B$_4$O$_7$ as solvent. Low cooling rates (2°C/h) and linear temperature profiles were applied in the temperature interval 1200-800°C, and a continuous flow of CO$_2$:H$_2$ in the ratio of 100/4 cm$^3$/min was adopted to obtain a reducing atmosphere (with the oxygen fugacity ranging from $10^{-8}$ to $10^{-15}$ bars at 1200 and 800°C, respectively).

Selected crystals were analysed by single-crystal X-ray diffraction (CCD detector), electron microprobe and optical absorption spectroscopy. The crystals obtained were found to be chemically homogeneous, with the Co$^{2+}$ content ranging from 0.06 to 1.00 atoms per formula unit, and varied in colour from light blue to intensely dark blue with increasing Co$^{2+}$ content. The progressive substitution of Co$^{2+}$ for Mg causes a large increase of tetrahedral bond length (from 1.919 to 1.944 Å), which is responsible for the observed increase of both unit cell parameter (from 8.079 to 8.100 Å) and oxygen positional parameter (from 0.2622 to 0.2635). Optimized structural formula show that the cation inversion between tetrahedrally- and octahedrally-coordinated sites is directly correlated with equilibration temperature.

At the constant temperature of 800°C, the inversion degree decreases from 0.23 to 0.14 with increasing Co$^{2+}$ content. With respect to Mg, Co$^{2+}$ shows a higher preference for tetrahedral coordination, and its site preference for octahedral coordination ($e.g.$, $^{\text{V}}\text{Co}^{2+}$/Co$_{\text{tot}}$) increases from zero to 0.14 with increasing Co$^{2+}$ content. The optical absorption spectra, measured between 4000 and 35000 cm$^{-1}$, show a set of three bands at $\sim$ 4300, 7200 and 17.000 cm$^{-1}$ marking spin-allowed electronic d-d transitions of Co$^{2+}$ in tetrahedral coordination. The absorption bands of Co$^{3+}$ are absent, in agreement with the highly reducing conditions imposed during crystal growth. The observed transitions are due to Co$^{2+}$ in tetrahedral coordination, and are the only responsible for the characteristic blue colour of cobalt spinels.
Ni-FREE, BLACK CERAMIC PIGMENTS BASED ON Co-Cr-Fe-Mn SPINELS: A REAPPRAISAL OF CRYSTAL STRUCTURE, OPTICAL PROPERTIES AND TECHNOLOGICAL BEHAVIOUR

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The pigments used to impart black shades to ceramic wares are mostly synthetic spinels. The best colouring performance in the industrial practice is ensured by complex mixed oxides (Cr, Fe, Mn, Co, Ni, and sometimes further transition elements). This turns the black pigments as the most expensive ceramic colorants after those based on noble metals or cadmium selenide. The design criteria followed in the industry basically consist in admixing different transition metal oxides in order to get into the spinel structure as much ionic species as possible (e.g. Cr³⁺, Fe²⁺, Fe³⁺, Mn²⁺, Mn³⁺, Co²⁺, Co³⁺, Ni²⁺) each able to absorb in the visible spectrum, so contributing to achieve the best black colour. From the colourimetric viewpoint, the target is a minimal brightness without significant chroma contributions. Besides spinels have been deeply investigated and the relationship between crystal structure and properties is well known for binary (and to some extent ternary) compositions, the complex systems used in ceramic pigments are not modelled and the application of conventional XRD and spectroscopic approaches is complicated by the occurrence of several transition metals. Both health regulations (preventing the use of carcinogenic compounds like Ni-bearing oxides) and technological innovation (digital decoration and particularly ink-jet printing) are changing the market demand towards high performance and safe pigments. This is not an easy task, because some pigment properties are ensured by the undesired elements (e.g. Ni was used to improve the chemical resistance in Zn-rich glazes). From this standpoint, a reappraisal of crystal structure, optical properties and technological behaviour of black spinels is needed to define the best compositions in the Co-Cr-Fe-Mn system and disclose the pigment-glaze interactions affecting the final crystallochemical features after the ceramic process. For this purpose, 21 ternary and quaternary spinel formulations were designed, using the crystallochemical criterion of Cr³⁺ occupancy of the octahedral site (with Co, Fe and Mn sharing the tetrahedral site): progressive decreasing of chromium (from 2 to 1.5, 1, 0.5, and 0). Spinel pigments were prepared from these batches, simulating the industrial processing (firing at 1300°C) and characterizing the powder samples through XRD (Rietveld refinement); optical and Raman spectroscopy; technological testing (in different glazes). Spinel pigments are monophasic (but when the sum Cr + Fe exceeds the occupancy of the octahedral site, resulting in spinel+hematite assemblages). The colour ex synthesis is uniformly black (but when Cr occupancy = 2). The colouring performance depends on the chemical composition and firing temperature of the glaze: black shades are kept when Cr occupancy is between 1 and 1.5 apfu, while for values < 1 the spinel reacts with the glass causing bubble formation and eventually bloating phenomena. Suitable black spinels exhibit unit cell parameter in the 8.35-8.40 Å range and anionic parameter in the 0.258-0.262 range. The best colouring performance in glazes rich in alkaline-earth elements correspond to quaternary batches; in particular, the best behaviour in zinc-rich glazes is ensured by high cobalt amounts (nominally half occupancy of the tetrahedral site). More suitable for high temperature glazes (rich in alkalis) are spinels richer in Fe and/or Mn. Therefore, the mechanisms controlling the colouring performance seem to be the partial occupancy of the octahedral site by Cr³⁺ and the amount of cations with a strong affinity to the tetrahedral site to contrast the formation of solid solution with Mg and Zn that would turn the colour to brown shades. Preliminary Raman observation has shown that samples with best colour are heterogeneous, with strong local spectral differences, and highly disordered, with large Raman peaks, prompting for further EDS and XRD characterization (run within the PRIN project SPIN GEO-TECH).
HIGH ANGULAR ANNULAR DARK FIELD (HAADF) MICROSCOPY: A NEW LOOK INTO CRIPTED SUB-NANO DOMAINS IN MINERAL SCIENCES

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A major challenge to the development of a full understanding of mineral and ceramic nano-structures, including unit cell defects and distortions and local charge balance problems, is to identify contaminant (< 10 ppm) elements and characterize their environment at the nano-scale.

Atomic-scale techniques, such as conventional transmission electron microscopy, although powerful, are limited by the extremely small amounts of material that are examined. However, recent advances in electron microscopy provide a number of new analytical techniques that expand its application in environmental studies, particularly those concerning trace elements with high atomic number compared to those of the hosting phase.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), STEM-energy-dispersive X-ray spectrometry (EDX), and energy-filtered TEM (EFTEM) can be effectively used to identify and characterize these elements. The technique of high-angle annular dark-field (HAADF) imaging, allows forming images by collecting high-angle scattered electrons using an annular dark-field detector in a dedicated scanning transmission electron microscopy (STEM) instruments. This technique, in contrast to common TEM ones, is not limited to fully electron transparent sample areas, but also slightly thicker sample volumes are good for investigations. The contrast of HAADF images is i) strongly dependent on the average atomic number of the scatterer encountered by the incident probe, ii) not strongly affected by dynamical diffraction effects, iii) not strongly affected by defocus and, finally, iv) not strongly affected by sample thickness variations; the spatial resolution is limited by the size of the focussed incident probe.

Furthermore, the high sensitivity of HAADF image contrast to the average Z-number of the specimen atomic columns has allowed the use of this methodology to study the presence of single atoms of dopants in a crystal structure, or to derive the chemical profile of buried layers in a host matrix.

As examples, both gold nano-crystals in olivine and iridium nano-clusters in rutile have been identified by HAADF-STEM and STEM-EDX mapping and subsequently characterized by high-resolution TEM (HRTEM). The combined use of these techniques greatly expands the effective application of electron microscopy in mineralogical studies, especially when applied to heavy elements of very low concentrations. Examples of how this electron nano-beam technique can be used to characterize a low concentration of heavy metals (a few ppm) on nano-scale particles are discussed.
This work aims at exploring the character and mechanisms of structural relaxation in minerals, through a detailed spectroscopic study of the real structure and compositional dependence of \( T-O \) and \( M-O \) bond distances of Cu centered \( T.O_4 \) and \( M.O_6 \) polyhedra in synthetic spinel-cuprospinel single crystals. Large (up to mm-sized) spinel single crystals with variable composition in the binary \( Mg(1-x)CuxAl_2O_4 \) were synthesized by the flux-growth method. This method employs a mixture of nutrient oxides (\( MgO \), \( Al_2O_3 \) and \( CuO \), in this case) and \( Na_2B_4O_7 \) as flux compound as starting material, which was put in a Pt crucible. The synthesis experiments were conducted in air in a muffle furnace. The temperature was first raised to 1200°C and then leaved constant for 24 hours, to allow complete dissolution of the nutrient oxides and homogenization of the melt. The temperature was then decreased by 4°C/hr down to 800°C, and subsequently cooled more quickly to ambient conditions. The proportions of the nutrient oxides and the flux compound were changed in order to obtain spinel single crystals of different compositions, aiming to cover the entire range between the two end members spinel \( sensu \ stricto \) \( MgAl_2O_4 \) and cuprospinel \( CuAl_2O_4 \). Up to now, we have successfully synthesized single crystals in the \( Mg(1-x)CuxAl_2O_4 \) series with nominal compositions in the range \( x = 0-0.7 \).

Single crystal optical absorption spectroscopy in the UV/VIS-NIR spectral range confirms that Cu actually entered the crystal structure. Furthermore, the optical absorption spectra demonstrate that \( Cu^{2+} \) is present in both \( T \) and \( M \) sites of the spinel structure, with a strong preference for the \( T \) sites. Absorption bands, resulting from spin-allowed electronic \( d-d \) transitions in \( Cu^{2+} \) at \( T \) and \( M \) sites, were observed at \( \approx 6900 \text{ cm}^{-1} \) and \( \approx 13900 \text{ cm}^{-1} \), respectively. The intensity of these bands increase with the Cu content of the spinel. The crystal field splitting energy for \( Cu^{2+} \) at the tetrahedrally coordinated \( T \) site is predicted by ligand field theory to correspond to \( 4/9 \) (\( \approx 0.44 \)) of the splitting energy for octahedrally coordinated \( Cu^{2+} \) at the \( M \) site. Considering that \( Cu^{2+}-O \) distances are somewhat shorter than \( M-O \) distances in Cu-substituted spinel, the experimentally derived value of 0.49 is in excellent agreement with theory. In addition, the fact that no significant composition dependent energy shifts of the absorption bands caused by \( Cu^{2+} \) at \( T \) and \( M \) sites are observed in the present spectra indicates that \( MO_6 \) and \( TO_4 \) polyhedra are structurally strongly relaxed in this solid solution series.

Both the synthesis experiments and the spectroscopic measurements were performed at the Department of Mineralogy of the Swedish Museum of Natural History (Stockholm). This project (SE-TAF_893) received support from SYNTHESYS which is financed by the European Community - Research Infrastructure Action under the FP7 “Capacities” Specific Programme.
THE EFFECTS OF TEMPERATURE ON THE CRYSTAL STRUCTURE OF A NATURAL EPIDOTE

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The effects of temperature on the crystal structure of a natural epidote from the intrusive/metamorphic complex of Val Sissone, Valmalenco, \([\text{Ca}_{1.925}\text{Fe}_{0.745}\text{Al}_{2.265}\text{Ti}_{0.004}\text{Si}_{3.037}\text{O}_{12} \text{(OH)}] \), \(a = 8.8924(7) \), \(b = 5.6214(3) \), \(c = 10.1547(6) \) Å and \(\beta = 115.396(8)\)\(^\circ\) at room conditions, Sp. Gr. \(P2_1/m\) have been investigated with a series of structure refinements at low T (293-100 K) by means of single-crystal X-ray diffraction (SC-XRD) and at high T (293 and 1070 K) by means of neutron single-crystal diffraction.

The low- and high-T experiments confirm that epidote is stable within the whole T range investigated (i.e. 100 K - 1070 K) and that the space group \(P2_1/m\) is maintained. At high T, a positive thermal expansion is observed along all the three crystallographic axes (with \(\Delta a/a \approx 0.55\%\), \(\Delta b/b \approx 0.91\%\), \(\Delta c/c \approx 1.00\%\) and \(\Delta V/V \approx 2.4\%\) between 293-1070 K). At low T, within the precision and accuracy of our CCD data, the unit-cell constants do not vary significantly, and only a slight decrease of the monoclinic angle is observed.

The refinements performed on the whole T range confirm that Fe\(^{3+}\) occupies, along with Al\(^{3+}\), the M(3) site [\%Fe(M3)\textsubscript{100K} = 69.6(4)\% X-ray data, \%Fe(M3)\textsubscript{1070K} = 74(2)\% neutron data]. In other words, the M(1) and M(2) sites are fully occupied by Al. Moreover, the high-T structural refinement shows that no dehydration effect occurs.

Over the whole T range investigated, the structure behaves without any drastic change on most of the geometrical parameters; only little variations on inter-atomic bond distances, thermal vibration of all the atomic sites, and inter-polyhedral tilting occur. The main low-T effect is observed on the vibrational regime of the atomic sites; a significant monotonic reduction of the magnitude of the thermal displacement ellipsoids, with a variation of \(U_{eq}\) (defined as one third of the trace of the orthogonalised \(U_{ij}\) tensor) by \(\approx 40\%\) is observed for both the Ca-sites between 293 and 100 K. However the vibrational regime of the two Ca-sites is slightly different within the T-range investigated: the Ca(1) site shows a lower \(U_{eq}\) and a less pronounced anisotropy, (represented by the ratio R1/R3 respectively the longest and the shortest components of the root-mean-square components of the thermal ellipsoids) with respect to Ca(2) at any temperature. This is basically due to the different coordination shell of the two cationic sites, with longer bond distances for Ca(2).

Within the T range investigated, the thermal displacement ellipsoids of the oxygen sites are only slightly pronounced; the most significant anisotropy is observed for the three oxygen of the two corner-sharing T-sites [O(3), O(8) and O(9) oxygen sites, with R1/R3 < 3 at low T and R1/R3 ~ 2 at high T]. This effect might be driven by rotation of the Si(2)-tetrahedron due to the presence of Fe\(^{3+}\) at the M(3) site.

The nuclear refinements show that two possible hydrogen bonds, with O(2) and O(4) as acceptors [\textit{i.e.} O(10)--H(1)..O(2) and O(10)--H(1)..O(4)] occur. However, the topological configuration of the bonds suggests that the O(10)--H(1)..O(4) is energetically more favourable, as H(1)..O(4) = 1.9731(28) Å, O(10)--O(4) = 2.9318(22) Å and O(10)--H(1)..O4 = 166.7(2)\(^\circ\), whereas H(1)..O(2) = 2.5921(23) Å, O(10)--O(2) = 2.8221(17) Å and O(10)--H(1)..O2 = 93.3(1)\(^\circ\) (at 293 K). The O(10)-H(1) bond distance at 293 K corrected for “riding motion” is 0.9943 Å.
The south-western area of the Mt. Etna volcano has been studied because the presence of peculiar mineralogical association. In our previous study we investigated the Biancavilla area, a dome and dyke system with autobrecciated portion. In the Biancavilla volcanic system the metasomatic process led to the formation of new minerals, fluoro-edenite and fluoroflogopite (Gianfagna & Oberti, 2001; Gianfagna et al., 2007), and some rare minerals, such as pseudobrookite and As-apatite(Ca, F) (under study).

In this work we studied the Santa Maria di Licodia area, a dome located on the East side of the Biancavilla volcanic area. Some significant differences are present respect to the Biancavilla, such as the presence of a fibrous orthopyroxene instead of fibrous fluoro-edenite. Fibrous orthopyroxene is rare, and was found in ultramafic xenoliths and interpreted as an autometasomatic product of hydrous magmas (Bryant et al., 2007).

With the aim to investigate a possible metasomatic process in S. Maria di Licodia area, a detailed sampling was executed on both the unaltered lava portion (massive rocks) and the altered portion (massive and brecciated rocks) of the dome. Combining mineralogical and petrographic data the presence of fibrous orthopyroxene in both massive and brecciated portion was evidenced. Besides the fibrous opx, the secondary mineral phases also include alkali-feldspars (Na), augitic clinopyroxene, apatite, Fe-Ti oxides.

Orthopyroxene show different morphology, such as prismatic, acicular and fibrous. In the massive rocks, fibrous orthopyroxene appears at the expense of probable olivine, in veins and in reaction rim. Here the orthopyroxene forms radiating aggregates totally replacing the previous crystal. The acicular morphology is only present in the pores of the rocks. Finally, in the brecciated portions the orthopyroxene is characterized by loose fibers.

Different morphology correspond to differences in composition, in particular in the iron content. The EMPA analyses on the orthopyroxene form the massive rocks evidenced high content of FeO (until 18 wt.%), while SEM-EDS micro-analyses on the fibers of the brecciated portion highlighted a more large variability, ranging from 4 to 14 wt.% FeO.

X-ray investigation on brecciated (fine) portion allowed to individuate and identify the orthopyroxene as an enstatite ferroan, as also confirmed by the EDS micro-analyses. Further mineralogical investigations are in progress to better define and characterize this rare fibrous orthopyroxene.

In the present project we have simulated the properties of ultrathin layers of nickel and iron oxide epitaxially grown on copper (001), which represent a new class of materials with potential applications in microelectronics, magnetic tunnel junctions, flat panel displays, model supports of catalytic systems, etc. The interest in these systems comes mainly from the theoretical possibility to tune the electronic and geometric properties of the films so as to obtain new desired properties by simply varying the lattice parameter through a proper choice of the appropriate metal substrate, by modifying the film thickness or the nature of the interface, by selectively introducing hetero-atoms or defects in the structure. On the other hand, the fact that sometimes the films possess a different geometric and electronic structure is one of the fascinating aspects of these materials, and opens new perspectives for their use in various applications. Another property of interest is related to the magnetic behavior. This can be modified in principle by interfacing a nonmagnetic metal with a magnetic oxide or simply by changing the lattice mismatch. The nature of the bonding at the interface is essential in determining the final magnetic properties of the system.

Bearing in mind the great interest in this field, we decided to undertake the present study where the properties of ultrathin layers of nickel and iron oxide epitaxially grown on copper (001) have been determined, by adopting a periodic slab model, consisting of five layers of Cu covered on both sides with NiO and FeO monolayers.

The choice of the metallic substrate was dictated by the need to improve and further develop applications based on copper, in view of recent advances in microelectronics and other advanced technologies. The electronic, magnetic and structural properties of the oxides and of the complex systems have been determined. Moreover, the topological analysis of the investigated structures in the framework of the Bader’s theory has been performed.

The calculations have been performed by exploiting the ab-initio CRYSTAL09 program at the HF/DFT level. Different Hamiltonians and basis sets have been tested in order to choose the computational setting which better reproduced the experimental observations.

The present studies have shown that the presence of the copper substrate modifies indeed the structural and electronic properties of an epitaxial oxide monolayer; for example, it has been noted that the conductive properties of the materials change significantly, as shown by the analysis of the density of states and band structures. Moreover the antiferromagnetic properties of the films supported by the metallic substrates don’t differ significantly from those of the unsupported ones; both unsupported and supported films show an antiferromagnetic ordering.
CHARACTERISATION OF SYNTHETIC SPINELS IN THE Fe\textsuperscript{2+}(Al,\textit{Cr})\textsubscript{2}O\textsubscript{4} SERIES BY MEANS OF SINGLE CRYSTAL XRD, ELECTRON MICROPROBE AND MÖSSBAUER SPECTROSCOPY

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Single crystals along the hercynite-chromite join were synthesised using a flux-growth method. Analytical grade Al\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3} powders were dehydrated and dried at 900°C for 12 h before mixing with Na\textsubscript{3}B\textsubscript{4}O\textsubscript{7}, used as flux compound. Around 6 g of starting material was ground under acetone in an agate mortar and mixed with flux/nutrient ratio ranging from 1.3 to 2.0 depending on nutrient compositions. The mixture was loaded in a 10 cc Pt/Au (5%) crucible with a lid. For thermal runs an ENTECH vertical tube furnace equipped with programmable temperature controller and controlled atmosphere flow system was used. In order to obtain a homogeneous melt, the load was heated at 1200 or 1300°C for 24 h. Subsequently the temperature was linearly decreased by 300°C with a cooling rate of 4°C h\textsuperscript{-1}. A reducing atmosphere was provided by a continuous flow of high-purity CO\textsubscript{2} and H\textsubscript{2} gases through the furnace. The CO\textsubscript{2}:H\textsubscript{2} ratio was maintained by TYLAN flow controllers and was kept constant at 1:2. Oxygen fugacity ranged from 10\textsuperscript{-11} to 10\textsuperscript{-17}bars at 1200 and 900°C, respectively. The thermal runs were ended turning off the furnace and the product was allowed to cool more rapidly to room temperature.

For single-crystal XRD analyses, synthetic spinels were mounted on an automated KUMA-KM4 (K-geometry) diffractometer, using MoK\alpha radiation monochromatized by a flat graphite crystal. The unit cell (\textit{a}_0) was determined by 24 equivalent reflections of (12 8 4) (about 90° of 2\textit{θ}), accurately centred at both sides of 2\textit{θ}. Data collection was made according to Della Giusta \textit{et al.} (1996) up to 2\textit{θ} = 55°. Structural refinement was carried out against Fo\textsubscript{2}hkl in the \textit{Fd}-3\textit{m} space group (with origin at -3\textit{m}), without chemical constraints, using the SHELX-97 program (Sheldrick, 1997). Cell edges varies within the range 8.1534(6) Å - 8.3672(1) Å, while the oxygen positional parameter is comprised between 0.2645(2) and 0.2628(1).

Structural parameters \textit{a}_0, T-O and M-O increase with chromite content while \textit{u} decreases.

Mössbauer spectra were acquired at room-temperature using a conventional spectrometer system operated in constant acceleration mode. The spectra are dominated by a relatively broad absorption envelope consistent with ferrous iron. Several samples show also weaker contributions from ferric iron, despite the strongly reducing conditions prevailing during the synthesis procedure. The amount of ferric iron appears to increase with the chromite component of the samples.

Arsenic sulfides are widely studied for their great technological potential and As₄S₄ compounds in particular are of interest to material scientists owing to their high infrared transparency, photo-structural sensitivity and doping ability (Nalwa, 2001 and references therein). Most of them consist of a packing of cage-like, covalently bonded As₄Sn (n = 3, 4, and 5) molecules held together by van der Waals forces, and the investigation of their thermodynamic properties, such as thermal expansion and compressibility, can usefully contribute to the understanding of the interactions governing the structure and its stability.

The crystal structure of the α modification of As₄S₄ (i.e., the mineral realgar) has been recently investigated by in situ X-ray single-crystal and powder diffraction methods up to 43 GPa (Többens et al., 2010). On the other hand, no data on the compressibility and structural behaviour of β-As₄S₄ at high pressure have been reported in the literature so far.

Under ambient-pressure conditions, β-As₄S₄ crystallizes in the C2/c space group with a = 9.957(3), b = 9.335(4), c = 8.889(5) Å, β = 102.48(4)° (Porter & Sheldrick, 1972). The structure consists of As₄S₄ cage-like molecules, characterized by a D₂d molecular symmetry, with each As atom bonded to one As and two S atoms. Crystals of β-As₄S₄ were obtained by heating crystals of realgar under vacuum at 295°C for 24 hours. The quenched product was used to collect single crystal intensity data at pressures up to 4.8 GPa using two different diamond anvil cells loaded with different crystals in a methanol-ethanol (4:1) mixture. Unit-cell measurements have been performed in a ETH-type DAC using a STOE STADI IV four-circle diffractometer equipped with a point detector (University of Padova). The measurement of unit-cell parameters became impossible beyond 2.8 GPa because of a dramatic broadening of reflections. The whole intensity data collections were carried out at different pressure steps up to 2.7 GPa using an Oxford Diffraction -Xcalibur2 diffractometer equipped with a CCD detector (Bayerisches Geoinstitut) using a Bolher-Almax DAC. The diffraction study has been combined with a microRaman investigation throughout the whole experiment. The compressibility data were fit through a Birch-Murnaghan equation of state truncated at the 3rd-order with resulting bulk modulus K₀ = 10.9(2) GPa, and its first pressure derivative K’ = 8.9(3). These values are substantially identical to those found for the low temperature polymorph (Többens et al., 2010) which is characterized by the same kind of molecule. The response to pressure is almost isotropic and the dramatic decrease of the unit-cell volume (from 805.17 to 702.7 Å³ at 2.7 GPa) is mainly due to the reduction of intermolecular distances, whereas molecules remain substantially unchanged. In particular, the volume of the As₄ disphenoidic group does not decrease significantly while the molecular volume contracts by approximately 1.6%, due to the shortening occurring along the S3-S3 [30-1] and S1-S2 [010] directions. Further experiments, carried out at higher pressures with a thinner crystal, only led to a rough measurement of the unit-cell parameters showing that β-As₄S₄ does not undergo any phase transition in the whole pressure range investigated, in spite of a compression to about 80% of the initial volume.

SYNTHESIS AT ROOM AND HIGH PRESSURE OF PYROXENES
ALONG THE JOIN CaCoSi2O6-Co2Si2O6

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The study of pyroxenes along the join CaCoSi2O6-Co2Si2O6 has an interest in mineralogy and in ceramic sciences. As for ceramics, Co-bearing silicates can act as blue to pink pigments. Blue color stems from Co in tetrahedral coordination, like in CoAl2O4 spinel (blue cobalt), whereas higher coordination drives to a pink hue. In CaCoSi2O6-Co2Si2O6 pyroxenes the substitution occurs in two different sites $M_1$ and $M_2$ at different coordination, being $M_1$ a regular octahedron and $M_2$ a distorted polyhedron with 6-8 fold coordination, and the effect of Co for Ca substitution on the pyroxene color can therefore be investigated. As for mineralogy the series is an analogue to the series diopside-enstatite (CaMgSi2O6-Mg2Si2O6) and hedenbergite-ferrosilite (CaFeSi2O6-Fe2Si2O6) of quadrilateral pyroxenes. The comparison on the crystal chemistry and phase transitions of the effect of the solid solution of Ca for Co on the $M_2$ site, vs. that of Ca for Mg and for Fe, can provide the basis for an extensive model of solid solutions in pyroxenes. Preliminary results on the synthesis and characterization of CaCoSi2O6-Co2Si2O6 pyroxenes are here reported.

Previous experimental data on CaCoSi2O6-Co2Si2O6 pyroxenes are confined to the end members, CaCoSi2O6 which was synthesized at room pressure, and Co2Si2O6 which was synthesized above 3 GPa and 7 GPa in the orthorhombic and monoclinic polymorphs respectively. In the present study eleven compositions along the series, at step of 10 mol% of the CaCoSi2O6 component, were synthesized at room and high pressure. Room pressure syntheses were achieved by calcinations at 1000°C for 12 hours of stoichiometric mixtures of the oxides. Combined SEM/EDS, Raman and XRD investigation gave evidence of an incomplete reaction for the starting materials, with the presence of residual amorphous silica. Clinopyroxene, with a composition close to (Ca0.9Co0.1)CoSi2O6, was found in all samples except that with stoichiometric composition CaCoSi2O6, where an assemblage of Co-olivine (Co2SiO4) and silica was found. Co-olivine was observed in all samples, less in Ca-richer compositions. Co-ackermanite (Ca2CoSi2O7) was observed between CaCoSi2O6 and (Ca0.6Co0.4)CoSi2O6. The color changes from pink to blue together with increasing ackermanite and decreasing olivine.

To obtain wider pyroxene solid solution, high pressure synthesis on the same starting materials was carried out with piston cylinder apparatus at P = 3 GPa and T = 1200°C, for 4 to 20 hours. XRD and Raman analyses show that between CaCoSi2O6 and Ca0.4Co0.6Si2O6 a clinopyroxene solid solution is the only phase. In the sample with starting composition Ca0.2Co0.8Si2O6 we obtain the coexistence of clinopyroxene, orthopyroxene and quartz, and in Co2Si2O6 only olivine and quartz, without formation of a pyroxene phase. Cell parameters follow the same trend with composition previously observed in C2/c pyroxenes along the series diopside-enstatite and hedenbergite-ferrosilite. Changes observed in Raman spectra may be interpreted as in pyroxenes along the diopside-enstatite.

Single crystal XRD and optical spectroscopy investigations, as well as attempts to synthesize Co2Si2O6 clinopyroxene by means of a multi-anvil apparatus, are in progress.
THERMOELASTIC BEHAVIOUR OF \(C2/c\) OMPHACITE

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Omphacite shows an intermediate composition along the binary jadeite-diopside join of the Na-pyroxene solid solution. Most of the interest in this mineral has been focused on the order-disorder phenomena which it undergoes, causing a \(P2/n \leftrightarrow C2/c\) phase transition (Carpenter et al., 1990). Although omphacite plays a key role in high-pressure and high-temperature geological environments, \textit{in situ} studies on its thermo-elastic behaviour under non-ambient conditions are definitively scarce. Some experimental results have been reported on the omphacite high-pressure \textit{in situ} behaviour (McCormick et al., 1989; Pavese et al., 2001) and, more recently, the thermal expansion and the thermal equation of state were studied by (Pavese et al., 2000) and by (Nishihara et al., 2003) respectively. However all these data were collected using different experimental conditions, by both powder materials and single crystals and often off the omphacitic composition. Therefore they do not provide a systematic on the high-pressure and high-temperature behaviour. In order to constrain the correct value of the compressibility and thermal expansion of omphacite we have studied a natural sample by high-pressure and high-temperature \textit{in situ} single crystal X-ray diffraction (in two separate experiments). Two twin and inclusion-free single crystals of \(P2/n\) omphacite from the Münchberg Mass (Bavaria) eclogitic rock were selected for this study. Its composition, Jd\(_{48}\)Di\(_{39}\)Hd\(_{6}\)En\(_{4}\)CaTs\(_{3}\), is very close to pure Jd\(_{50}\)Di\(_{50}\) omphacite. In order to obtain fully disordered \(C2/c\) omphacite crystals, isothermal annealing at 1000°C for 300 hrs was carried out using a vertical temperature control furnace. Intensity data collections were performed to verify the absence of the \(h+k=2n+1\) reflections, and data were refined in the \(C2/c\) space group. Unit-cell parameters were determined by SCXRD at 16 different pressures up to about 7 GPa. A continuous decrease of the unit-cell parameters and volume was observed as a function of pressure up to the maximum \(P\) reached (volume decreases about 5.2% up to 7 GPa). A third order Burch Murnaghan equation of state was used to fit the experimental pressure-volume data. We obtained the following coefficients: \(V_0 = 421.04(7)\), Å\(^3\), \(K_T = 118.65(1.84)\) GPa, \(K' = 5.7(6)\). The compressibility scheme \(\beta_b > \beta_c > \beta_a\) is similar to that of other clinopyroxenes. High-temperature experiments were carried out measuring lattice parameters at intervals of 50°C in the 25-800°C T range both on increasing and decreasing temperature. Continuous increasing of the unit-cell parameters and volume was observed as a function of temperature with a volume increase of about 2.3% up to 800°C. The thermal expansion obtained using the approach by (Gottshalk, 1997) yielded \(\alpha = 3.03(3) \times 10^{-6} \text{ K}^{-1}\).

We obtained two different behaviours as a function of pressure and temperature: 1) even if further experimental data are necessary for intermediate compositions, our data show that the bulk modulus value for disordered omphacite is in very good agreement with a linear combination of the bulk moduli of the Jd and Di end-members; 2) otherwise the thermal expansion value is slightly higher than that expected for a linear combination of the volumetric thermal expansion of the two end members.


FeCr$_2$O$_4$ SYNTHETIC SPINEL: 
HEATING EXPERIMENTS AND OXIDATION KINETICS

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Single crystals of FeCr$_2$O$_4$ were synthesized using a flux-growth method. Analytical grade Cr$_2$O$_3$ and Fe$_2$O$_3$ powders were dried at 900°C for 12 h before mixing with Na$_2$B$_4$O$_7$, used as flux compound. About 5-6 g of starting material was ground under acetone in an agate mortar and mixed with flux/nutrient ratio. The mixtures were loaded in 10 cc yttria-stabilised Pt/Au (5%) crucibles and covered with a lid. For thermal runs, an ENTECH muffle furnace with a programmable temperature controller were used.

In order to obtain a homogeneous melt, the load was heated at 1200°C for 24 h. Subsequently the temperature was linearly decreased to 900°C with a 4°C h$^{-1}$ cooling rates. The thermal runs were ended turning off the furnace and the product was allowed to cool rapidly to room temperature. The reducing atmosphere was provided by a continuous flow of high-purity CO$_2$ and H$_2$ gasses into the furnace. The CO$_2$:H$_2$ ratio was maintained by TYLAN flow controllers and was kept constant at 1:2. Oxygen fugacity ranged from 10-11 to 10-17 bars at 1200-900°C, respectively, which is ca. -0.1 log units from the iron-wüstite solid buffer. Additional details on the spinel syntheses can be found in Lenaz & Skogby (2003). Previous studies (Lenaz et al., 2004) showed that Cr completely fills the octahedral site, and that iron occurs almost exclusively as tetrahedral Fe$^{2+}$.

As Cr should not be oxidized in spinels, we would expect that heating affects only the iron cations present in the $T$ site. Heating in hercynite spinels, FeAl$_2$O$_4$, causes exchange of the Fe and Al cations between the two non-equivalent sites and oxidation of Fe$^{2+}$ to Fe$^{3+}$ (Lavina et al., 2005). Consequently, as Cr cannot fit into a tetrahedral site, the only possible effect is the oxidation of Fe$^{2+}$ to Fe$^{3+}$ and, possibly, the formation of $T$ site vacancies.

To reach this purpose crystals were put in a thin-walled quartz tube and heated in a vertical tube furnace at different temperatures from 600 to 1000°C. Heating runs were performed at room pressure in air. Run temperatures were accurately measured and controlled by means of a calibrated Pt / Pt-Rh thermocouple located near the sample; the uncertainty is estimated to be about ±5°C. Since the cell parameter ($a$) and the oxygen positional parameter ($u$) changes with time and temperature, a strongly correlated relationship between the heating process and the iron oxidation was supposed. At the end of the oxidation process the crystals were polished to about the median plane in order to see if and how the oxidation develops into the crystals.

In order to verify the presence of ferric iron and the formation of vacancies, SEM EBS as well as EMPA analyses have been performed and successively compared with previously performed data obtained from single crystal XRD, EMPA and Mössbauer spectroscopy.

Northern Victoria Land (Antarctica) mantle, sampled by spinel peridotite xenoliths found in basalts of Mt. Melbourne Volcanic Province, brings evidence of a metasomatic event related to Cenozoic volcanism. This metasomatic signature varies across the volcanic province: at Baker Rocks (BR) metasomatism is characterized by the occurrence of amphibole as disseminated grains or in veins hosted in lherzolite and harzburgite xenoliths carried by alkali basalt; at Greene Point (GP, about 80 km north of BR) cryptic metasomatism provides variable enrichments of incompatible elements in clinopyroxenes from lherzolite/harzburgite xenoliths that were transported to the surface by a nepheline-basanite lava.

In this work we check the effects of the two styles of metasomatism on oxygen fugacity, estimating the redox state of anhydrous xenoliths with different metasomatic signatures, by means of the spinel-orthopyroxene-olivine oxybarometer. At BR, we estimated also the redox state of the metasomatic agent (the crosscutting amphibole-bearing veins) by applying the Popp et al. (2006) method to the crystal-chemical data obtained from amphiboles crystallized in the veins.

Xenolith mineral chemistry was determined by electron microprobe, and the ferric iron content of spinels and amphibole were measured by $^{57}$Fe Mössbauer spectroscopy. Amphiboles were also characterized by single-crystal X-ray structure refinement, which allowed quantification of dehydrogenation by the method proposed by Oberti et al. (2007).

Results show that oxygen fugacities recorded by the xenoliths range from -0.2 to -1.6 log-bar units ($\Delta \log f_O^2$) with respect to the fayalite-magnetite-quartz (FMQ) buffer. The $\Delta \log f_O^2$ values calculated from amphiboles are about -0.6 log-bar units, thus in the range found for metasomatic amphibole of mantle xenoliths from the same area of northern Victoria Land ($\Delta \log f_O^2 = -1.4 : -0.4$ log-bar units, Nazzareni et al., 2010).

In detail, $f_O^2$ data shows that i) beneath Greene Point, metasomatism increased $f_O^2$ by ~ 1 $\Delta \log f_O^2$ log-bar units, whereas in Baker Rocks lithospheric mantle the metasomatic melt/rock interactions did not produce any significant change in $f_O^2$; ii) within each suite, there is no evident correlation between $f_O^2$ and the degree of mantle depletion, as indicated by spinel Cr#$^{2+}$; iii) in GP xenoliths no direct correlation is found between $f_O^2$ and the enrichment in incompatible elements in clinopyroxenes.

In conclusion, as evidenced by Baker Rocks xenoliths, mantle metasomatism leading to amphibole formation does not necessarily imply mantle oxidation; in contrast, the variability of $f_O^2$ obtained for Greene Point xenoliths highlights that the silicate melts responsible for the last metasomatic event recorded by xenoliths acted as an effective oxidiser of the depleted shallow upper mantle.
THE ROLE OF THE LONE ELECTRON PAIRS AND Fe$^{2+}$ IN THE HIGH-PRESSURE BEHAVIOR OF BERTHIERITE

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Berthierite is a sulfosalts with composition FeSb$_2$S$_4$ (space group Pbam) presenting several interesting aspects like magnetic properties (Winterberger et al., 1990) and phase transition in the temperature range 323-365 K (Łukaszewicz et al., 2001). Moreover, berthierite structure features antimony in a trivalent state and is characterized by its lone electron pair (LEP) with pronounced steric effect. In this study, high-pressure single crystal X-ray diffraction experiments have been performed on a natural sample of berthierite in order to determine its equation of state (EoS) and high-pressure crystal structure evolution.

Structural relation to stibnite and galenobismutite is also presented and the high-pressure development of the three structures compared. The purpose of this work is to contribute to the compressibility systematic for LEP compounds with the aim to outline a mechanism of their structural deformation and to define better the changes in the LEP activity as a function of pressure. Two needle-like single-crystals of berthierite were selected from a natural sample collected in the Herjia deposit (Romania), the first one for high-pressure unit-cell determination (183 x 80 x 40 m$^3$) and the other one for intensity data collection (175×75×40 m$^3$).

High-pressure single-crystal diffraction experiments were performed for each sample in an ETH-type diamond-anvil cell (DAC), equipped with diamond culets of 600 m in diameter and diamond backing plates. Stainless steel gaskets preindented to a thickness of 90 m and with a spark eroded hole of 250 m in diameter were used. A mixture of methanol and ethanol (4:1) was used as a pressure-transmitting medium and a single-crystal of quartz as an internal pressure standard. For the EoS determination, the measurements were performed using a four-circles STOE STADI IV diffractometer equipped with a point detector and controlled by the SINGLE software. No phase transitions were indicated in the investigated pressure range. The third-order Birch-Murnaghan equation of state calculated using high-accuracy volume-pressure data up to 8.046(12) GPa gave the following coefficients: $V_0 = 608.78(7)$ Å$^3$, $K_{0T} = 37.2(2)$ GPa and $K' = 7.0(1)$.

The crystal selected for structure analysis was measured from room pressure up to 7.408 GPa, including one measurement on decompression. Complete intensity data collections were performed using a STOE STADI4 four-circle diffractometer, equipped with an Oxford Diffraction CCD detector. As in the case of stibnite and bismuthinite, the crystal structure can be divided into rods comprising the short Sb-S bonds and the intervening space, which is sterically affected by the lone electron pairs of Sb. In all three structures the latter space accommodates most of the compression.

The LEP activity has been quantified by the eccentricity of the Sb coordination polyhedra. With increasing pressure the eccentricity decreases indicating a reduction of the LEP activity. The Fe octahedron, which is the stiffest coordination polyhedron in berthierite, increases its distortion between 3 and 5 GPa exhibiting an increasing in the Jahn-Teller effect with a more clear distinction between two shorter and four longer bonds.
An efficient protocol, based on advanced statistical diagnostics and robust fitting techniques applied to the least-squares processing of cation ordering-disordering kinetic data, is here presented and discussed.

The study of the inter-site cation exchange in rock-forming minerals constitutes a powerful tool for modeling the thermal history of the host rocks. In recent decades many experiments have been conducted on cation ordering-disordering in different rock-forming silicates with the aim of quantifying cation ordering as a function of chemical composition, equilibration temperature, and time. This makes it possible to estimate both the closure temperature and the cooling rate of silicates from terrestrial rocks and meteorites. The kinetics of cation ordering in minerals is less well known than the thermodynamics. This is mainly due to the scarcity of experimental data and to difficulties in interpreting the kinetic data. Moreover, as a consequence of a number of factors, kinetic data are often affected by the presence of strong outliers, i.e. data points markedly distant from the main part of the system. This fact turns into a large discrepancy between the observed and calculated data points and into an incorrect modeling of the experiment. The effect of trying to fit an outlier is to make the fits of all other data points a little bit worse with consequent biasing of the parameter estimates. This is particularly true when the outlier is also an influential point (i.e., a point that remarkably affects the model).

Bearing in mind these considerations, we proposed a protocol for processing cation ordering-disordering kinetic profiles aimed at obtaining a greater accuracy of the estimates of the least-squares optimizing procedures. The procedure, which consists in the identification of the outliers that remarkably impair the fitting by means of the so-called “leverage analysis” and some related diagnostics, has been applied to different set of synthetic data generated on the basis of the Mueller kinetic model. Random errors taken from a normal population with mean and standard deviation comparable to those obtained from experimental measurements have been added to the calculated data points. The effect of the number of experimental data points and of the distribution of them across the kinetic profile, on the reliability of the procedure and on the parameter estimates, has been also investigated.

It has been found that the proposed approach allowed the elimination of the actually aberrant observations from the data set and/or their robust weighting to inhibit the negative effects induced on the data fitting, with consequent reduction of the bias introduced into the parameter estimates and a significant improvement in the regression results.
Fe-Mg SUBSTITUTION IN PIGEONITE: A STUDY BY RAMAN SPECTROSCOPY

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The Raman spectra of 10 samples containing the mineral pigeonite, a Ca poor \( P_{21/c} \) variety of the mineral pyroxene, were measured. Seven of the studied samples come from the achondritic meteorites belonging to the family of ureilites, two are from volcanic rocks, and one is synthetic; the studied samples have an mg content \( [\text{mg} = 100\text{Mg}/(\text{Mg}+\text{Fe})] \) between 52 and 100.

The differences in Raman spectra with \( C_{2/c} \) and Pbca pyroxenes are highlighted; the peak position of the main peaks changes linearly with mg, whereas, likely for the small difference in Ca content, no correlation is present with Wo. Changes in peak position with mg of the major peaks at 340 and 670 cm\(^{-1}\) are significantly lower in \( C_{2/c} \) compared to Pbca and \( P_{21/c} \) pyroxenes. This feature is interpreted as changes in the major peaks are most related to major structural modifications in the \( M_2 \) polyhedron; such structural modifications are lower in \( C_{2/c} \) pyroxenes. Peak width in natural pigeonite is higher than in synthetic one, owing to the defective texture of the former.

The present results may provide a basis for on site analysis of pyroxenes by means of Raman spectroscopy of planetary bodies in space exploration.
Ni-Ti CO-DOPED HIBONITE (CaAl_{12}O_{19}) CERAMIC PIGMENTS:
SYNTHESIS, CRYSTAL STRUCTURE AND OPTICAL PROPERTIES

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Hibonite, with general formula \( [12]A[6]M1[5]M2[4]M3[6]M4[2]M5[6]O_{19} \), is the natural counterpart of the synthetic calcium hexa-aluminate (CaAl_{12}O_{19}) which crystallizes with the magnetoplumbite-type structure (space group \( P6_3/mmc \), \( Z = 2 \)). Calcium occurs in a 12-fold coordination site (\( A \)), whereas Al\(^{3+} \) ions are distributed over five different sites, including three distinct octahedra (\( M1, M4, \) and \( M5 \)), a tetrahedra (\( M3 \)), and an unusual trigonal bipyramid (\( M2 \)) that gives rise to a fivefold oxygen-coordinated site. Minerals of the magnetoplumbite-group habitually contain significant amounts of metals with different valences (e.g. divalent as well as tetravalent and pentavalent cations). Of great importance is the tendency of these metal ions to be hosted at definite sites. As a matter of fact, \( M2^+ \) ions are usually hosted at \( M3 \) site, while \( M4^+ \) and \( M5^+ \) ions are preferentially accommodated at the \( M4 \) site. The ions of different charges tend to improve the local charge balance in the crystal structure. Therefore, the introduction of divalent ions is thought to be achieved by co-incorporation of tetravalent or pentavalent cations which are mainly ordered over the octahedral sites in the face-sharing interlayer doublet. This ability to accommodate such a wide variety of ions, with different valence and coordination, makes the hibonite structure very interesting to be used as a ceramic pigment. In this work, the electroneutrality of the hibonite lattice was ensured by the following coupled substitution: \( 2\text{Al}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ti}^{4+} \).

Hibonite (CaAl_{12-2x}Ni_{x}Ti_{x}O_{19} where \( x = 0.1-2.0 \)) is a refractory phase hard to synthesize by the conventional solid state reaction. Therefore, kinetic hindrances were overcome through a combustion synthesis performed at 400 and 1200°C. In order to maximize the exothermic effect, fuel mixtures (urea, glycine, beta-alanine) were selected, based on their compatibility with metal nitrates used as raw materials. These synthesis strategies allowed the formation of hibonite structure directly during the combustion reaction, without any further annealing. The behavior during combustion was monitored by thermal analysis, which revealed that highly exothermic redox processes are responsible for the formation of the designed oxide compound. The hibonite characterization was performed by X-ray powder diffraction, microstructure analysis (SEM), and diffuse reflectance spectroscopy (DRS). At the lower combustion temperature, the hibonite structure is the main phase, but secondary phases were also detected, such as spinel (NiAl_{2}O_{4}), perovskite (CaTiO_{3}), and gamma alumina (\( \gamma \)-Al_{2}O_{3}). With the increasing of the combustion temperature to 1200°C, the XRD profile exhibits sharper peaks and a better peak to background ratio. The hibonite structure shows an expansion of lattice parameters that is proportional to the degree of nickel and titanium substitution for the smaller aluminium ion. In terms of optical parameters, \( \text{Ni}^{2+} \) is incorporated at two different coordination sites, \( M3 \) and \( M4 \), preferentially in tetrahedral coordination up to saturation of the \( M3 \) site. The crystal field strength of nickel in tetrahedral coordination is regularly decreasing implying an elongation of the local Ni-O distance, coherent with the volume increasing from AlO_{2} to NiO_{2} tetrahedra. Ti\(^{4+} \) ions are accommodated at the octahedral site \( M4 \), in competition with Ni\(^{2+} \), and secondarily at the 5-fold coordinated site \( M2 \). The combined XRD + DRS approach allows to understand the mechanisms of dopant incorporation into the CaAl_{12}O_{19} structure and the origin of its colour on the right track for engineering of hibonite ceramic pigments.
Sessione tematica J5:
Petrofisica e deformazione delle rocce:
dai rischi naturali alle implicazioni sociali

Conveners:
Rosalda Punturo (Università di Catania);
Sergio Vinciguerra (INGV, Roma)*
Alba Zappone (ETH, Zurich)
PHYSICAL AND MECHANICAL CHARACTERIZATION OF POTENTIAL RESERVOIR AND CAP ROCKS FOR GEOLOGICAL STORAGE OF CARBON DIOXIDE IN SWITZERLAND: WORK IN PROGRESS

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The potential for storage of CO₂ in geological formations in Switzerland has recently been evaluated by Chevalier et al. (2010). A score was assigned to each aquifer/seal pair in the Swiss Molasse basin and Jura mountains, based on an international reference scale (Bachu, 2003). The upper Muschelkalk/Gipskeuper aquifer/seal pair scored highest.

However, the spatial heterogeneity of this aquifer, combined with lack of data coverage, warrants a thorough investigation of the potential aquifer/seal pair, with emphasis on the following questions:

1) How is porosity and permeability spatially distributed in the Muschelkalk?
2) Can we use existing geophysical data (i.e., seismic lines) to provide information about the physical properties of the Muschelkalk?
3) How has the physical properties of the Muschelkalk developed over geological time?

To answer these questions we aim to compile existing published data and gather new data by laboratory measurements, where it is needed. Several sources for information are available at present, including academic literature and industry records.

Laboratory investigations on elastic properties, density, porosity and permeability are ongoing, using experimental equipment at the rock deformation laboratory in Zurich.

The work will present a state of the art of the of these studies in the perspective of a feasibility study of a pilot project of Carbon capture and Storage in the Swiss Molasse Basin.
MECHANICAL CHARACTERIZATION OF THE SERGNANO RESERVOIR BY ULTRASONIC WAVE VELOCITY MEASUREMENTS

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Proper design and planning of gas storage in natural reservoirs takes advantage of the numerical modeling of the injection process. The numerical simulation must be supported not only by a thorough knowledge of the geological and structural features of the concerned area, but also by an adequate geomechanical characterization of the involved units. Static and dynamic methods can be applied, by in situ tests or at laboratory scale.

With the final goal to furnish the input data for numerical modeling, the mechanical properties of the rocks making up the Sergnano oilfield were preliminarily investigated by ultrasonic wave velocity measurements on rock samples.

The Sergnano oilfield (CR-Italy) is located in the Pliocene-Quaternary foredeep of the Po basin; discovered in 1953, it was converted into a methane gas storage tank in 1965.

The reservoir rocks belong to the “Ghiaie di Sergnano unit”, overlying the Gallare marl (Marne di Gallare). The cap rock is represented by the Santerno shale (Argille di Santerno).

Samples were collected from the two cores gently offered by ENI S.p.A.: six in the cap rock at the depth between 1330-1340 m, and two at the base of the reservoir at about 1710 m b.s.l..

The mineralogical clay nature of the Santerno shale was derived from X-ray diffraction analysis and their behavior defined by the Atterberg limits. The physical properties of bulk and specific unit weigh were measured and porosity calculated, both for the cap rock unit then for the bottom one.

P and S high frequency wave velocities, measured in different directions, normal and parallel to the bedding plane, allowed to define a poor anisotropic behavior. The effect of increase confining pressure, up to 290 MPa, was explored and correlation equations between wave velocity and pressure were attempted. The dynamic elastic properties were then calculated: Bulk modulus (K), Elastic modulus (E), Shear modulus (G), Poisson’s ratio (ν).
ULTRASONIC EMISSIONS RELATED TO ROCKS CRACKING PRECURSORS:
FIRST RESULTS FROM ROCK SAMPLES TESTS

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The analysis of stress accumulation and crack-induced vibrations of an unstable slope before failure is
considered an effective tool in rock-fall disaster forecasting. The national project SMILAND (Innovative
Integrated Systems for Monitoring and Assessment of High Risk Landslides) aims at development of innovative
solutions for rocky landslide early-warning based on optical fiber sensors. Within this project, a petrophysical
characterization, based on different laboratory methods aims to detect the elastic properties, has been carried out
on different type of rock samples.

The acoustic emissions (AEs) released during the rock fracturing of laboratory samples has been also
studied. Nowadays, the implemented AE monitoring techniques, used both in laboratory and in the field, are
mainly based on seismometers, geophones or also microphone arrays. These devices, although accurate and
reliable, may be difficult to install in the field and are liable to lighting and electromagnetic interference (EMI).

In recent years, the interest in fiber optic-based sensors (FOS) has experienced a rapid increase, fostered
by the advantages that these sensors offer in comparison with the classical ones. In particular, their intrinsic
robustness to EMI and lightning, their remote operability and distributed sensing ability, make the FOS suitable
to the distributed monitoring of several parameters (e.g. strain and temperature) in hard environment conditions
too. The application of such sensors to landslides and cliff collapses is nowadays mainly limited to displacement
measurements. Nonetheless, the application of fiber sensors to the characterization and monitoring of seismic
precursory patterns of unstable rocks or cliffs is still an unexplored research field. Interferometric sensors have
shown very high sensitivity, that consists an extremely important feature for detecting small wave amplitude
precursor AEs related to initial rock cracking development. Considering that the correlation between the rock
behavior to different stress conditions and internal resistance variation is principally due to the mechanical
properties of the rock mass, different rock types samples (marble, dolomite and trachyte) has been used in
laboratory tests to detect the elastic properties of rocks related to mineral composition, fabric, structure and
porosity. Elastic properties of rock samples have been measured by using different laboratory methods such as
uniaxial apparatus, ultrasonic static and dynamic multifrequency instrument. The comparison of data results have
shown a substantial homogeneity from elastic modulus obtained by different methods.

In this frame, all the rocks involved in the testing phase have been characterized from the mineralogical-
petrographical and structural point of view. Such a complete characterization has been carried out on three
mutually perpendicular sections with respect to the macroscopic fabric elements of the rock. Grain and bulk
densities of the rocks will be also measured.

Laboratory testing of FOS have been carried out coupling the developed sensors with several rock
samples, having different lithological, structural and mechanical features.
As argued by the European Commission - Directorate General for Energy and several international bodies, like among the others the Carbon Sequestration Leadership Forum (CSLF), the Carbon Capture and Storage (CCS) is accepted as a reasonable solution for reducing greenhouse gas emissions, figuring in perspective as a countermeasure against the climate change. In particular, there is a general agreement to consider the CO₂ storage in geological formations as a feasible technique and Weyburn-Midale CO₂ Project (Canada Saskatchewan) and Sleipner Project (Norway - North Sea) seem to demonstrate it. Yet the safe and effective approach in a long-term perspective (500-1000 years) is still largely not proven. Thus the understanding of the long-term transport and fate of CO₂ and associated physical processes is still a crucial issue in view of the deployment of the technology.

CO₂ can be stored in different geological reservoirs as: depleted oil and gas fields, unminable coal seams and deep saline aquifers. The porous rocks with salt waters offer the highest CO₂ storage potential and the injection should take place in geological reservoirs located at least 800 meters of deep where the conditions of temperature and pressure are suitable for injecting CO₂ in supercritical conditions and with the characteristics of a fluid. The reservoir must be covered by a clay (or equivalent) geological formation, which can prevent the leakage of CO₂ into geological formations above.

The characterization of the caprock-reservoir system for CO₂ geological storage includes several processes as for example: well integrity, chemical reaction, thermal flux, multiphase flow and transport, stress/strain change, induced fracturing and fault reactivation. In this complicated contest, it is undeniable that the numerical modeling is the only tool available for predicting the long-term behavior of CO₂.

The paper describes the geological models created for three different potential reservoirs in Italy: a) Offshore Sibari basin (denominated Calabria Ionica) where the geological caprock is represented by a thick clay formation (Pleistocene) locally with thin silt or sand layers and the reservoir is represented by high porosity and salt water arenaceous/gravel-sand formation (upper Miocene), b) Offshore North Adriatic sea where the caprock is represented by clay with silt and thin layers of sand (Pleistocene) and the reservoir is represented by high porosity and salt water sands with few thin clay intercalation (Pleistocene-Middle Pliocene), c) Area onshore around Malossa oil and gas field in Lombardia region in which the caprock is represented by a clay formation known as Santerno Clay of Pliocene age and the reservoir is a conglomerate formation with salt water known as Sergnano Gravel of upper Messinian age.

The numerical modeling results of CO₂ injection and fate by using the Integrated System for Modeling Analysis (SIAM) developed by RSE Company are also shown with particular relevance to CO₂ plume extension during the 30 years of supposed injection and extended to more than 500 years after the start of the CO₂ injection process itself. The stress conditions generated around the injection wells, inside the reservoirs and at reservoir-caprock interfaces are also shown to verify the safety pressure criteria. The injection of 1 Mton/year of CO₂ for a 30 years period is considered for case a) and b) while, for case c) we considered a CO₂ injection rate of 0.3 Mton/year. The CO₂ storage capacity of each saline-aquifer reservoirs has been estimated by using the method proposed in the EU Geocapacity Project with different values of the storage efficiency factor and compared with the more sophisticated procedures related to numerical modeling.
RELATIONSHIP BETWEEN STRUCTURAL, PETROLOGICAL AND PETROPHYSICAL FEATURES ON STRAIN EVOLUTION IN THE KAVALA SHEAR ZONE (RHODOPE MASSIF, NORTH-EASTERN GREECE)

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Mylonitic shear zones represent the binary which drives the structural evolution of mountain belts; for this reason they can be considered as “natural laboratories” where it is possible to observe and concentrate the investigation on microstructural and textural characteristics related to the changes in physical and mineralogical properties of progressively deformed rocks.

Our attention focussed on the Kavala (Symvolon) pluton, which crops out in North-Eastern Greece and is mainly composed of early-Miocene granodiorite deformed at various extents during syn-shearing emplacement. According to the Authors, it represents the South-Western termination of the Rhodope Core Complex, which was exhumed as a result of large scale extension from mid-Eocene to mid-Miocene times.

Structural features of mylonitic textures highlighted the presence of a NE-SW monotone stretching lineation consistent with the shape elongation of the outcropping pluton, with intensity in deformation increasing towards the contact with the host gneiss. Despite gneiss rocks experienced a longer deformation history, any previous fabric was completely reworked by the Alpine mylonitic shearing activity. Such a peculiar outcrop conditions set aside samples to be collected by taking into account progressive deformation.

Bulk rock geochemical and petrographic investigation allowed the characterisation and selection of representative samples for both Kavala granitoid and country gneiss rocks. They mostly classify as metaluminous to weakly peraluminous granodiorite and strongly peraluminous granite, respectively, and define distinct parallel trends in specific major and trace element variation diagrams. Geochemical trends have been used to check for any possible modification of the different rock types associated with mylonitization, as well as to identify original magmatic compositions. Mineral chemistry investigation accompanied by multivariate statistical analysis of multispectral X-ray maps highlighted well preserved original porphyroclast zoning within low strain domains, whereas a complete compositional re-homogenisation was observed in widespread high-strain domains. Moreover, several generations of syn-mylonitic mineral growth inducing local strength-softening have been detected.

Quantitative microstructural investigation was performed on thin sections cut parallel to the stretching lineation. Optical assisted-image technique analysis on quartz grains (800 ca. grains per sample) revealed a mean axial ratio (AR, i.e. the ratio between major and minor axis of particles) ranging between 2.2 and 3.2 (AR max = 15) and average grain size of 20 µm². Calculated flow-law equation describing the rheological properties of quartzite suggests a mean shear strain rate value of 4.87 × 10⁻¹² (s⁻¹) for the studied samples.

Finally, petrophysical investigation on progressively deformed granodiorite at confined pressure conditions (up to 400 MPa) highlighted that Vₚ are distributed with the highest and lowest values orientated within and normal to the main foliation plane, respectively. Vₚ related seismic anisotropy ranges from 2.16 to 6.92%. Vₚ related acoustic birefringence shows its maximum along the stretching lineation direction. Vₚ/Vₛ ratios are in the range of 1.67-1.70.

Preliminary correlation between petrophysical and quantitative microstructural features opens new perspectives in the calculation of strain rate estimates of progressively natural sheared rocks.
REMAINING GAPS FOR A “SAFE” GEOLOGICAL STORAGE OF CO₂:
THE CO₂GAPS VISION CHALLENGES OF “LEARNING BY DOING”

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CO₂GAPS vision of the INGV (which is jointed recently with other research groups of CNR, ETHZ, EUCENTRE, etc., by an European Proposal still confidential and under evaluation, as a whole) intends to fill key GAPS concerning the main risks associated to the storage of CO₂ and the consequent liability of the “storage” part in the entire Carbon Capture and Storage (CCS) process. These still constitute a real obstacles for the large scale industrial development of CCS. A better “site specific” risk assessment and the development of reliable multi-disciplinary monitoring protocols will be then supported by “peer reviewed” processes and patented analytical procedures and techniques. The outcome results should be also embedded in the updating of the Annex 2, EU Dir. 2009/31/EC. The vision of the INGV group, as part of the partnership, is to apply a multidisciplinary approach, integrating geomechanical-geochemical data with seismic tomography and crustal rocks anisotropy, induced/triggered seismicity, gravimetry, EM techniques, and “early alarm” procedures for leakage in shallow geo-spheres and abandoned wells.

Moreover geomechanical and geochemical data are necessary for a reliable 3D-Earth modelling and a full merging with reactive transport codes, as well as the improvement of numerical modeling codes itself (updating “site specific” siting - Annex 1). CO₂GAPS vision will apply and verify these themes working on several European selected sites, taking also into account complex systems such as “inland” active faulted blocks close to the off-shore storage sites, ECBM faulted prone-areas, “inland” injection test site, and CO₂ natural analogues. The purpose of these future activities will focus on the study of long-term fate of stored CO₂, leakage mechanisms through the cap-rock/abandoned wells, geochemical/geomechanical reactivity of cement wells, as well as the effects of impurities in the CO₂ streams, their removal costs, the use of tracers and role of biota.
RADON AND THORON EMISSIONS FROM HIGH TO LOW POROSITY ROCKS UNDER INCREASING DEFORMATION


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Anomalous radon and thoron emissions are regarded as valuable precursors of earthquakes and volcanic eruptions and are related to increasing damage of the medium. However both positive and negative anomalies are observed in the field prior ruptures, thus indicating competing deformation mechanisms. Initial porosity (P) plays a key role for natural lithologies in controlling damage accumulation and strain localisation processes. Thus investigating how elastic properties of low to high porosity rocks are affected from increasing loading is required to quantitatively interpret the positive and negative anomalies observed.

Here we present an experimental dataset where measurements of radon (222Rn) and thoron (220Rn) emissions are carried out on low to high porosity lithologies incrementally loaded up to failure. The following samples are investigated: a high porosity lithophysae-rich tuff (P = 47.0%) and a low porosity phonolitic lava flow (P = 3.6%). Cylindrical samples of 120 (length) × 60 (diameter) mm, have been uniaxially loaded at constant strain rate in servo-controlled uniaxial machines. Samples have been either 1) mechanically damaged to the end of the elastic phase, before the onset of dilatancy or 2) loaded up to the failure. Radon and thoron exhalation rates are carried out by using a solid-state alpha detector, connected to a small accumulation chamber kept at the constant temperature of 60°C. Measurements are performed on two samples at once to achieve stronger signals and repeated several times in order to verify their reproducibility.

Results show that a decrease of radon and thoron emissions are evidenced at the end of the ‘damage phase’ for the high porosity tuff, while a slight increase is observed for the low porosity lava flow. At the end of the elastic phase the tuff reduces its radon and thoron exhalation rates, because of pervasive pore collapse of the macropores, with a P reduction up to 40.1%. In contrast, for the lava flows the loading slightly increases the crack damage and, consequently, P increases up to 5.1%. This change does not significantly affect the radon exhalation. At the failure, new rupture surfaces are generated. The total exhaling surface of the samples increases and an increase of radon emission is observed for both lithologies.
CAN CARBONATE FAULTS BE MELT-LUBRICATED?
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There is natural and experimental evidence that faults are normally lubricated during seismic faulting. In particular, carbonate fault lubrication is thought to be driven principally by decarbonation reactions. Here we present the natural example of the Canalone Porta fault (Grigna Massif, Southern Alps, Italy) which shows the existence of carbonate pseudotachylytes, suggesting that low-viscosity melts can promote melt lubrication processes.

The Canalone Porta fault, developed within dolomitic and marly limestones, hosts fault- and injection-veins of dominant carbonate composition. Vein texture is characterized by a fine-grained reddish matrix supporting millimetre-sized clasts. This matrix is composed of micrometre-sized globular aggregates of micrometre- to nanometre-sized calcite and dolomite crystals, bound together by a K-bearing aluminosilicate glass. Bulk-rock geochemical compositions of veins are very similar to those of the host fault-core rocks. However, veins display a Mg/(Ca+Mg) ratio ($X_{\text{Mg}}$) definitely lower than the host rocks.

In the calcite-dolomite system, carbonate melting occurs in the $\sim$ 660-1100°C range of temperature, depending on the water content. The estimated melting temperature of the studied rocks falls within this temperature range ($\sim$ 700°C). Besides, the average $X_{\text{Mg}}$ of the matrix (0.26) is in keeping with the theoretical value (0.2-0.3) for similar compositions at crustal pressures. The observed aluminosilicate glass can be derived from disequilibrium melting of muscovite.

Structural, chemical, mineralogical and petrological observations suggest that the Canalone Porta veins have not been formed by simple mechanical comminution, but are the quenching product of friction-induced carbonate-rich melts (i.e., carbonate pseudotachylytes) produced at $T \approx 700^\circ\text{C}$ and $P \approx 0.1-0.2 \text{ GPa}$. The existence of pseudotachylytes of dominant carbonate composition along faults implies the presence of low-viscosity melts promoting fault lubrication during those earthquakes nucleating in the carbonate sedimentary levels of the shallow crust.
CARMA – CARBON MANAGEMENT IN POWER GENERATION
GEOLOGICAL STORAGE IN SWITZERLAND

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The CARMA project aims to explore the potential for and the feasibility of Carbon Capture and Storage (CCS) in Switzerland within the framework of future energy scenarios. We aim to exploit the available expertise to develop new CCS technologies and know-how, which might be applied in Switzerland and worldwide. We intend to evaluate the economic, environmental, societal, and institutional implications of CCS and to assess the potential CO₂ geological storage capacity in Switzerland. We also intend to build on the strengths, experience and available equipment of the research groups involved, focusing on mineral carbonation, as a means of fixing CO₂ in stable, mineral form. CARMA brings together the research groups from various universities and industries in Switzerland. The project started in January 2009, with a total runtime of 4 years. This poster reports the achievements with respect to geological storage of CO₂ in Switzerland during the first half of the project.

An estimate of the theoretical storage potential in the subsurface was completed in August, 2010. The methodology followed an existing evaluation scheme developed in Canada, based on geological criteria only. Modifications were introduced to suit the geological setting and available data in Switzerland. The study relies on quantitative and semi-quantitative attributes derived from analysis of existing laboratory, drill-hole, geological, and geophysical data. The weighted combinations of these attributes have been ranked in order to visualize Switzerland’s storage potential in the form of a contour map. The theoretical storage capacity of the suitable sandstone and limestone aquifers is approximately 2.6 Gtons of CO₂, i.e. 65 times Switzerland’s current annual CO₂ emissions. Thorough geological investigations, laboratory testing and one or multiple field tests would be imperative to prove its feasibility and safety.

The potential seismic hazard related to CCS operations is carefully assessed within CARMA. The activities that have been carried out focused on the compilation of known cases of induced seismicity due to fluid injection. The compilation includes enhanced geothermal systems, passive geothermal plants, liquid waste disposal, and CCS projects. A classification methodology has been proposed according to the type of operation, operative plant parameters, tectonic regime, state of stress and background seismicity of the injection area.

An alternative approach to that offered by subsurface storage is ex situ mineral carbonation in a controlled industrial setting. This involves the dissolution of CO₂ into an aqueous phase, leaching of magnesium/calcium from a natural mineral feedstock and the precipitation of Mg-/Ca-carbonates, thus fixing CO₂ in a stable, environmentally benign form. The reactions involved are exothermic overall, but their kinetics is slow under ambient conditions. This makes an energy intensive mechanical or thermal activation of the mineral feedstock inevitable. While this adds to costs, mineral carbonation offers the possibility of fixing CO₂ directly from an industrial off gas stream, thus obviating the costly capture step. Within CARMA, we are investigating an aqueous process, where a flue gas is bubbled through a stirred tank containing the mineral feedstock in suspension. We have built a set-up to perform mineralization experiments under a variety of temperature, pressure, gas composition and solution chemistry conditions, using several optical and physicochemical analytical techniques to monitor the different phases in situ and online further downstream. Currently, the dissolution behavior of thermally activated serpentine is being studied. Hitherto, olivine was found to be the natural silicate feedstock exhibiting fastest dissolution kinetics. When directly compared to olivine, we found that activated serpentine dissolves 2 to 3 orders of magnitude faster under identical conditions.
Sessione tematica J7:

I siti anionici nei fillosilicati: implicazioni cristallografiche, cristallochimiche e petrologiche

Conveners:

Maria Franca Brigatti (Università di Modena e Reggio Emilia) *
Annibale Mottana (Università Roma Tre)
Alessandro Pavese (Università di Milano)
Raffaele Sassi (Università di Padova)
Fernando Scordari (Università di Bari)
CHARACTERIZATION OF GENTAMICIN-BENTONITE COMPLEX

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Clays are common ingredients in pharmaceutical and cosmetic formulations, used as active substances (gastrointestinal protector, osmotic oral laxatives, antidiarrhoeaics, topical antibacterials and antinflammatories) and excipients in solid (tablet, capsules, powder), liquid (suspensions, emulsions) or semisolid (ointments, creams) forms.

The present work aims to evaluate the intercalation of gentamicin molecules into a montmorillonite rich clay (i.e., bentonite, here after BNT) to obtain a drug delivery carrier for antibiotic treatment in a perspective to decrease gentamicin side effects and to improve systemic adsorption. In addition clay antibacterial activity could produce a synergistic effect.

BNT-gentamicin complexes, obtained via a batch treatment, were characterized by chemical analyses, thermal analyses (thermogravimetric and thermo-differential) coupled with evolved gasses mass spectrometry, and X-ray powder diffraction at non-ambient temperature conditions.

Chemical analyses indicates that gentamicin is adsorbed by the clay in a percentage varying between 2.0 and 2.3 (weight %) in relation to the pH of the treating solution. Thermal analyses show that the gentamicin treatment influences both the dehydration and the dehydroxilation reactions of montmorillonite and, in particular, highlights that in the treated sample the dehydroxilation reaction related to cis-vacant sites is shifted to an higher temperature respect to the natural clay. Basal periodicity was measured via XRPD diffraction on (00l) oriented mounts of the air-dried samples in the temperature range 25-400°C (heating rate 2°C/min) using a powder diffractometer equipped with an area detector. In the natural sample the layer periodicity reach the closest 2:1 packing (i.e., 0.99 nm) at about 160°C, whereas this value in the gentamicin treated sample is reached only after 400°C (i.e., after the thermal decomposition of the organic molecule).
SODIUM HEXAMETAPHOSPHATE INTERACTIONS WITH ILLITE AND MONTMORILLONITE: PRELIMINARY OBSERVATION ON THERMAL BEHAVIOR

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The interaction of an efficient deflocculant, sodium hexametaphosphate (NaHMP), with two different illites (IMt-1 from Silver Hill, Montana USA and from Schwäbisch Hall, Würtenberg Germany) and two different Ca-montmorillonites (STx-1 from Gonzales County, Texas, USA and from Santa Rita, New Mexico, USA) was investigated.

Adsorption measurements of the NaHMP anion were performed on Na-exchanged illite IMt-1 as a function of temperature by means of inductively coupled plasma technique (I.C.P.). The thermodynamic parameters of the adsorption process, together with an estimation of the maximum adsorbed amount on the Na-illite were obtained and compared to the corresponding data previously obtained for Na-kaolinite.

The effect of NaHMP on the natural illites and montmorillonites was analyzed using different techniques. I.C.P. measurements of the concentration of P, Na, Si, Al, Ca, Mg, and K of the deflocculant solutions in contact with the clays were performed in order to detail the adsorption, dissolution and exchange phenomena which accompany the deflocculant activity.

Thermal analysis (thermo-gravimetric, thermal-differential) and XRD measurements at non ambient temperature conditions were used to characterize the clay solid samples after the interaction with NaHMP. Thermo-gravimetric analyses indicate that NaHMP-treated illites and montmorillonites are less hydrated than natural samples, whereas the dehydroxilation reaction seems to be not influenced by the NaHMP treatment. Basal periodicity was measured via XRPD diffraction on (00l) oriented mounts of the air-dried samples in the temperature range 25-400°C (heating rate 2°C/min) using a powder diffractometer equipped with an area detector. No significant variation of layer periodicity was observed, thus indicating that NaHMP molecules are adsorbed on the edge and/or in the interlayer without modifying natural layer periodicity.
ON THE CRYSTAL CHEMISTRY AND ELASTIC BEHAVIOUR OF A PHLOGOPITE 3T

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The crystal chemistry and the elastic behaviour under isothermal conditions up to 9 GPa of a natural, and extremely rare, 3T-phlogopite from Traversella (Valchiusella, Turin, Western Alps) \([(K_{0.99}Na_{0.05}Ba_{0.01})(Mg_{2.60}Al_{0.20}Fe^{2+}_{0.21})[Si_{2.71}Al_{1.29}O_{10}](OH)_2, \text{ space group } P3_112, \text{ with } a = 5.3167(4), c = 30.440(2)\AA, \text{ and } V = 745.16(9) \text{ \AA}^3]\) have been investigated by electron microprobe analysis in wavelength dispersion mode, single-crystal X-ray diffraction at 100 K and in situ high pressure synchrotron radiation powder diffraction (at room temperature) with a diamond anvil cell. The single-crystal refinement confirms the general structure features expected for tri-octahedral micas, with the inter-layer site partially occupied (using the potassium scattering curve alone), iron almost homogeneously distributed over the three independent octahedral sites, and the average bond distances of the two unique tetrahedra suggesting a disordered Si/Al-distribution (i.e. \(<T_1-O> \approx 1.658 \text{ and } <T_2-O> \approx 1.656 \text{ \AA} \)).

The location of the H-site confirms the orientation of the O-H vector nearly perpendicular to (0001). The refinement converged with \(R_f(F) = 0.0382, 846 \text{ unique reflections with } F_0 > 4\sigma (F_0) \) and 61 refined parameters, and not significant residuals in the final difference-Fourier map of the electron density (+0.77/-0.37 e/\AA^3). The high-pressure experiments showed no phase transition within the pressure range investigated. The P-V data were fitted with a Murnaghan (M-EoS) and a third-order Birch-Murnaghan equation of state (BM-EoS), yielding: 1) M-EoS, \(V_0 = 747.0(3)\text{\AA}^3, K_{T0} = 44.5(24)\text{GPa and } K' = 8.0(9)\); 2) BM-EoS, \(V_0 = 747.0(3)\text{\AA}^3, K_{T0} = 42.8(29)\text{GPa and } K' = 9.9(17)\). A comparison between the elastic behaviour in response to pressure observed in 1M- and 3T-phlogopite is carried out.
Layer charge value and location are commonly considered key factors for predicting interaction of layer silicates with external agents, such as, for example, pollutants, bio-molecules, and, more generally, ionic complexes. Several methods are discussed in literature for the experimental determination of layer charge, always, however, giving an average value from the different micro-crystals used for the analysis. The most commonly used methods are: the structural formula method (Newman & Brown, 1987; Laird, 1994), the alkylammonium method (Lagaly & Weiss, 1969) and the potassium saturation method (Christidis & Eberl, 2003). The purpose of this paper is to demonstrate that the determination of the average value of the layer charge can sometimes lead to inconsistent results, as not correctly representing the layer charge location at mineral surface. This goal was achieved by analyzing crystal chemical results obtained from different crystals of muscovite characterized by a different content of celadonitic substitution.

Muscovite sometimes presents heterovalent substitutions both in tetrahedral (e.g. Al$^{3+}$ for Si$^{4+}$) and in octahedral sites (e.g. Mg$^{2+}$, Fe$^{2+}$, and vacancies for Al in octahedral sites). Our results seem to demonstrate that these substitutions can be ascribed to trioctahedral cells, all occupied by cations different than Al, in a dominating dioctahedral pattern, with cis-octahedral sites entirely occupied by Al and the trans-site vacant. This interpretation suggests that mean layer charge may not represent effective layer charge at mineral surface because it refers not to randomly distributed substitution, but to domains showing different chemistry which can be locally charge-neutralized. Furthermore, also distortion parameters which affect tetrahedral topology and that can also affect the formation of surface complexes, such as $\alpha$ angle and $\Delta z$ oxygen plane flattening, can be different inside a same structure and locally not corresponding strictly to the determined mean value via single crystal diffraction.

CRYSTAL CHEMISTRY AND SURFACE FEATURES OF A 2M₁ PARAGONITIC MUSCOVITE

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The paragonitic muscovite considered [K₁.72(₂Na₀.25₁Ba₀.₀₁₀)[VI](Fe²⁺₀.₁₄₀Al³⁺₃.₇₆₉Cr³⁺₀.₀₀₃Mg₀.₀₇₄Tb₀.₀₁₂Mn₀.₀₀₂)[IV] (Al₁.₈₉₇Si₆.₁₀₃)O₂₀ (F₀.₁₀₉ OH₃.₈₉₁) came from Antarctica, it is monoclinic, 2M₁ polytype, with symmetry C2/c and unit cell parameters a = 5.1969(1), b = 9.0138(3), c = 20.0835(7) Å and β = 95.763(2)°.

By using a multi-analytical approach this study describes the crystal chemical features of muscovite determined both in the bulk and on the uppermost surface layers.

The bulk structure was refined by single crystal X-ray diffraction and the final refinement yielded the following agreement factor R = 0.0299. The two tetrahedral sites, T₁ and T₂, present similar distances (<T₁-O> = 1.643 Å and <T₂-O> = 1.647 Å) and distortion parameter values, thus evidencing a disordered distribution of [IV]Si and [IV]Al in tetrahedral sites. Tetrahedra ring is significantly distorted (α = 11.2°) and the tetrahedral basal oxygen atoms plane is remarkably wavy (Δz = 0.224Å). tetrahedral ring distortion affects not only the topology of the cleavage plane, but also the coordination of the interlayer cation, which reduces from twelve to eight.

Crystal chemical modifications at mineral surface were investigated via X-ray Photoelectron Spectroscopy (XPS), by comparing data related to surface to the ones characterizing the bulk.

A peculiarity of muscovite from Antarctica is a limited Na for K interlayer substitution, which was found in the bulk as well as on the mineral surface. It is well known that in micas the coordination of the interlayer cation can vary from twelve to six, depending on the distortion of the hexagonal tetrahedral ring, as measured by α angle, as observed and predicted by Weiss et al. (1992).

The interlayer cation K (binding energy = 293.36 eV) is confirmed to be eight-fold coordinated (Zakaznova-Herzog et al., 2008). Na (binding energy = 1071.02 eV) substitutes K both in the bulk and at the surface. Na coordination, at mineral surface, reduces from eight to six. The six-fold coordination presented by Na is consistent with α = 16°, which is typical for paragonite, whose interlayer is completely occupied by Na. Chemical composition at the surface was compared to bulk chemical composition obtained by electron microprobe analysis. This comparison highlights a decrease in K content, which can be explained by its location on the cleavage surface, since the cation is expected to be distributed equally along the two surfaces generated after cleavage, and an increase in Na which can be related to Na domains close to the cleavage surface.

These aspects may relate muscovite cleavage processes to the presence of “defects”, or better inhomogeneities in layer crystal chemistry. This fact may thus suggest that Na content in paragonitic muscovite could not be only attributed to a solid solution mechanism, where this cation substitutes for K, but rather to the presence of Na-dominant clusters.

THE PHYLLOSILICATE LAYERS:
AN OVERVIEW ON TOPOLOGY AND MODULARITY

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On the basis of the specific purposes of Symposium J7, the keynote aims to present an introductory overview on the structural characteristics of the phyllosilicate layers. With particular reference to the TOT layer, emphasis will be given to the features that support complex crystal chemistry, polytypism, polysomatism and twinning.
CRYSTAL CHEMISTRY OF TRIOCTAHEDRAL MICAS-2M₁ FROM BUNYARUGURU (SW UGANDA) KAMAFUGITE

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In trioctahedral micas, polytype 2M₁ occurs less frequently than 1M one. For such a reason, trioctahedral 1M-polytype has been extensively studied up to date whereas studies on 2M₁-polytype are relatively rare. In several cases 2M₁-micas have been reported as coexisting with 1M-micas (Takeda & Ross, 1975; Ohta et al., 1982; Bigi & Brigatti, 1994; Laurora et al., 2007; Aldega et al., 2009). Other studies were focused on the characterization of phlogopite-annite 2M₁ micas with peculiar composition (Bigi et al., 1993; Brigatti et al., 2000; Brigatti et al., 2005; Brigatti et al., 2008; Pini et al., 2008). The crystal chemistry of 2M₁ micas from Bunyaruguru (south west Uganda) kamafugite was studied by Electron Probe Microanalysis, Single Crystal X-ray Diffraction, Mössbauer and Fourier Transform Infrared spectroscopy. To the best of our knowledge, this is the first integrated crystal chemical study of phlogopite from Ugandan kamafugites, and was undertaken to get an insight into the crystal chemistry of the trioctahedral mica 2M₁-polytype.

Chemical analyses showed that the studied crystals are Ti-rich, F-poor phlogopites with an annitic component, 

\[ \text{Fe}_{\text{tot}}/(\text{Fe}_{\text{tot}} + \text{Mg}) \text{, ranging from 0.15 to 0.23. Unit-cell parameters from single crystal X-ray data are in the range: } 5.3252(1) \leq a \leq 5.3307(1), 9.2231(3) \leq b \leq 9.2315(3), 20.1550(6) \leq c \leq 20.1964(8) \text{ Å and } 94.994(2) \leq \beta \leq 95.131(2). \]

Anisotropic structure refinements, in the space group C2/c, converged to 2.80 \leq R₁ \leq 3.56% and 2.91 \leq wR₂ \leq 4.08%. Mössbauer spectroscopy showed that the studied sample has: \( \text{VIFe}^{2+} = 60(1)\% \), \( \text{VIFe}^{3+} = 24(1)\% \) and \( \text{IVFe}^{3+} = 16(1) \% \). FTIR investigations pointed to the occurrence of Fe³⁺-oxy substitutions and ruled out the presence of vacancy mechanisms. The overall crystal chemical features are consistent with the following substitutions: tetraferriphlogopite; Ti-oxy and Al, Fe³⁺, Cr-oxy; Al, Fe³⁺-Tschermak; kinoshitalite and 

\[ \text{XII}^+ + \text{IV}^{12}\text{Al}^{3+} \leftrightarrow \text{IV}^{14}\text{Si}^{4+} + \text{XII}^+ \].

The estimation of the OH⁻ content for Ugandan mica-2M₁ was obtained, for the first time, from the linear regression equation \( c = 0.20(2) \times \text{OH}^- (\text{gpfu}) + 19.93(2) \) derived from literature data of 2M₁-samples with known OH⁻ content. The orientation of the O-H vector with respect to \( c^* \) was found in the range from 2.8 to 12.6°, consistently with literature values (Schingaro et al., 2001).

This study investigates the crystal chemical features of six lizardite-1T crystals sampled in four ophiolitic outcrops (Pompeano, Sassomorello, Varana, and Santa Scolastica) in the Modena Apennines (Italy). Notwithstanding the extensive contributions already present in literature, this is the first study dealing with lizardites from Modena ophiolites. As evidenced by one of our samples, the whole rock composition affects lizardite composition, which results to be sensible to the overprint of secondary, metasomatic events. In our study, particular attention was devoted to the effects of octahedral Fe for Mg and of Si$_{1.1}$Al(Mg,Mn,Fe)$_2$(Al,Cr,Fe)$_3$ exchange mechanisms on the structure.

Our results suggest that Fe for Mg substitution induces an increase in the octahedral M-O$_4$ length, and a decrease in the octahedral site distortion. Both these effects are also observed to influence unit-cell parameter \(c\). The effect of the Si$_{1.1}$Al(Mg,Mn,Fe)$_2$(Al,Cr,Fe)$_3$ substitution is a decrease in the M-O$_1$ distance and a concomitant increase in the T-O$_1$ distance.
TEXTURAL STUDY OF METAMORPHIC ROCKS
BY MEANS OF A CONVENTIONAL X-RAY SOURCE

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The aim of this study is the textural characterization of very low to greenschist facies metamorphic rocks by means of a conventional X-ray source, possibly establishing a relationship between the extent of morphological orientation of mineral grains and metamorphic degree.

For a long time geologists investigated the morphological orientation of mineral grains in polycrystalline rocks by means of petrographic microscope equipped with a Universal stage. More recently diffraction of conventional X-ray sources as well as diffraction (or transmission) of hard X-rays, electrons and neutrons has been applied to these kind of study. However, whereas X-ray conventional sources can be regarded as a routine technology, hard X-ray, electron and neutron sources are only available in a few facilities around the world.

Phyllosilicates such as smectite, illite, muscovite, chlorite and biotite play a key role in the textural characteristics of the mineral assemblages of rocks characterized by increasing metamorphic degree. The present study is focused on the variation of the X-ray intensities of selected reflections of these phases. In short, if a morphologic orientation of the grains of a certain phyllosilicate is present, a variation of the intensity of these reflections will be measured when the rock sample is rotated in a goniometer keeping constant both the incident beam angle and the position of the detector.

The samples selected for the study are the following: 1) a Ms, Chl, Qtz, Pl fine grained metapelite from Frassenetto (UD, Italy) (very low grade metamorphism, Anchizone) with some detrital muscovite flakes recognizable by their coarser grain size; 2) Ms, Chl, Qtz, Pl fine grained metapelite from Chiadenis (UD, Italy) (low grade metamorphism, Epizone) with some detrital muscovite flakes recognizable by their coarser grain size; 3) a Ms, Chl, Ilm, Qtz, Pl layered phyllite from Villabassa (BZ, Italy) (Greenschist facies metamorphism, Ms-Chl-Bt), with crenulated main foliation and axial planes defining a second spaced foliation; 4) a Ms, Bt, Grt, Ilm, Qtz, Pl layered phyllite from Luson (BZ, Italy) (Greenschist facies metamorphism, Ms-Bt-Grt), with crenulated main foliation and axial planes defining a second spaced foliation.
ADVANCED TECHNIQUES TO DEFINE INTERCALATION PROCESSES

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Intercalation means the reversible insertion of a guest chemical species (atom, ion, molecule) in a virtually unchanged host crystal structure. Any type of layer-structured material may give rise to intercalate compounds, the guest species being inserted between the host sheets without loss of their planarity. Layer silicates, in particular, may be considered intercalated structures in which interlayer guest species and complexes are inserted between the silicate layers.

The most common guest species is water, which is generally present under natural conditions in layer silicates such as smectites, vermiculite and halloysite. From the outset, attention was focused on their swelling/shrinking behaviour with respect to water, and also on the non-stoichiometric, heterogeneous complexes they formed with organic liquids such as ethylene glycol and glycerol.

At present, the unique combination of the layer-silicate features (small crystal size, high surface area) and the low concentrations necessary to effect a change in the matrix, both coupled with the advanced characterization techniques now available, have generated much interest for the special field of nanocomposites, as far as for graphene, which can also be considered as an intercalated layered structure.

In general, any guest material inserted into an interlayer space causes a main modification in the structure, with size changes in a particular crystallographic direction ($d$-spacing). After a brief introduction on conventional and synchrotron-based X-ray techniques used to define crystal size and thickness, the essentials of the grazing-incidence diffraction (GIXRD) technique will be given.

The additional, complementary information arising from X-ray absorption spectrometry (XAS) such as short-range order and detailed local information on atomic positions by angle-resolved X-ray near-edge structure (AXANES), polarized extended X-ray absorption fine structure (P-EXAFS), and near-edge extended absorption fine structure (NEXAFS) spectroscopies will also be analyzed and discussed.
INFLUENCE OF UNCERTAINTIES AFFECTING ELASTIC PARAMETERS ON THE GIBBS ENERGY CALCULATION: THE CASE OF 3T - 2M1 PHENGITE

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The stability of 2M1 (S.G. C2/c) versus 3T (S.G. P312) polytype is dependent on the P/T ratio of formation: large P/T values are supposed to promote crystallisation of 3T phengite, presumably because of 3T having a more flexible structure than 2M1 to arrange cations in the octahedral sheet. In fact, the trigonal polytype provides two symmetry-independent octahedral sites (M2 and M3), against only one in 2M1 (Ferraris & Ivaldi, 2002 and references therein).

All this is related to the occurrence of cation order, which Pavese et al. (2003 and references therein) have extensively investigated by neutron powder diffraction. However, the stability of 3T vs. 2M1 phengites is still an open question. On the basis of experimental works (Curetti et al., 2006; Gatta et al., 2010) we infer that the stability of 3T increases as a function of P, though the Gibbs energy difference between the two polytypes still keeps small. Such a behaviour is due to that K’(3T)< K’(2M1), and K0 (3T) is very similar to K0(2M1): at sufficiently high pressures 2M1 becomes less compliant to P than 3T, and therefore the deformation energy contribution to the Gibbs energy is supposed to favour the latter.

The relative stability between trigonal and monoclinic polytypes remains a matter of thermodynamic inference. In this view, hence, the ability to fix the uncertainty on the elastic properties, and to determine how it propagates onto the calculated deformation energy, is a fundamental step to support any prediction of stability of a given polytype at high pressure. In a study about the accuracy of the calculated Gibbs energy, depending on the uncertainties on elastic parameters (bulk modulus, its first derivative versus pressure and molar volume) we revised the relative stability, controlled by pressure, between 3T-2M1 phengite. Above a few GPa the uncertainty due to the deformation energy and dependent on the parameters governing the equation of state grows the dominant contribution to the total uncertainty on G(T,P), and it is imperative to make efforts to abate the uncertainties on K0 and K’ so that one can achieve fully distinguishable deformation energy contributions. Using another approach to discuss on how to manage the role of the elastic properties in the relationship between polytypism and stability for phengite 2M1 and 3T, we developed the general concept of “distinguishibility” between sets of elastic parameters used to calculate the contribution of deformation to the Gibbs energy. This notion bases on that different contributions of deformation are actually observed if the related elastic parameters sets lie in the K0-K’ spaces sufficiently apart, in terms of a variational principle formulated using the experimental uncertainties.

The results of the comparison between the two polymorphs of mica showed that a P increase does favour their distinction and promote the stabilization of 2M1 even if this behaviour is appreciable only in the high pressure, a regime very different from the actual field of stability of micas but that stresses the role of pressure in differentiating the two polytypes. Once more the large errors that affect the elastic observables and the relevant proximity between the elastic parameters are responsible of the difficulties in distinguishing the behaviours of the considered polytypes off ambient conditions.

3T-trioctahedral micas are rarer than it is thought. This is likely due to the occurrence of apparent polytypism, so that 1M polytype twins result in a diffraction pattern simulating a 3T periodicity (Nespolo & Kuwahara, 2001; Scordari et al., 2011). Most of the 3T trioctahedral micas found in nature to date belong to muscovite-polythionite-annite system (Brown, 1978; Pavlishin et al., 1981; Weiss et al., 1993; Brigatti et al., 2003). X-ray diffraction studies on these micas have often reported partial tetrahedral ordering and/or different patterns of octahedral ordering (Brown, 1978; Brigatti et al., 2003).

In the present work, a 3T trioctahedral mica from Kasenyi (south west Uganda) kamafugite was studied via Electron Probe Microanalysis (EPMA) and Single Crystal X-ray Diffraction (SCXRD).

Main EPMA data gave: SiO$_2$ = 38.7(2), Al$_2$O$_3$ = 13.08(9), MgO = 20.4(2), TiO$_2$ = 4.8(1), FeO$_{tot}$ = 5.1(9), Cr$_2$O$_3$ = 0.90(7), K$_2$O = 9.64(5), Na$_2$O = 0.29(1), BaO = 0.15(5) and F = 0.13(5) wt.%. The analysed crystal may be classified as a Ti-rich, F-poor mica with a composition intermediate between the annite and phlogopite end members.

Anisotropic single crystal X-ray refinement was performed in the $P3_112$ space group and converged to $R_1 = 4.34$ and $wR_2 = 3.33\%$. Unit cell parameters were: $a = b = 5.3235(3)$ and $c = 30.188(2)$ Å. Mean bond length distances of $M_1$, $M_2$ and $M_3$ follow the pattern $M_1 = M_2 < M_3$, suggesting partial octahedral cation ordering. Conversely, mean bond lengths of $T1$ and $T2$ point to a disordered cation distribution over tetrahedral sites.

Finally, the overall crystal chemical features indicates the occurrence in the studied sample of the following substitution mechanisms: tetraferriphlogopite; Ti-oxy and Al, Fe$^{3+}$, Cr-oxy; Al, Fe$^{3+}$-Tschermak; kinoshitalite and $^{XII}K^+ + ^{IV}Al^{3+} \leftrightarrow ^{IV}Si^{4+} + ^{XII}O$. Such substitutions are the same as those found in 1M-2M$_1$-coexisting micas from the same rock sample (Scordari et al., 2011).

ADSORPTION OF WATER MOLECULES ONTO 1:1 DIOCTAHEDRAL CLAY MINERALS: A BADER’S TOPOLOGICAL ANALYSIS OF THE AB-INITIO ELECTRON DENSITIES

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The interaction between water molecules and clay minerals has been investigated by means of ab-initio computational methods. The interest in this field comes from the considerations that water-clay systems play a central role both in natural and industrial processes. Clays, as natural inorganic component of soils, significantly affect transport, distribution, and stability of dissolved chemical species. In this context, special focus has to be paid to toxically active species, such as radionuclides, pesticides, heavy metals. Clays also found a lot of industrial applications as effective storage materials for nuclear waste or as potential catalysts for refining processes used in the oil industry. In many of the above processes, water plays a crucial role as a natural solvent and as a transport medium for chemical species, therefore the understanding of the structure and chemistry of the water-clay interface is of considerable importance.

In spite of the great number of experimental investigations in this field, a thorough understanding of clay mineral-water interactions is still lacking. Computer simulation techniques can provide interesting insight concerning a structural characterization of adsorption sites and of interactions between surfaces and adsorbed molecules at the molecular level.

In the light of these considerations, the present computational study has been undertaken in order to make a theoretical characterization of each compound and then to get strategic information in predicting its behavior. In particular, we decided to investigate two polytypes of the kaolinite group, namely kaolinite and dickite, since it is well known that the holes in the tetrahedral and octahedral surfaces of these structures are favorable interaction sites for adsorption of different molecules.

Bulk and slab geometry optimizations have been performed and the topology of the electron density and its Laplacian distribution have been studied on the basis of Bader’s “Atoms In Molecules” (AIM) theory to determine the conditions required for the adsorption of different organic molecule on the tetrahedral and octahedral surfaces of the mineral. The analysis of the Laplacian critical points allowed to recognize the reactive sites of the structures and provided an efficient tools that guides in the determination of the sites of adsorption and of the geometry of the reactant relative to the surface site. The results of this analysis indicated that the octahedral and tetrahedral holes in both basal surfaces are favorable interaction sites for adsorption of small polar molecules and that the electronic reactivities of the two different polytypes are very similar, which means that the chemical behavior of the analyzed structures is comparable.

In a second step, in order to test the possibility of absorbing water in each position predicted by the topological analysis the geometrical optimization of mineral-water system has been performed.

The information coming from both the theoretical prediction of the reactivity of the molecules involved and the simulated structural and energetic features of the investigated system actually represent an engineering approach that can allow to “calibrate” the experimental work as well as to explain the experimentally observed behaviors.

Moreover, this kind of data base actually represents a good “launching pad” for all the subsequent theoretical simulations of the interactions between clay minerals and different guest molecules of interest.
MULTIMETHODIC INVESTIGATION OF COEXISTING 1M- AND 2M1-MICAS FROM KASENYI (SW UGANDA) KAMAFUGITE

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Several diffraction studies on coexisting 1M and 2M1 polytypes have been carried out to date (Takeda & Ross, 1975; Ohta et al., 1982; Bigi & Brigatti, 1994; Laurora et al., 2007; Brigatti et al., 2008; Aldega et al., 2009) in order to draw informations on their differences by comparing unit layer structure and/or the crystal chemical details of the two polytypic forms. Some of the quoted studies contain implications on polytype formation in micas (Takeda & Ross, 1975; Ohta et al., 1982).

In the present work, the crystal chemistry of 1M and coexisting 2M1 micas from Kasenyi (south west Uganda) kamafugite was investigated by Electron Probe Microanalysis, Single Crystal X-ray Diffraction and Mössbauer spectroscopy. The aim of the present study is to compare crystal chemical and unit layer structural features of the coexisting polytypic forms and to make comparisons to literature data.

EPMA investigation yielded similar composition for 1M and 2M1 polytypes. They are Ti-rich, F-poor phlogopites with an annitic component, $\text{Fe}_{\text{tot}}/(\text{Fe}_{\text{tot}} + \text{Mg})$, of about 0.14. The room temperature Mössbauer spectrum of the sample yielded three Fe-species: $^{\text{VI}}\text{Fe}^{2+} = 58(1)\%$, $^{\text{IV}}\text{Fe}^{3+} = 23(1)\%$ and $^{\text{IV}}\text{Fe}^{3+} = 19(1)\%$. A typical crystal chemical formula is:

$$\text{(K}_{0.96}\text{Na}_{0.04}\text{Ba}_{0.01})(\text{Mg}_{2.29}\text{Al}_{0.09}\text{Fe}_{0.21}^{2+}\text{Fe}_{0.08}^{3+}\text{Ti}_{0.28}\text{Cr}_{0.04}\text{Ni}_{0.01})(\text{Si}_{2.87}\text{Al}_{1.06}\text{Fe}_{0.07}^{3+}\text{O}_{10.65}\text{F}_{0.05}\text{OH}_{1.30}.$$

Average cell parameters are $a = 5.326$, $b = 9.224$, $c = 10.231$ Å, $\beta = 100.06^\circ$ for polytype 1M and $a = 5.325$, $b = 9.223$, $c = 20.206$ Å, $\beta = 95.08^\circ$ for polytype 2M1. The interatomic distances are similar for the two polytypes and consistent with the relevant site chemistry.

The comparison among atomic coordinates of 1M and 2M1 micas from this study and from the literature in the 2M1 setting evidenced a remarkable agreement between all atomic coordinates, with the exception of the y values of the octahedral oxygen atoms. Specifically, the difference between y values was 0.004 in the study samples, 50 times the estimated standard deviations. Similar differences were found for the literature data (Takeda & Ross, 1975).

In the present study, a systematic investigation of fluorophlogopite from Mt. Etna volcano (Italy) was performed. The mica sample studied here is among the most Fe- and Ti-rich fluorophlogopite found in nature. It occurs in a benmoreitic lava from the prehistoric volcanic activity of Mt. Etna (post-caldera phase of the “Ellittico” volcano; ~15 ka BP; Nicotra et al., 2010). Fluorine-rich minerals are important indicators of the halogen activity in magmatic systems, so that their investigation offers the opportunity to get important information on the processes of magma differentiation acting in the shallow portions of the volcano plumbing system. This study was based on electron probe microanalyses (EPMA), and single-crystal X-ray diffraction (SCXRD).

EPMA data yielded the following chemical formula for the mineral under consideration: 
\[
(K_{0.817}Na_{0.148}Ca_{0.003})(Fe^{2+}_{0.535}Cr_{0.004}Mg_{0.223}Al_{0.003}Ti_{0.227}Mn_{0.008})(Al_{0.958}Si_{3.042})O_{10}(Cl_{0.010}F_{1.388}OH_{0.152}O_{0.450}).
\]
The X-ray analysis indicated that the sample represents an example of twinning of 1M polytype simulating the diffraction patterns of a 3T polytype (Nespolo & Kuwahara, 2001). Structure refinements, which was performed on three crystals using twin laws, converged at \( R = 0.03-0.04 \), with cell parameters in the range \( a = 5.323-5.324, b = 9.219-9.222, c = 10.116-10.119 \) Å, \( \beta = 100.13-100.25^\circ \). Major substitutions are \( OH^- \leftrightarrow F^- \), and the Ti-oxy substitution: \( V Hi^{2+} + 2(OH)^- \leftrightarrow VITi^{4+} + 2O^{2-} + H_2^+ \).

The replacement of \( OH^- \) with \( F^- \) affects mainly the octahedral sites reducing the misfit between tetrahedral and octahedral sheets. The short \( c \) parameter is due to the reduced repulsion between the interlayer cation and the hydrogen depleted anion sited in \( O4 \). In the studied sample the structural effects due to the high-F content are enhanced by those due to oxy-type substitution. The crystal chemical features of this fluorophlogopite from the summit portions of Mt. Etna are intermediate between those from Biancavilla (Gianfagna et al., 2003) and the Ti-rich fluorophlogopite from Presidente Olegario, Brazil (Schingaro et al., 2011). Although the fluorophlogopite from Biancavilla and that studied here were found in products of the same eruptive period at Mt. Etna, the different structural and chemical features may reflect distinct physico-chemical conditions of crystallization.

The Biancavilla fluorophlogopite occurs as phenocryst together with the “classical” Etna mineral assemblage, whereas those of the summit portion crystallized inside the lava vesicles during the post-eruptive phases (Nicotra et al., 2010). In the last instance, the fluorine available during crystallization of fluorophlogopite crystals should be lower than that of the active Biancavilla lava domes, where the continuous volatile flux by halogen-rich fluids may have brought to such fluorine enrichment. The anomalous high Fe content of the studied fluorophlogopite may have been inherited by the lower degree of differentiation of the hosting lava than that of the Biancavilla volcanic rocks.

Sessione tematica LI:
Le Alpi dal break up della Pangea alla strutturazione della catena:
una sessione in onore di Luciano Cortesogno e Mario Vanossi

Conveners:
Giorgio Dallagiovanna (Università di Pavia) *
Laura Gaggero (Università di Genova)
Silvio Seno (Università di Pavia)
In this work we want to show the present-day advancements on the geology of the Ligurian Alps, with emphasis on central Liguria. A major contribution to the knowledge of the geology of this area is due to Lucio Cortesogno and Mario Vanossi: the present state of the art could not have been the same without their contributions and we want to dedicate to Lucio and Mario this work.

Central Liguria, i.e. the Voltri Massif and the Sestri-Voltaggio Zone, is in a key geological position, as it represents the easternmost part of the Ligurian Alps, and the physical link with the northern Apennine belt. On the basis of twenty five years of geological mapping and structural analysis, here we want to focus on the structural architecture and the mutual relationships between the main tectono-metamorphic units that characterize this area: the Voltri and the Palmaro-Caffarella units. They derive from mantle and oceanic crust and show different peak metamorphic conditions: the Voltri Unit (as defined by Capponi & Crispini, 2008) re-equilibrated in the eclogite facies, whereas the Palmaro-Caffarella Unit shows blueschist facies peak metamorphic conditions. According to the recently published Geological Map of the area (Foglio 213-230 “Genova” of the CARG project, Capponi & Crispini, 2008), the eastern sector of the Voltri Unit largely consists of serpentinites that enclose bodies of eclogitised metagabbros, metasediments and serpentinised peridotites, that achieved slightly to severely different P-T conditions, even if they attained peak conditions within the metamorphic eclogite facies.

On the whole, at the regional scale, the Voltri Unit is limited to the east by the Palmaro-Caffarella Unit, in contact along folded and sheared boundaries; nevertheless detailed geological mapping and structural analysis revealed a more complex architecture, showing that disrupted portions of the blueschist Palmaro-Caffarella Unit are boudinated and sheared along the regional foliation inside the Voltri Unit. The result is that highly sheared serpentinites and metasediments of the Voltri Unit host various HP rock slices re-equilibrated at different P-T peak conditions. Metagabbro and peridotite bodies display strong strain partitioning, being much less deformed than the country rocks. Such evidence indicates that bodies with different metamorphic (eclogite vs. blueschist facies) and tectonic evolution float in a low competence “matrix” and therefore suggests that the Voltri Massif, at least its eastern sector, matches the requirements of a tectonic mélangé. In particular the Voltri Massif displays a strong strain partitioning, with low deformed rock bodies inside highly sheared country-rocks; such bodies (from m-scale to km-scale) show heterogeneous metamorphic peak conditions, ranging from eclogite to blueschist facies.

The occurrence of a tectonic melange in the Voltri Massif has been proposed by Federico et al. (2007) that interpreted in this way an hectometric outcrop of foliated chlorite-actinolite enclosing lenses of less deformed metabasites and metasediments, at Cascine Parasi, in the western part of the Voltri Massif. We like to recall that we were introduced to the geology of the Cascine Parasi area by Lucio Cortesogno, who also led the petrographic studies during our Geological Mapping of the CARG project.

FROM FIELD GEOLOGY TO PALEOGEOGRAPHIC AND GEODYNAMIC RECONSTRUCTIONS: THE SYNERGY OF LUCIANO CORTESOGNO AND MARIO VANOSI

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This session is jointly dedicated to the memory of Luciano Cortesogno and Mario Vanossi who passed away in 2005 and 2009 respectively. Since 1970, Luciano Cortesogno developed investigations addressed to primary, ocean floor and orogenic processes in the oceanic lithosphere. In those years, starting from extensive, accurate, interpretive field survey and mapping, through deep and exhaustive mineralogical, petrographic, petrologic analyses, he elaborated original petrogenetic and geodynamic interpretations and resulted a first rank contributor to the Alpine and Tethyan ophiolite geology.

A distinctive character of Lucio was the capacity to collaborate and integrate the contribution from other disciplines than petrography: stratigraphy, structural geology, geochemistry and mineralogy. His scientific interests spread then to the Paleozoic petrogenetic processes in the continental crust of the Ligurian Pennidic terranes: Lower Palaeozoic stratigraphy and metamorphic evolution, Late Variscan volcanism, plutonism, stratigraphy, Triassic volcanism. His research, in a fruitful collaboration with Pavia colleagues and friends, firstly Mario Vanossi, was developed across many years of field and laboratory work.

Mario Vanossi has been one of the most complete geologists in the national and international scientific community, endowed with great abilities of analysis and synthesis and helped by a formidable power of concentration. He wrote about 150 publications as only author or in collaboration with Italian and foreign colleagues. In about twenty years, between the ‘sixties and the end of the ‘seventies, he collected a huge amount of stratigraphic and structural data, then expressed in more than forty scientific publications, edited in ten years only, as well as in several geological maps. One of these was the second edition of the Albenga-Savona Map of the C.G.I., 1:100.000 scale, printed in 1970, which he managed as survey co-director. At the same time, ranging from the Helminthoid Flysch to the Briançonnais and Piedmont successions, and everytime dealing with different topics, from the stratigraphic-sedimentologic to structural, paleogeographic and geodynamics ones, he outlined a general framework for this sector of the Alpine belt which is, up to now, a milestone.

As from the early ‘eighties the collaboration Vanossi-Cortesogno started and continued for over twenty years producing basic contributions about the genesis and metamorphic evolution of the Paleozoic basements, the stratigraphy of the late-Variscan successions of the Ligurian Briançonnais and their metamorphic Alpine evolution. Even during the draft of his last paper, co-authored with colleagues and friends in the University of Pavia, Mario Vanossi still addressed the structural evolution of the Penninic nappes of the Ligurian Alps, and honoured his scientific engagements, but also accomplished his teaching commitment, another face of his great passion towards the Earth Sciences.
GEODYNAMIC RECONSTRUCTION OF ALPINE PRE-COLLISIONAL STAGES BETWEEN VARISCAN HERITAGE AND TECTONO-SEDIMENTARY EVOLUTION IN THE LIGURIAN ALPS: A REVIEW

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The renewed interest that has arisen around passive margins leads us to reconsider the stratigraphy and geodynamics of this peculiar and misunderstood sector of the Italian Alpine belt. The Western Italian Alps comprise one of the most extensively studied areas in geological sciences, but the Ligurian Alps, are left out from recent debates and are rarely cited in papers on pre-collisional geodynamic reconstructions. In our opinion this is due to the scarcity of international literature on this Alpine sector, and to the widespread metamorphism and tectonic displacement affecting almost all the sedimentary covers, discouraging field research. Nevertheless, once the complex puzzle of tectonic units has been restored, the Ligurian Alps represent one of the best places to observe a complete section of a Mesozoic passive margin. In addition, in the Ligurian area there is no field evidence of multiple oceans (as in other sectors of the Western Alps), giving the researcher an opportunity to pass directly through the margin towards its transition to the undeformed foreland and to the oceanic domain. Furthermore, the preserved geological records pertain to two distinct orogeneses, the late-Variscan and the Alpine events.

The Early-Middle Permian tectonics, considered as the product of a megashear zone evolution or as a response to a changed geodynamic context, affected the Ligurian Alps, as we can see in the Briançonnais domain, with the rejuvenation or birth of new faults bordering graben/half-graben or pull-apart structures during the emplacement of the different volcanic bodies.

During Late Permian-Early Triassic times, the Ligurian sectors underwent extensional tectonics only. At first, graben/half-graben structures filled by Upper Permian K-rhyolites developed, followed by the establishment of suitable gradients for erosion and transport of clastic components of the Verrucano Formation. From the Middle Triassic onwards, the Ligurian Alps area was affected by diffuse extension caused by southeastern subduction of Palaeotethys which led to the opening of multiple oceanic troughs (i.e. Pindos, Maliac and Meliata). At these times, the study area was located in a sector approaching the convergence of the axes of basins, opening like a fan toward the East. The climax of this activity occurred in the Ladinian. Nevertheless, our data show that the extensional basin axes at this time were markedly different from the Alpine Tethys ones that overprint the whole pre-Jurassic geological record.

The Late Carnian to Norian was a key point in the evolution of the Mediterranean area: in the Ligurian Alps it represented the transition between the Middle Triassic back-arc/rifting stage and the Alpine Tethys rifting s.s. Field evidence is in favour of an overlap of the two extensional mechanisms rather than a complete switch-off of the first. The Alpine Tethys rifting developed from the Norian and reached its climax in the Early Jurassic, when subsidence increased until the collapse of the margin. This led to the formation of emerged rifting shoulders and deeper inner domains, creating the Briançonnais-Prepiedmont differentiation. It follows the oceanisation and successive cooling of the margins. Our research highlights that the Ligurian Alps were a domain in which for over a hundred million years orogenesis, rifting and oceanisation strongly affected the integrity of the upper crust. The rare volcanic effusions testify to a complex chemistry, sometimes apparently in contrast with the supposed geodynamic environment. This may be related to the heterogeneity of the crust that was affected by multiple mantle uplifts, partial melting and extensive faulting over a long period. Thus the last and most important rifting (the Alpine Tethys) developed around a narrow, elongated area of crustal weakness generated by multiple geodynamic events.
Towards a Chronostratigraphic Definition of the Paroxysmal Phase of Rifting in the Ligurian Alps (Case Morteo Rhyodacites)

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Cortesogno \textit{et al.} (1981) pointed out the presence of rhyodacite lavas and pyroclastites that form metre-thick layers interfingering with the M. Galero Breccia near Albenga, SV (Case Morteo rhyodacites). Two volcanic events can be recognised: the first led to the deposition of altered acid lava, about 4 metres thick, the second event is formed by 5-6 metres-thick level of altered acid lava that overlies a breccia horizon, reworking and englobing its clasts, testifying to the true stratigraphic position of the volcanics. The original mineralogical composition of massive lava and pyroclastites was interpreted (Cortesogno \textit{et al.}, 1981) to be formed by plagioclases, amphibole, biotite and quartz and thus considered to be an alteration product of a primary felsic suite that ranges from rhyolite to dacite.

The age of volcanics remained unsolved due to both the incertitude of the chronostratigraphic position of the embedding breccia (traditionally referred by regional comparison to Dogger \textit{s.l.}) and to the lacking of minerals for the radiometric datation (zircons were searched but not found). Recently, a revision on the stratigraphy of this sector of the Ligurian Alps, (Decarlis & Lualdi, in press) leads to the definition of new lithostratigraphic unit that allow to reconsider the chronological position of some units also by comparison with key-successions in the Western Alps used as geodynamic markers. On this base, the M. Galero Breccia, \textit{i.e.} megabreccias produced by the dismantling of northern margin of Tethys, has been referred to a Late Liassic age rather than Dogger \textit{s.l.}

Since the opportunity to date this huge amount of clastics (and their equivalent in the Western Alps, \textit{e.g.} Formation Detritique Rousse, Breche \textit{s.l.} of the Breccia Nappe) that marks the paroxysmal phase of rifting that closely predates the oceanisation. The relevance of these volcanites is also to be a unique witness of synrift flow on continental crust on the whole Western Alps. The existence of these outflows may proves their run-up in Liassic times along pre-existing faults and their mixing with the falling blocks. As a consequence, they can be considered to be strictly linked to the geodynamic context of the pre-oceanic rifting of the Prepiedmont sector of the European margin. It is worth considering that similar pyroclastic product emplacements took place during the Pliensbachian to Toarcian in the Betic cordillera, preceding the effusion of basic lava associated with the western Tethys oceanisation.

Unfortunately, the U/Pb radiometric analyses on zircon separates by the ELA ICP MS (excimer laser ablation Inductively coupled plasma mass spectrometry) method (CNR - IGG Pavia) did not provide a reliable age due to the alteration of the volcanics and to high normal-Pb content. The latter is probably due to a late hydrothermalization associated with rifting and emplacement of the oceanic crust, recorded by the complex vein network affecting the overly radiolitares. Recently, a detailed sampling has been performed on the coarser grained fraction of the flow that provided a few zircon crystals. Further U-Pb analyses on zircons in progress by SHRIMP (Sensitive High Resolution Ion Microprobe) are aimed to improve the response in order to achieve regional scale correlations.


THE “URBE” 212-2 QUADRANGLE: NEW GEOLOGICAL MAPPING IN THE HP POLYDEFORMED VOLTRI MASSIF (WESTERN ALPS)

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We performed a new geological mapping of the western part of the Voltri Massif at 1:10,000 scale, between autumn 2009 and 2010. The investigated area is approximately 160 Km² and covers a hilly to mountainous region in Liguria (spanning the Savona and Genova provinces), with the highest peak of Mt Beigua (1287 m) at only about 8 Km from the Ligurian Sea.

The mapped area falls inside the HP metaophiolitic Voltri Massif of the Western Alps and thus encompasses rocks belonging to the Ligurian-Piemontese Domain. The bedrock is made up of serpentinites and metasediments, with minor occurrence of metabasite, lherzolite and metagabbro. Metagabbros frequently crop out as lenses and bodies inside serpentinites and are either eclogite-facies Fe-Ti-oxyde gabbros or Mg-rich HP gabbros, largely retrogressed in greenschist facies. Along the contacts between serpentinites or metabasites and metasediments, levels of hybrid rocks (schists containing chlorite + actinolite/tremolite ± carbonate ± ores) often occur, resulting from shearing and metasomatic exchanges; such rocks are schists containing chlorite + actinolite/tremolite ± carbonate ± ores Metabasites encompass rocks with either a magmatic (“Prasinite” Auct.) or metasedimentary origin (pristine mafic breccias or greywackes), completely retrogressed in greenschist facies conditions.

The bedrock is covered by late- to post-orogenic deposits, either belonging to the basal horizons of the Tertiary Piedmontese Basin (TPB) or to Pliocene marly sediments. The metamorphic rocks are commonly highly deformed and the more evident foliation in the field is a composite fabric (CF) that is parallel to the lithological contacts. More than 2200 CFs have been measured, together with axes and axial planes of folds. The structural analysis and the development of mesoscopic fold interference patterns point out to the occurrence of at least three phases of folding. The older deformation event (F1+2) is characterized by tight to isoclinal transpositive folds, with generally subhorizontal axial planes and subhorizontal axes; the second one (F3) is characterized by open folds with E-W to NE-SW trending and low plunging axes, that don’t produce an axial plane cleavage. Dispersion of AP3 suggests the occurrence of a further folding event (F4) with N-S to NW-SE subhorizontal axes. The resulting interference patterns are both of type 2 and 3, that occur also at the cartographic scale. In general the CF dips 40-50° towards E-SE in the eastern side of the mapped area, whereas it is subhorizontal in the western part. This structural feature, combined with the fact that further to the east the CF in the Voltri Massif is commonly steeply dipping (Capponi & Crispini, 2008), points to a general recumbent geometry already depicted in literature but variably interpreted (e.g., Capponi & Crispini, 2002; Vignaroli et al., 2010). This 3D-structural architecture is going to be discussed on the basis of our analysis. In the studied area brittle structures are widespread and associated to mappable fault rocks. We measured fault surfaces and associated kinematic indicators in the field and mapped the tectonic lineaments resulting from photo-interpretation as well. Even if lithologic boundaries generally follow the CF, they are locally reworked by brittle tectonics, that in places can be constrained in time by the occurrence of the Pliocene sediments (in the southeastern part of the map) and of the TPB deposits in the northwestern corner. The new detailed mapping and structural analysis allowed us to make a direct comparison with data recently collected in adjacent areas (CARG Project - Capponi & Crispini, 2008) to obtain a better insight into the structural setting of the Voltri HP-ophiolites.


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POST- AND LATE COLLISIONAL VOLCANISM IN SOUTHERN VARISCIDES: A KEY TO COLLAPSE AND DISRUPTION OF AN OROGEN

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The late to post orogenic evolution in southern Variscides is characterized at the Early Permian, by a transtensional geodynamic regime developed along the southern Palaeoeuropean margin, as a result of a dextral megashear between Gondwana and Laurasia. In West-Mediterranean southern Variscides, magmatism and tectonics interplayed during the opening of intracontinental alluvial to lacustrine basins.

The most significant issues to address in the characterization of post-orogenic succession in Southern Variscides are the following: i) within the generalized orogenic collapse, sediment- or volcanic-dominated series develop as a consequence of local tectonic and lithospheric setting. The volcanic units are characterized by a common stratigraphic succession, beginning with early calc-alkaline andesites and rhyolites, followed by conspicuous rhyolites, and by dacites infilling fault-bounded pull-apart basins. Both andesites and rhyolites show K-normal and high-K calc-alkaline character. However, in different regions and settings, differences in timing, areal distribution and outpoured volumes arise. ii) Opening of pull apart basins is associated with strike slip basins iii) when tectonic unroofing is active, the volcanism could be associated with HT/LP metamorphism iv) along with areal distribution of the volcanic field, a chemical zoneography is possible parallel to the orogen axis. This character has been evidenced in the Ligurian Alps and also in the collapse of the Balkan orogen (Bulgaria) the relationships between calcalkaline and alkaline volcanism have been demonstrated to occur as subsequent or coeval. In the Ligurian Alps, the volcanic activity is confined between calc-alkaline rhyolites dated 285.6±2.6 Ma and rhyodacites-rhyolites aged 272.7±2.2 Ma (U/Pb LA ICP MS on zircon). In between, intermediate lavas and associated tuffites that have been interpreted as the result of mixing and fractional crystallization originated in partial melting at boundary between lithospheric mantle and lower crust. The interaction with the overlying thickened crust was constrained at ~ 34% crystallization by adding ~ 27% of contaminant to the parental magma. The final volcanic event is represented by K-alkaline rhyolites at 258.5 ± 2.8 Ma after a Mid-Permian amagmatic and sediment-starved time gap of ca. 14 Ma.

Conversely, in Nurra, a midly alkaline activity occurs at Santa Giusta at 291 Ma; here the basement was a structural high bounded by E-W trending faults since the Late Carboniferous-Lower Permian, and also controlled the development of Mid Permian and Lower Triassic successions. The Lower Palaeozoic medium- to high-grade metamorphic basement, the Sardinia-Corsica batholith and the Stephanian-Autunian calc-alkaline effusives are cut by transitional dolerite dikes with a N-S trend and subvertical dip. 40Ar-39Ar ages on amphibole at 253.8±4.9 and 248±8 Ma probably represent the emplacement interval.

Finally, a role of volcanic dominated series in plate reorganization has been envisaged: the end of calc-alkaline magmatism and the gap in the sedimentary record may correspond to the major displacement along the megashear zone between Laurussia and Gondwanaland as supported by palaeomagnetic constraints. In the Ligurian Alps, the age of the alkaline volcanic rocks matches the end of the plate reorganization and the onset of the Alpine cycle.
In the European Alps the exposure of Variscan structural and metamorphic imprints within the present-day Alpine structural domains indicates that before the Pangaea break-up, the continental lithosphere was thermally and mechanically perturbed by Variscan subduction and collision. When continental rifting does not develop on a stable continental lithosphere, geodynamic interpretation of igneous and metamorphic records, as well as structural and sedimentary imprints of rifting-related lithospheric extension, can be highly ambiguous since different mechanisms can be responsible for regional HT-LP metamorphism. While the metamorphic and igneous records of Variscan orogeny are widespread in the European continental crust, a diffuse igneous activity associated with HT metamorphism accounting for a Permian-Triassic high thermal regime is peculiar to the Alpine area.

The overprint of HT Permian-Triassic evolution on the HP relics of the Variscan subduction and collision has been interpreted as induced either by late-orogenic collapse or by lithospheric extension and thinning leading to continental rifting (e.g. Lardeaux & Spalla, 1991; Diella et al., 1992; Ledru et al., 2001). Even the interpretation of the geodynamic environment responsible for the development of intracontinental basins hosting the Permian volcanic products allows two possible alternatives: one envisaging a strike-slip dominated regime (Arthaud & Matte, 1977; Cassinis & Perotti, 1994), which is compatible with the evolution of a mature collisional setting (Molnar & Lyon-Caen, 1988), the other a continental rifting tectonic setting (Siletto et al., 1993; Selli, 1998; Staehle et al., 2001). In both cases the continental rifting promoting Mesozoic opening of the ocean in a lithosphere thermally softened and thinned by slab break-off processes is generally accomplished in the final stages of continental collision.

Recently the integrated use of geological data and numerical modeling shows that active extension is required to achieve the thermal conditions allowing partial melting of the crust accompanying gabbroic intrusions and HT-LP metamorphism (Spalla & Marotta, 2007; Marotta & Spalla, 2007; Marotta et al., 2009).

U-Pb CHRONOLOGICAL CONSTRAINTS FOR THE LATE TO POST-VARISCAN MAGMATISM AND METAMORPHISM IN THE LIGURIAN ALPS (ITALY)

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The Alpine chain comprises two major rock groups: one of these only experienced tectonics related to the Alpine cycle, while a second shows pre-Alpine relict metamorphism. The latter recorded a polyphase ante-Alpine history, both Variscan or pre-Variscan in age. The Alpine overprint on the Variscan relict units in general obscures our interpretation of the preceding history. In particular, the Penninic nappes of the Western Alps comprise several gneissic units, whose age, origin, pre-Alpine metamorphism and tectonic significance are debated. In the Ligurian Alps, one of the basement units of the Briançonnais domain (Barbassiria massif) is made up of orthogneisses derived from K-rich rhyolitic protoliths and, subordinately, rhyolitic dykes cutting a main igneous body. The pervasive Alpine metamorphic and tectonic overprint under blueschist facies conditions on the Barbassiria Orthogneisses preserves little evidence of the Variscan metamorphism.

New U-Pb excimer laser ablation ICP-MS dating on zircon separates from the orthogneisses and dykes has been undertaken to unravel the relationships between effusive emplacement and Variscan metamorphic overprint. The results suggest an age for the eruption of the rhyolite protolith of the Barbassiria Orthogneisses of ~ 320 Ma (i.e. Late Carboniferous), and a subsequent dyke emplacement at 260.2±3.1 Ma. The Variscan high-temperature metamorphic event (amphibolite-greenschist facies) is thought to be related to a mechanism of tectonic burial associated with the compressive tectonics during the uppermost Carboniferous late stage of the Variscan collision.

The dykes cutting the Barbassiria Orthogneisses at ~ 260 Ma belong to the diffuse K-rhyolite volcanism emplaced at 258.5±2.8 Ma. This age represents the end of the orogenic phase in this segment of the southern Variscides, and enhances the evidence of a ~ 10-15 Ma Mid-Permian sedimentary/magmatic gap in its volcano-sedimentary cover.
EARLY PERMIAN LATE CARBONIFEROUS VOLCANO-SEDIMENTARY SUCCESSION THERMOMETAMORPHOSED BY COMPOSITE GABBRO-GRANODIORITIC PERMIAN PLUTON: LU FALZU BASIN (NORTH SARDINIA)

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In North Sardinia a volcano-sedimentary succession made of clastic sediments and by a thick stack of pyroclastic flows crops as remnant of a Permo-Carboniferous basin. The outcrop to the south is buried by the the Tertiary sediments of the Castelsardo basin, whereas to the north it rests on granitoids that intrude the Variscan High Grade Metamorphic Complex, which mainly consists of migmatites. Among the different intrusions in touch with this late Variscan basin, a small intrusion consisting of intergradational, quartzose gabbro-diorite, diorite and voluminous mafic-to-felsic granodiorite is the closest to the best exposition of its infilling. The clastic sediments consists of fine-grained quartzites, arcoses with silty intercalation and conglomerates; these consist of mud-sustained angular to sub-rounded clasts, derived from the metamorphic basement. The facies of the deposits recall that of some Stephano-Autunian basin of southern Sardinia. The clastic succession is capped by tuffs and by welded lava-like ignimbrites with an exposed thickness of 700 m. The intrusive relationships between the plutonic rocks of the area with the late variscan deposits were already evidenced by Del Moro et al. (1996), who evidenced some metamorphic assemblage in the Permo-Carboniferous sediments. Actually, the fine-grained sedimentary rocks in contact with the intrusives are deeply transformed, in place resembling those of the High Grade Metamorphic Complex. In any case in thin section they show abundant andalusite ± cordierite, graphyte and decussate aggregates of muscovite and biotite. Graphyte is particularly abundant in some dark beds as metamorphic product of carbonaceous matter. New U/Pb zircon analyses on the gabbroic portion of the composite intrusion yielded an age 285.8±1.9 Ma. Such an age is coherent with both the Rb/Sr blocking ages and newly performed Ar/Ar ages - which resulted few hundred thousand years younger - on muscovite and biotite with decussate texture of the thermoetamorphic sediments. Moreover amphibole thermobarometry confirmed the shallow emplacement level (2-3 km) for the composite granodioritic intrusion.

Taking in account that the High Grade Metamorphic Complex on which the Lu Falzu sediments rest is affected by the neo-Variscan HT/LP (≈ 4 Kb - 650°C) event at about 303 Ma (Macera et al., 1989) and that erosion and sedimentation must had occurred before the gabbro emplacement, uplift and exhumation of the migmatite that equilibrated at least 13-14 km occurred within a time span as short as ten million years.


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THE PERMIAN GABBROS OF THE WESTERN ALPS CONTINENTAL CRUST: THE FLY-RECORER OF THE JOURNEY FROM PANGEA BREAK-UP TO ALPINE CONVERGENCE

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Gabbro emplacement in the continental lithosphere is a marker of lithospheric thinning: association of mantle peridotites, gabbros and continental crust is an important key for the understanding of passive margins. Gabbros included in continental units of orogens are therefore basic tools to infer duration and mechanisms active during ocean opening. Moreover gabbro compositions are diagnostic to develop critical parageneses in subduction-collision environment.

In the Austroalpine domain several gabbro bodies have Permian ages and are often intruded into metamorphic rocks deformed under high-temperature and intermediate- to low-pressure conditions. They are interpreted, with the contemporaneous metamorphism often developed in their country rocks, as signals of a positive thermal anomaly associated to lithospheric thinning, indicated by some authors as precursor of the continental rift that led to the Mesozoic ocean opening (Marotta et al. 2009 and references therein). Amongst these, mainly in the western portion of the Austroalpine, numerous bodies underwent HP-LT Alpine metamorphic re-equilibrations but still preserve, at places, relics of pre-Alpine evolution.

Corio and Monastero and Sassa gabbro bodies are here investigated to reconstruct their structural and metamorphic evolution in order to decipher the geodynamic scenarios characterizing their pre-Alpine and Alpine tectonic history. The polyphase Alpine deformation of these gabbros is highly heterogeneous; our detailed structural investigations allow to discriminate between emplacement structural levels: the Sassa body maintains at best the igneous characters over huge weakly deformed volumes and the pre-Alpine subsolidus evolution accounts for an exhumation from the intermediate crust.

The Corio and Monastero gabbro is pervasively eclogitized but few low strain domains preserve pre-Alpine fabrics and mineral assemblages pointing to a deep crustal emplacement. Similarly the Alpine evolution differs in the two bodies: Sassa gabbro underwent Tertiary blueschist facies re-equilibration whereas Corio and Monastero gabbro underwent Upper Cretaceous-Paleocene eclogite-facies conditions. Differences in the PT/dt paths characterizing the pre-Alpine and Alpine evolutions are the key to unravel differences in the thermal state affecting pre-Alpine continental crust during lithospheric thinning and the Alpine evolving thermal state of the subduction zone.
Sessione tematica T2:
Micro e nano-particelle minerali in ambienti atmosferici, idrici, biologici

Conveners:
Elena Belluso (Università di Torino) *
Antonio Gianfagna (Università di Roma “La Sapienza”)
Alessandro Gualtieri (Università di Modena e Reggio Emilia)
Caterina Rinaudo (Università del Piemonte Orientale)
HIGH RESOLUTION ELEMENTAL MAPPING OF FERRUGINOUS BODIES FROM LUNG TISSUE USING SYNCHROTRON RADIATION

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It was not until the late 1950s that asbestos was recognized as a human carcinogen and exposure to fibers started to be associated with several different lung injuries, including respiratory diseases, asbestosis, mesotheliomas, and lung cancer. Since that time, the mechanism by which asbestos causes cancer has been intensively studied, but, however, it is still not well-understood. Ferrouginous Bodies (FB) consist of a coating of inorganic fibers (usually asbestos fibers, but not only) composed of inorganic and organic material. If the core of these bodies consists of asbestos, FB are known as Asbestos Bodies (AB), and their count is one of the most valuable tools for establishing if a subject underwent professional exposition to asbestos, or to estimate the degree of asbestos exposure among the general population (Churg & Warnok, 1981). It was generally accepted that the coating of embedded fibers to form AB is a protective mechanism produced by macrophages trying to segregate the cytotoxic fibers from the organic tissues (Mace et al., 1980). However, more recently, other authors suggested that the coating material may enhance the cytotoxic properties of the asbestos fibers by increasing the production of free radicals (Ghio et al., 2004). Therefore, the exact knowledge of the composition of the AB, and of FB in general, is of fundamental interest. Accordingly, iron on the surface of AB was shown to be catalytically active (Hardy & Aust, 1995) and capable of inducing the formation of single strand breaks in phiX174 RFI DNA (Lund et al., 1994).Earlier studies, exploiting Transmission Electron Microscopy and X-ray diffraction on split AB, showed that the coating contained crystalline particles of the same order of size quoted for the inorganic iron core of the ferritin molecule (Pooley, 1972). More recently, synchrotron radiation soft X-rays imaging and fluorescence microscopy revealed novel properties on the composition of FB (Pascolo et al., 2001). In this work, samples of human lung tissue rich in FB, due to professional exposure, were collected from three subjects died of lung cancer. Tissues were digested using NaClO to produce a suspension of inorganic material that was filtered on porous membranes. The membranes were preliminarily characterized by optical microscopy and Scanning Electron Microscopy, in order to estimate the number of the filtered particles. The samples were brought to the European Synchrotron Radiation Facility in Grenoble (France), a high brilliance X-ray source. Exploiting the high spatial resolution provided by the micro-focused X-ray beam (down to 0.5 microns), \(100 \times 100\) microns\(^2\) fluorescence maps of selected bodies were acquired. The fluorescence maps revealed that, except for bodies containing the asbestos fibers (which also contain Si, Mg, and Al), the FB are mainly composed of Fe, Cu, Zn, As, and, for certain subjects only, Ge and Ba. X-ray Absorption Spectroscopy at the Fe K-edge was also performed on selected FB in order to unravel the speciation of iron. The near edge part of the absorption spectra (XANES) revealed features that are in excellent agreement with the ferritine standard. The results obtained will help solving a long time debate and lead to a better understanding of the toxicological mechanism of a large class of air pollutant particles that, nowadays, constitutes a serious risk for human health.

CHARACTERIZATION OF THE MINERALOGICAL COMPONENT
OF MILAN PM$_{10}$

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Samples of summer and winter (2010-2011) atmospheric particulate (PM$_{10}$) of Milan urban area were collected and characterized for some classes of components with health impact. Moreover, the PM chemical characterization of the main components (i.e. inorganic compounds, organic compounds, and elemental carbon) was performed by XRF and ICP-MS. Toxicity test on pulmonary immortalized cell lines showed different effects produced by summer and winter samples.

Indeed, the summer PM$_{10}$ fraction has a more pronounced inflammatory effect, due to the presence of endotoxins. Nevertheless, their inhibition did not completely vanish the inflammatory effect, which may be related also to both silicic materials of crustal source and transition metals. The quantity of such materials is significantly higher in the summer PM$_{10}$.

The morphology and chemistry of this fraction components were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Further SEM and EDX analysis will enable to a better characterization of this particulate. Moreover, the analysis at transmission electron microscopy (TEM) will allow to discriminate the mineralogical phases that contribute to the PM$_{10}$ silicon and transition elements.
STUDY ON THE POTENTIAL TOXICITY OF NATURAL CHRYSOTILE
NANOFIBERS: PREPARATION OF PROPER SAMPLES
AND PRELIMINARY CELLULAR AND CELL-FREE TESTS

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Inhalation of asbestos fibers causes asbestosis, lung cancer and pleural mesothelioma. Fiber length,
biopersistence and surface reactivity are involved in the development of the respiratory diseases. The fiber length
was the first parameter correlated with asbestos toxicity. In vivo studies on rodents showed that long (> 8 µm)
and thin fibers the have highest potential to induce mesothelioma. Nevertheless, a large number of fibers in the
mesothelial tissues of exposed workers has diameter < 0.2 µm and length of few µm. Nanofibers (NFs) have also
been recovered in subjects only exposed to environmental pollution. NFs could result from the splitting up in the
lung of long fibers - mainly of chrysotile asbestos - in sub-micrometric fibrils, or might be inhaled already in
nanometric size. In the past NFs, were released from several products, e.g. brake pads, following mechanical
stress. They are also detectable in the natural environment, e.g. in turbulent waters from mountain streams that
flow trough serpentinite outcrops.

The pathogenic potential of the asbestos NFs is still unclear. Therefore the main goal of the present work
are a) to develop a size selective procedure for preparation of short (< 5 µm) and thin (< 200 nm) chrysotile NFs
and b) to compare their potential toxicity by respect to long fibers.

We investigated the effect of ultrasonic treatments on size, shape and structure on a pure sample of
chrysotile asbestos from the Italian Central Alps widely characterized in previous investigations, in order to
identify the best conditions to produce a homogenous batch of short asbestos fibers. Ultrasonic treatments were
carried in water for different time periods (from 3 to 24 h) and the final products were subjected to
morphological analysis to verify change in shape and size distribution (Scanning Electron Microscopy) and to
crystallographic (XRD, micro-Raman spectroscopy) and elemental analysis (X-Ray Fluorescence) to detect any
change in structure/composition. The preparation of asbestos NFs was performed also on a commercial
chrysotile sample (from the Balangero mine, Italy) and the potential toxicity of the two samples was compared
with the well known toxicity of the original asbestos. First we examined the surface properties considered
relevant to pathogenicity then some cellular responses in human epithelial cells.

Among the most relevant surface properties involved in asbestos toxicity we examined the potential to
cause oxidative injury within the lung by measuring free radical generation and depletion of antioxidant
defenses. The potential of NFs to generate hydroxyl and carboxyl radicals when in contact with biological fluids
has been investigated by means of the spin trapping technique. The potential to consume the antioxidant defenses
has been evaluated by monitoring the depletion of cysteine and ascorbic acid, during the incubation of the
sample over time. The amount of bio-available iron on the sample surface was also evaluated by mobilization of
ferric and ferrous ions using specific chelators. In all cases NFs showed a lower reactivity than the long fibers.

Cellular responses were measured as leakage of lactate dehydrogenase (LDH) into the extracellular
medium, ROS and nitric oxide (NO) production, and lipid peroxidation.

The data of the cell test showed a different toxicity of the fibers correlated to their length. Nanofibers are
less toxic than the long fiber of the same asbestos source.
MICRO-RAMAN SPECTROSCOPY AND VP-SEM/EDS TECHNIQUE APPLIED TO THE CHARACTERIZATION OF INORGANIC PARTICLES OR FIBRES IN LUNG AND PLEURAL TISSUES FROM PATIENTS AFFECTED BY RESPIRATORY DISEASES

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During the XX Century Italy was a big producer and importer of asbestos until 1992 when asbestos was banned: for this reason it results still now affected by a lot of asbestos-related diseases, as proved by the data published by ReNaM (Registro Nazionale dei Mesoteliomi).

The correlation between inhaled fibrous materials and diseases of the respiratory system - asbestosis, mesothelioma, pulmonary carcinoma - is demonstrated by a large scientific literature.

These pathologies are typically characterized by a long latency time, i.e. the time interval between exposure and the disease onset, therefore the effects on the human health of asbestos exposures occurred in the past appear decades later. Scientific studies indicate, despite the ban of these materials, an occurrence peak of asbestos-related diseases in the next decade.

Moreover, not only occupational and/or family exposure, but also the environmental one may today represent a cause of asbestos-related pathologies onset.

Previous works carried out in our laboratories proved that micro-Raman spectroscopy is a technique able to recognize mineral phases on untreated samples. In particular recently micro-Raman spectroscopy, using 632.8 nm laser beam as excitation source, has been coupled with VP-SEM/EDS - Variable Pressure Scanning Electron Microscopy with annexed Energy Dispersive Spectroscopy - to characterize, without digestion of the biological matrix, particles/fibres directly in the histological sections used for the medical diagnoses. In particular a methodology allowing the characterization of the same particle/fibre under the two techniques, on thin sections of lung and pleural tissues from patients affected by Malignant Pleural Mesothelioma, due to past professional exposures, have been studied. All the inorganic phases, fibrous or not, have been characterized on their spectroscopic and chemical aspects. The results obtained on all the analysed sections indicate on the silicate particles/fibres inhaled and detected in the respiratory system an interaction cell-particle/fibre affecting the crystalline structure.

Also the “asbestos bodies”, where the inhaled fibre is coated by an iron rich protein material, have been characterized. The laser beam was addressed either on the material coating the fibre either on the portion more free from the coating. By this way identification about the mineral phase corresponding to the fibre in the core can be achieved.
ULTRAFINE PARTICLES NUMBER MONITORING IN TURIN METROPOLITAN AREA - YEAR 2010 RESULTS

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Like all large urban areas of Po Valley, Turin metropolitan area is very critical with respect to particulate concentrations in ambient air. The measures which are carried out by Environmental Protection Agencies concerning institutional purposes are focused on mass concentration, which is the indicator provided for by law. In recent years, however, concern for number concentration measures is greatly increased, due to its importance for the evaluation of particulate toxic effects, in particular in respect of ultrafine fraction. The need for a deeper knowledge in this field was explicitly highlighted in the results of European Commission Programme CAFE (Clean Air For Europe).

In this context a research project was promoted in order to collect ultrafine particles data in the Turin metropolitan area through long-term measures carried out both at ground level and at an altitude comparable to winter planetary boundary layer height. A specific instrumentation was acquired (UFP Monitor 3031-TSI Incorporated), specifically designed for routine use within air quality monitoring networks.

This instrument was installed at the beginning of October 2009 in the first monitoring site which is located on the fifteenth floor of Province of Turin headquarters in the city centre at an altitude of about 50 meters.

The UFP operates continuously and provides both the size distribution and the number concentration of particles between 20 and 1000 nm. The set up channels of size resolution are six (20-30 nm, 30-50 nm, 50-70 nm, 70-100 nm, 100-200 nm, 200 -1000 nm).

The average number concentration in the year 2010 is approximately 7200 particles/cm³. The calculation was carried out on the basis of hourly average concentrations of particles whose size is between 20 and 200 nm.

About 70% of the particles measured in the range 20-200 nm have a diameter between 20 and 50 nm, and the higher concentrations are recorded in the class 20-30 nm.

The data were correlated with other pollutants monitored at two traffic stations placed at ground level in the city centre (Torino Consolata and Torino-Rivoli) and at the background station of Torino-Lingotto. The comparison shows a good correlation with the concentrations of nitrogen monoxide, PM₁₀ and PM₂.₅. The lowest correlation coefficients were found for nitrogen dioxide and benzene. The mean variability during the day for classes 20-30 nm and 30-50 nm is relatively high, whereas other classes have a more constant trend.

Monthly averages trend shows a relative maximum in July which does not seem to be explainable just on the basis of the weather situation and will require further investigation.

The analysis of critical events during cold weather shows that the concentration of ultrafine particles is related to the inversion layer height.
MATERIAL METHODS FOR THE CHARACTERIZATION OF 2.5 PARTICULATE MATTER IN THE URBAN AREA OF ROME, ITALY

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The characterization of the airborne particulate represents a real issue. Many studies have examined the effects of the particulate matter on human health suggesting that the small particles represent a severe problem.

In the present work chemical and mineralogical investigations on the particulate matter of the city of Rome were carried out. The particulate samples (PM2.5) were collected in Rome since April 2010. Polycarbonate filters were used to trap and recover airborne particles according to a standard procedure, and then utilized for different analytical techniques. Preliminary investigations on PM2.5 filters (SEM-EDS, X-ray and DTA) provided information about the inorganic compound. High iron content was highlighted as oxides, hydro-oxides, and sulphates. In particular, the presence of melanterite FeSO₄·7(H₂O) was evidenced. Ca-sulphates and clays were also found. Moreover, innovative methodologies, such as Atomic Force Microscopy (AFM), resulted useful for morphological and dimensional investigations of the micro and nano-particles.

Hygroscopic properties of mixed urban aerosol can be monitored by FT-IR. Furthermore a complete functional group characterization of PM2.5 phases in the 4000-400 cm⁻¹ spectral range, with a procedure based on diffuse reflectance (DRIFT), is in progress.

The association in the atmospheric dust particles of amorphous phases and heavy metals is known to increase the release of these dangerous chemical elements. To obtain the bulk chemical composition of the particulate material the Regional Protection Agency usually utilize ion mass spectrometry (ICP-MS) on a little amount of particulate matter (2 mg; D.M. 60/2002). In this work ICP-MS analyses were performed on a high content of material (35 mg). The high amount was here used to investigate the presence of heavy metals and their release in biological environment. Data on PM2.5 samples was fully comparable with those typically observed by Regional Protection Agencies (ARPA). Test of release were executed in physiological solution (pH 7.4, 37°C, 30 days). Release evidence were obtained for Fe, V, Pb, As and Cr. These results confirm that the release of heavy metals in the biological environments already occurs from the first hours. In vitro experiments are in progress to assess the relation between the fine and ultrafine particles and the health effects.
ORIGIN, SOURCES AND DYNAMICS OF DISPERSION OF PARTICULATE POLLUTANTS IN A HEAVILY INDUSTRIALIZED BASIN VALLEY: THE CASE OF TERNI (CENTRAL ITALY)

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In this paper combined PCA/APCS factor analysis on bulk chemical analyses and individual particle analyses by SEM/EDS have been applied to the characterization of airborne particulate matter sampled at urban and regional background sites near Terni, Central Italy, in order to discriminate local sources from long range dust intrusions of both natural and anthropogenic particulate pollutants. The distinctive morpho-chemical features of particulate matter of various origins (industrial, anthropogenic, long-range transport) have been characterized by an year long extensive sampling campaign at urban and remote background sites. These data were integrated by a 15-day long wintertime campaign exploiting a tethered balloon equipped with real time instrumentations, able to continuously sample the lower troposphere from ground up to 600 m height.

Five distinct PM sources were identified, namely crustal/road dust, industrial (steel plant), traffic direct, oil combustion/incineration and secondary aerosol, and the contribution of each source to the particle size ranges modelled accordingly. Results show direct vehicular and industrial metallurgical activities be the main sources for PM in the fine fraction, and soil/road dust as the main contribution to the coarse fraction. Individual particle analyses revealed six different classes of particles in the aerosols, namely silicates, carbonates, carbonaceous and metal particles, sulphates and Ca-phosphates. They were included in the statistical analysis leading to three main clusters of crustal, secondary/transport and direct combustion/industrial sources. Except for silicates and carbonates, the rest of particles are from urban and industrial anthropogenic sources. Metal particles, in particular, result from a mix of sources from ground (car exhaust) to upper level (steel plant smokestacks) in the troposphere. A general tendency towards increasing size and size heterogeneity is observed when passing from atmospheric stability to convective conditions.

Multivariate source apportionment turned out to be a powerful tool in discriminating natural from anthropogenic sources of particle pollutants, but failed to distinguish local from long range transported soil dust. At this point discrimination between local and long range soil sources was focused on the correlation between individual particle analyses and bulk chemical composition of the coarse fraction in the aerosols. Based on the mineral chemistry of the constituent particles, corroborated by back-trajectory calculations and atmospheric vertical profile analyses, it was also possible to estimate the extent of the contribution of local and Saharan dust to the soil source.

The presence of local and mid- to long range anthropogenic sources of particulate pollutants has been put in evidence in this study. With regards to short range anthropogenic particles, those coming from automotive exhausts tend to be confined within the lower level in the atmosphere, whereas those coming from industrial emissions tend to permeate at higher levels in the atmosphere. On the other hand, long range anthropogenic sources of secondary aerosol from NE-Europe have been found to explain the observed increasing amounts of gypsum for increasing altitude upon Terni. Vertical dispersion of particle pollutants appears to be highly influenced by topography (which protects from ventilation), and also by thermal inversion within the mixing layer.
The increase of air pollution is one of the most important issues due to its effect on the human health and the European laws require a steady monitoring of suspended Particulate Matter (PM) (Directive 2008/50/EC). Deep investigation of the different components into the PM$_{10}$ (particles with aerodynamic diameter less than 10 $\mu m$) 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 effects on the human health (Senlin et al., 2007). PM$_{10}$ is usually monitored by high volume device, collecting the suspended material onto specific membranes, made either in fused silica (commercially “quartz”) or in glass fibres and measuring the concentration of the suspended PM$_{10}$ by the gravimetric method, defined as the total mass of the PM$_{10}$ per cubic meter of air within 24 hours (Directive 80/779/EEC). This type of analyses provides only the weight of suspended materials without information on their chemical composition. Moreover, the European Community is recently showing an increasing interest in assessing the chemical characterization of the different components occurring in the PM.

By our research group a quickly and not expensive methodology to characterize the PM starting from the filters routinely collected by the environmental protection agencies to determine the air quality- has been elaborated (Fornero et al., 2010). A procedure for removing the solid components of the PM from the sampling filters and deposit them onto polycarbonate supports, more suitable for the VP-SEM/EDS, instrument used for the characterization study. The developed procedure proves able to:

a) distinguish easily particles/fibres of the original support from those composing the PM;
b) detect the inorganic/mineral phases on the basis of the EDS analyses;
c) propose an apportionment 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) notice the presence of fibrous phases, in particular those ascribed to the minerals defined “asbestos” by the law (Directive 2003/18/EC).

The results obtained in different environmental situations: urban, rural and outskirts areas, localities characterized by various anthropogenic sources of pollution will be presented.


NATURAL AND ARTIFICIAL INORGANIC FIBERS IN LUNGS OF UNGULATES LIVED IN THE REGIONAL PARK OF “LA MANDRIA” (PIEMONTE REGION, NW ITALY)

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It has long been established that occupational exposure (high dose) to certain fibrous minerals is harmful to human health. The effects of environmental exposure (low doses) is still rather difficult to determine. Recent publications show the advantage in using animal population called Animal Sentinel System (ASS), in alternative to the human ones, as indicator of environmental contaminants.

The aim of this work has been to assess the presence of fibers in general and asbestos in particular (breathable fibrous inorganic fraction: bfif) airborne in the Regional Park of “La Mandria” (entrance of the Lanzo Valley, Torino) monitoring their presence in samples of lung tissue of ASS lived in that area with a natural environmental exposure (continuative and at low doses).

In the Regional Park of “La Mandria”, in fact, some fibrous minerals are present both in the composition of the lithologies naturally present end in the debris from the ex-mine of Balangero, used in the past to cover the footpaths.

Samples of lung tissue from 15 ungulates were examined. The investigations were carried out by using the scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) and have allowed us to obtain qualitative and quantitative data on breathed “bfif” and in particular on asbestos. The fibers found in the lung tissue of ungulates are chemically related to 2 main groups: silicate and non-silicate fibers. The different types of the detected silicate fibers are listed in decreasing order of abundance: artificial silicate with Na and possibly Mg, Al, Ca, K, chrysotile/antigorite; illite/smectite/montmorillonite, hornblende, tremolite asbestos, micas, phyllosilicates not better identified, vermiculite, crocidolite, Na-Ca feldspar, chlorite, edenite, pyrophyllite, kaolinite, diopside, zeolite. The two different types of the found out non-silicate fibers are listed below in decreasing abundance order: titanium dioxide, gypsum or anhydrite. Both crocidolite and tremolite asbestos and chrysotile/antigorite fibers were found in 40% of the samples. Globally, these three groups were present in 47% of the samples.

The antigorite fibers are released from both outcropping local serpentinitic rocks (natural source) and the debris from the ex-mine of Balangero (natural source), while those of chrysotile can come both from the local rocks (natural source) and the asbestos-containing materials (anthropogenic sources) such as the roofs of buildings.

The tremolite asbestos come from serpentinitic rocks (natural source) and not from the debris of the ex-mine of Balangero because this species has not been detected in the rocks of that area.

Crocidolite come exclusively from the asbestos-containing materials (anthropogenic source, such as the roofs of buildings) because this type of asbestos isn’t naturally present in Italian lithologies.

Although it is not possible to establish from which of the two sources (natural and anthropogenic) the chrysotile/antigorite fibers come, as regards tremolite asbestos and crocidolite the ASS represent a good model for assessing environmental exposure in relation to topographic features, geological and human environment in which they lived.
Sessione disciplinare GEO/06: Mineralogia

Conveners:
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Andradite, of ideal composition Ca₃Fe₂Si₃O₁₂ and space group Ia₃d, is a rock-forming garnet typically found in metamorphic rocks (i.e. serpentinites and skarns). The structure consists of a framework of alternating SiO₄ tetrahedra and FeO₆ octahedra, with cavities containing Ca cations in eight-fold coordination (Novak and Gibbs, 1971). Because relatively few studies are devoted to the trace-element composition, including REE profiles, of Ca-Fe³⁺ garnets (Gaspar et al., 2008), we have undertaken a study of andradite, in particular focusing on gem-quality green-colored crystals (variety “demantoid”). A suite of 28 andradite samples, occurring both in serpentinites and skarns, coming from the most notable localities worldwide (Italy, Russia, Iran, Pakistan, Madagascar, Namibia, and Romania) has been investigated by means of EMPA and LA-ICP-MS. More details about geology and garnet formation are reported by Bocchio et al. (2010) and Pezzotta et al. (2011). Our work aims to provide a chemical characterization of these stones and so contribute to a quantitative evaluation of the crystal chemistry of andradite.

The analyzed crystals cover a restricted range of composition, from almost pure andradite (Adr ≥ 98 mol%) to members of andradite-uvarovite (Adr₉₆-UV₃₋₁₈) or andradite-grossular (Adr₆₈-94-Grs₆₋₁₂) solid-solution series. They are homogeneous, with the only exception of a sample from the skarn deposit of Namibia, showing a composition varying from pure andradite up to almost pure grossular (Grs₈₉Adr₁₁), which frequently occurs in garnets from skarn (Smith et al., 2004; Gaspar et al., 2008). The chondrite-normalized diagrams of selected trace elements (Sc, Ti, Cr, Co, Ni, Zn, Sr, Y, Zr) indicated that all the examined garnets, both associated with serpentinites and skarn deposits, display a comparable pattern of distribution. However, the garnets occurring in the skarn rocks (i.e. samples from Madagascar, Namibia, and Romania) contain minor amounts of the chromophore elements, in particular of chromium, which is almost absent. The chromium contents detected in specimens from serpentinites are instead very variable, ranging from a few ppm up to 1 wt.%. With regard to the profile of REE, we observed that (i) all the samples showing a composition close to pure andradite, both associated with serpentinites and skarns, exhibit LREE-enriched and HREE-depleted patterns with a strong positive Eu anomaly, whereas (ii) the uvarovite-enriched samples show flatter patterns with a small positive Eu anomaly, and (iii) grossular rich samples are LREE-depleted with no Eu anomaly or negative one. These results indicate that the incorporation of REE in andradite is mainly controlled by the crystal chemistry. In particular, the substitution of Fe³⁺ (and Cr³⁺) for Al expands the framework and consequently favors the incorporation of the larger LREE. However, also the bulk composition of the host rocks and the physicochemical conditions occurring during the growth may contribute to the REE incorporation (Whitney and Olmsted, 1998; Smith et al., 2004; Gaspar et al., 2008).

THERMAL BEHAVIOR OF AFGHANITE, AN EIGHT-LAYERS MEMBER OF THE CANCринITE GROUP

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Thermal behavior of afghanite, \((\text{Na}_{15}\text{K}_{5}\text{Ca}_{11})_{233}[\text{Si}_{24}\text{Al}_{24}\text{O}_{96}]\text{(SO}_{4})_6\text{Cl}_6\), s.g. \(P\bar{3}1c\), \(a = 12.7961(7) \text{ Å}\), \(c = 21.4094(13) \text{ Å}\), an eight-layers member of the cancrinite group, has been investigated by combined electron microprobe analysis, X-ray single-crystal diffraction, and high-temperature X-ray powder diffraction. Non-ambient data were collected in the 323-1223 K thermal range on a specimen from Case Collina, Latium, Italy. RT structural data, from single-crystal work, provided improved details on cation partition with respect to reference data. The framework consists of columns of cancrinite cages ([4\(\bar{6}\)6\(\bar{5}\)] polyhedra following the IUPAC nomenclature) stacked along \([0 0 z]\), and regularly alternating liottite ([4\(\bar{6}\)6\(\bar{1}\)7] polyhedra) and cancrinite cages piled along \([2/3 1/3 z]\) and \([1/3 2/3 z]\). It has been observed that the cancrinite cages alternating with the liottite cages are more compressed along \(z\) than the remaining ones.

As result the chlorine atom, located at the centre of the cages, is driven off-axis in order to obtain a favourable coordination with the neighboring calcium atoms. Repeated heating-RT-cooling cycles led to the partial afghanite structure disruption and the partial conversion, \(\text{vita}\) an intermediate disordered phase, to haüyne. Thermal expansion shows a discontinuity at 448 K for both \(a\) and \(c\) cell parameters, a feature previously reported for other cancrinite-like minerals. In fact, up to 448 K the \(c\) cell parameter expands significantly and more than the \(a\) cell parameter. Above the discontinuity temperature \(T_d\), the thermal expansion is reverted becoming greater for the \(a\) cell parameter.

Afghanite shows a significant microstrain at RT that increases up to ca. 700 K and subsequently decreases as a function of \(T\). Cooling to RT permits a significantly release of \(\varepsilon_0\) microstrain and this process is coupled with a significant expansion of the \(c\) cell parameter as compared to the starting RT data. The expansion of the \(c\) axis has been prevalently attributed to the full expansion of the cancrinite cages alternating with the liottite cages. Upon reheating at 1173 K, the microstrain increases back to approximately the same value calculated for the first heating process. Repeated heating/cooling cycles did not modify the \(\varepsilon_0\) values both at RT and at HT.
MINERALOGICAL APPLICATION OF NANOINDENTATION TESTING

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The study of elastic properties of rocks and minerals had a significant development because these data are crucial for the interpretation of the propagation of seismic waves on which all models of Earth’s internal structure are based. In addition, these properties are essential for determining the equation of state of geological materials (Schreuer & Huassühl, 2005; Price, 2009). Other physical properties related to elasticity, such as hardness, fracture toughness, contact stiffness, creep resistance, can be used to understand the mechanisms of ductile deformation of rocks at the level of the mantle or deep crust, and of the brittle behavior of rocks at the level of upper crust. Finally, since the elastic properties are closely related to the crystal-chemistry of minerals, they can be used to probe the structural deformations induced by phase transitions and/or ionic substitutions (Carpenter & Salje, 1998; van Westrenen et al., 1999). The measurement of the elastic properties of minerals is essentially based on three methods: 1) direct mechanical methods; 2) sound wave velocity measurements and 3) electromagnetic wave scattering methods (Brillouin, inelastic X-ray/neutron). All of these methods are now well established, mature and widely used however they have an inherent limitation: they do not allows the measurement of elastic properties of materials at micro to nano scale (Angel et al., 2009).

Nanoindentation testing (introduced by Oliver & Pharr, 1992) has been widely adopted in the last two decades for the surface mechanical characterization of bulk materials and coatings. The method involves the controlled penetration of a diamond pyramidal indenter into the material: by measuring the load and displacement during the loading and unloading parts of the test, hardness (i.e. resistance to plastic deformation) and elastic modulus can be calculated (Oliver & Pharr, 1992; Schuh, 2007). In this way, a very accurate characterization of the elastic properties at material’s surface can be achieved, with a depth resolution and a lateral spatial resolution of the order of few nanometers. Three factors motivate the use of nanoindentation for the study of the mechanical properties of minerals. Firstly, in such tests the load and displacement of the indenter tip, are continuously monitored thus the method is ideal for probing local gradients and heterogeneities in samples. Second, no extensive sample preparation is required prior to mechanical testing. Third, most nanoindentation instruments provide experimental control that allows for a variety of different deformation modes. The data so far published are scarce and cover a limited number of minerals (some phyllosilicate, kyanite, K-feldspar, periclase, garnet, quartz and the first nine minerals of the Mohs scale; Broz et al., 2006; Whitney et al., 2007; Mikowski et al., 2008; Zhang et al., 2010). However, the results show the possibility of very interesting developments in the field of mineralogy, applied mineralogy and gemology.

TOBERMORITE 11 Å: ONE MINERAL SPECIES, SEVERAL THERMAL BEHAVIORS

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Tobermorite 11 Å, $\text{Ca}_{4+x}\text{Si}_{6}\text{O}_{15+2x}$(OH)$_{2-2x}\cdot 5\text{H}_2\text{O}$, with $0 < x < 1$, is a calcium silicate hydrate characterized by a variable content of “zeolitic” calcium cations. Its crystal structure is formed by calcium polyhedra layers, continuous in the plane (001), connected to wollastonite-like chains on both sides. These structural elements form the so-called “complex module”, common to all the phases of the tobermorite group. This module is C-centered, with cell parameter $a$ 11.2 Å, $b$ 7.3 Å, and width $c$ 11.2 Å. Two kinds of complex module exist, due to the two different ways of placing the “bridging” tetrahedron with respect to the “paired” tetrahedra in wollastonite-like chains on the two sides of the calcium layer. The stacking of these two different complex modules forms clinotobermorite and tobermorite 11 Å, with monoclinic and orthorhombic subcells, respectively (Bonaccorsi & Merlino, 2005). The 11 Å phases, both monoclinic and orthorhombic, are characterized by double silicate chains, and their polyhedral framework shows cavities that may host “zeolitic” cations and water molecules.

Three kinds of thermal behaviour were distinguished at 300°C (Mitsuda & Taylor, 1978): “normal” (tobermorite 11 Å shrinks to a 9 Å phase at 300°C), “anomalous” (the 11 Å phase does not shrink at 300°C), and “mixed” (both the 11 and 9 Å phase coexist at 300°C). However, further investigations (Merlino et al., 2008) indicated that the thermal behavior of tobermorites is more complex than that depicted by the previous authors.

In order to understand the involved processes during dehydration, several natural tobermorites were studied through a multi-technique approach. Tobermorites from N’Chwaning II mine (South Africa) and San Vito di Leguzzano (Italy) showed an “anomalous” behavior at 300°C but the former shrunked to a 10 Å phase at ≈ 420°C, whereas the latter preserves its 11 Å basal spacing. TG curves showed different weight loss patterns; in particular, tobermorite from N’Chwaning II mine lost 10 wt.% at 300°C, corresponding to 4 water molecules, whereas the sample from San Vito Leguzzano showed a weight loss of 8 wt.% (3 H$_2$O pfu). Chemically, the only difference between the two specimens is related to the presence of 0.5 Al pfu in the Italian tobermorite; the introduction of Al in tobermorite is possible through the substitution Si$^{4+} +$ O$^{2-} \rightarrow$ Al$^{3+} +$ OH$^{-}$. The different amount of OH groups in the two studied specimens may give rise to different hydrogen bond schemes; the important role of “zeolitic” water molecules in stabilizing the position of H$_2$O and OH bonded to the calcium layers was hypothesized by (Churakov, 2009). The occurrence of additional hydrogen bonds, related to the introduction of Al in tobermorite, may contribute to the stabilization of the 11 Å phase. On the contrary, their absence may result in structural changes upon dehydration that can lead to the shrinking to 10 Å. The 10 Å phase was characterized through SC-XRD, $^{29}$Si NMR and micro-Raman spectroscopies. It shows an orthorhombic (or pseudo-orthorhombic) subcell with $a$ 11.2 Å, $b$ 3.67 Å, $c$ 20.4 Å; spectroscopic data point to the maintenance of double wollastonite-like chains. It is interesting to note that a clinotobermorite-like phase appeared during the transition from the 11 to the 10 Å phase.

“Normal” tobermorite from Montalto di Castro (Italy) was studied through in situ X-ray powder diffraction. At 300°C, tobermorite 9 Å appears. Also in this case, the diffraction patterns suggest the occurrence of a clinotobermorite-like phase as an intermediate product between the 11 and the 9 Å phases.

**IN SITU STUDY OF THE THERMAL BEHAVIOR OF PLOMBIÈRITE**

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Plombièrite is the most hydrated phase belonging to the tobermorite group; it is characterized by a basal spacing of 14 Å. The structure solution and refinement by Bonaccorsi et al. (2005) indicated that the chemical formula of plombièrite is Ca₅(Si₆O₁₆)(OH)₂·7H₂O. Similarly to other members of the tobermorite group, its structure is composed by the stacking along c of a complex module, which is formed by a calcium layer, decorated on both sides by wollastonite-like single silicate chains. The modules are shifted each other of b/2 and are separated by a layer of additional calcium cations and H₂O molecules.

The thermal behavior of plombièrite is apparently simple: at 110°C plombièrite shrinks to a 11 Å phase, which transforms into tobermorite 9 Å upon heating up to 300°C. However, some authors (Farmer et al., 1966; Mitsuda & Taylor, 1978) describe a more complex behavior, with the appearance of a new phase at higher temperature, with basal distance of $\approx 10$ Å. Another matter of discussion is represented by the polymerization of the silicate chains in the 11 Å tobermorite formed through the dehydration of plombièrite: all the so far studied samples of natural tobermorite 11 Å show double wollastonite-like chains, whereas the 11 Å phase obtained upon heating might show single chains (Wieker et al., 1982; Yu & Kirkpatrick, 1999).

Specimens of plombièrite from Crestmore (California, USA) and Zeilberg (Baviera, Germany) were studied in situ through the experimental apparatus described by Meneghini et al. (2001) at the GILDA beamline of ESRF (Grenoble, France). The results obtained by the two specimens confirmed that at 110°C plombièrite shrinks to a 11 Å phase; the refinement of the cell parameters showed clearly the decreasing of the c parameter, whereas $a$ and $b$ maintain their values. These data pointed to the approaching along c of unmodified complex modules.

At the beginning, the so-formed 11 Å phase presented a basal spacing of nearly 11.7 Å, in accordance with the results of a previous study by Yu & Kirkpatrick (1999); this value progressively decreased down to 11.3 Å at about 250°C. At 300°C, the 11 Å phase is replaced by a 9 Å phase. As already observed by previous authors, the higher the temperature, the longer is the basal spacing of the 9 Å phase, which shifts toward 10 Å.

To investigate the condensation degree of the silicate chains in the 11 Å phase formed by dehydration of plombièrite, either double or single, we collected the micro-Raman spectra of the heating product of plombièrite from Crestmore, and compare them with those of other phases with known structure. Our results points to the occurrence of single silicate chains, in agreement with that reported by Yu & Kirkpatrick (1999).

In principle, it is possible to hypothesize that 11 Å phases characterized by single chains occur also in nature, due to the possible dehydration of plombièrite under mild metamorphic conditions. However, up to now this kind of phase was not yet discovered in natural samples.

MONTE ARSICCIO MINE: THE FIRST THALLIUM ORE IN APUAN ALPS

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Together with the magmatic hydrothermal system of La Fossa Crater (Vulcano, Eolie Islands, Sicily, Italy; Campostrini et al., 2011), the Monte Arsiccio mine is the second Italian locality showing the presence of thallium-bearing mineral assemblages. In particular, it is an interesting locality for the study of thallium sulfosalts in metamorphic environment. Notwithstanding over two centuries of mineralogical studies on the Apuan Alps ores, only recently the first thallium mineral, chabournéite, was identified from the Monte Arsiccio mine (Bonaccorsi et al., 2010); at the same time, Moëlo et al. (in press) detected the presence of minor Tl in Sb-rich sterryite from Pollone mine, confirming the geochemical complexity of the hydrothermal paragenesis of the ore deposits from Apuan Alps. Successively, boscardinite and routhierite were also discovered. These minerals have been identified by X-ray diffraction and chemical analyses. These sulfosalts are associated with baryte, calcite, cymrite, dolomite, pyrite, quartz, realgar, sphalerite, stibnite, and zinkenite in Triassic dolostones of the Sant’Olga level.

Chabournéite occurs as black metallic veins; chemically, it agrees with the general formula Tl₃₋ₓPbₓ(Sb,As)₂₁₋ₓS₃₄, with x ≈ 1.2 and 1.5 in the two analyzed samples. Therefore it is one of the Pb-richest chabournéites ever described; in addition, this new occurrence shows the lowest As contents, with As/(As+Sb) equal to 0.20 and 0.10 in the two samples. The crystal structure of chabournéite from Monte Arsiccio has been determined in the space group P-1; it confirms the general features given by Nagl (1979) but on the basis of a simpler and more symmetrical unit cell, without any visible superstructure, that may be due to the higher Sb contents of chabournéite from Monte Arsiccio.

This mine is the type locality of boscardinite (IMA 2010-079), a recently approved new mineral that occurs as lead-grey masses in quartz veins or in dolostones. Its simplified chemical formula is TlPb₄(Sb₇As₂)S₁₈; minor Ag is also present. Boscardinite is the Tl-Sb homeotype of baumhauerite. Its crystal structure was determined and refined to \( R = 4.5\% \) for 4319 observed reflections, in a cell with \( a = 8.0929(4) \), \( b = 8.7610(5) \), \( c = 22.4497(11) \) Å, \( \alpha = 90.868(4) \), \( \beta = 97.247(4) \), \( \gamma = 90.793(4) \), space group P-1. The crystal structure of boscardinite can be described in the sartorite homologous series, as formed by the 1:1 alternation of sartorite type and dufrénoyite type layers.

Finally, routhierite was identified on the basis of X-ray powder diffraction and qualitative chemical analysis. It occurs strictly associated with chabournéite, boscardinite, and stibnite, as small cinnabar red anhedral crystals, up to 1 mm. A full characterization of this new occurrence is planned.

The occurrence of a thallium-rich sulfide ore in the Apuan Alps constitutes a very interesting topic according to two points of view. First, it is a new field of exploration of the crystal chemistry of thallium sulfosalts, whose occurrences are extremely rare in the world. Secondly, the geochemistry of this ore, with (Sb,As, Pb, Zn, Tl, Cu, Hg)-sulfides and sulfosalts associated with pyrite is very similar to that described at Jas Roux (French Alps - Johan & Mantienne, 1974), and may be related to the same type of metallogenic process related to Alpine orogeny.

Bonaccorsi, E. et al. (2010): 20th General Meeting IMA, 6, 714.
DOES HOLLANDITE CONTAIN WATER?
PHASE TRANSITIONS IN HOLLANDITE INDUCED BY TEMPERATURE

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As a part of an ongoing study on the crystal-chemistry of the so-called “tunnel oxides”, we aimed at clarifying the possible presence of water in hollandite and in the other minerals of the cryptomelane group, whose general formula is \((\text{A}^+, \text{A}^{2+}_{0.5})_4(\text{M}^{4+}_{x-8}\text{M}^{3+}_x)\text{O}_{16} (x \approx 2)\). Due to the microporous nature of these minerals, it cannot be excluded that the tunnels may host water molecules, together with the A exchangeable cations (K+, Na+, Ba2+, Pb2+, Sr2+). So far specimens of Fe-rich hollandite from Vagli were studied. Their chemical formula can be expressed as \((\text{Ba}_{0.79}\text{Sr}_{0.22}\text{Na}_{0.02}\text{K}_{0.01})\sum_{\text{A}}=1.04(\text{Mn}^{4+}_{5.70}\text{Ti}_{0.32}\text{Fe}^{3+}_{1.05}\text{Mn}^{3+}_{0.79}\text{Al}_{0.13})\sum_{\text{M}}=7.99\text{O}_{16}\). As almost all members of the cryptomelane (all but mannardite), hollandite is nominally anhydrous. The ideal topological symmetry of hollandite is tetragonal, space group \(I\bar{4}/m\), with \(a \approx 10\), \(c \approx 2.9\) Å. A single-crystal X-ray diffraction study of hollandite from Vagli carried out with a conventional Siemens P4 four-circle diffractometer proved that its \(c\) axis is doubled and the actual symmetry is monoclinic. The observed cell parameters are \(a 10.152(4)\), \(b 9.938(4)\), \(c 5.828(2)\) Å, \(\gamma 90.71(3)^\circ\), space group \(P2/1\). The doubling of the \(c\) parameter has been related to the ordering of Ba cations between two split positions within the tunnels. The crystal structure of anhydrous hollandite has been refined to \(R = 5.01\%\) for 1641 observed reflections.

Assuming an actual electron density equal to \([\text{Ba}_{0.8}\text{Sr}_{0.2}]\), as indicated by EPMA data, we tried to include water molecules, alternating with Ba along the tunnels. This would result in a better coordination of barium and would avoid unlikely Ba...Ba interactions between neighbor cations. Notwithstanding the difficulty in accurately refining the occupancy of water molecules sharing the same sites with heavy cations (also because of the high mobility of both), a plausible and self-consistent crystal-chemical model has been depicted; in addition, the refinement converged to \(R = 4.97\%\).

In order to confirm the presence of water in hollandite, TG/DSC runs have been carried out with powdered samples (ca. 25 mg), using a Netzsch STA 449C equipment in N2 atmosphere, from room temperature up to 1200°C, with a thermal gradient of 10°C/min. After each run, the products were identified through powder X-ray diffraction using a Philips PW1050/25 diffractometer. The collected data suggest the presence of three steps of weight loss: i) at \(T \approx 730°C\), a small endothermic hump related to a weight loss of 1.2 wt.\%, maybe due to molecular water loss; ii) at \(T \approx 895°C\), a broad endothermic peak, probably related to the appearance of bixbyite and minor hausmannite in the heated products, as indicated by PXRD pattern; finally, iii) at \(T \approx 950°C\), a marked endothermic peak is observed. The final product consists of hausmannite and, maybe, of a new-formed Ba-bearing Mn phase. The total final weight loss is approximately 9 wt.\%.

Further thermo-gravimetric data on other specimens of hollandite from different localities are planned to verify the extent of the weight loss observed for the sample from Vagli. Preliminary data seems to confirm the above-described trend.
MENCHETTIITE, A NEW Ag-Pb-Mn-SULFOSALT FROM UCHUCCHACUA POLYMETALLIC DEPOSIT, LIMA DEPARTMENT, PERU, BELONGING TO THE LILLIANITE SERIES

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Menchettiite was found at the Nivel 890, Uchucchacua polymetallic deposit, Oyon district, Catajambo, Lima Department, Peru, that is the same type locality for three other Mn-bearing sulfosalts, uchucchacuaite, Pb₃AgMnSb₅S₁₂ (Moëlo et al., 1984), benavidesite, Pb₃MnSb₅S₁₂ (Oudin et al., 1982), and the newly approved manganocubanite, AgMnAsS₃ (Bonazzi et al., 2011). The new mineral has been named after Silvio Menchetti, full professor in mineralogy and crystallography at the University of Florence.

Menchettiite occurs in a calcite matrix associated with orpiment, minerals of the tennantite-tetrahedrite series, and other, still unnamed, minerals of the system Pb-Ag-Sb-Mn-As-S. Electron microprobe analyses carried out on the same crystal used for the structural investigation led to the following empirical chemical formula: 

\[ [\text{Pb}_{4.81}\text{Mn}_{3.20}\text{Ag}_{1.95}\text{Cu}_{0.01}\text{Fe}_{0.02}\text{Zn}_{0.01}\text{Sb}_{6.09}\text{As}_{3.94}\text{Bi}_{0.01}]\sum = 20.04[\text{S}_{23.95}\text{Se}_{0.01}]\sum = 24.96. \]

Menchettiite is monoclinic, space group \( P2_1/n \), with \( a = 19.233(2) \), \( b = 12.633(3) \), \( c = 8.476(2) \) Å, \( \beta = 90.08(2)° \) and \( V = 2059.4(8) \) Å³, and it is ubiquitously twinned on \{100\}. Its crystal structure \([ R = 0.0903 \text{ for } 2365 \text{ reflections with } F_o > 4\sigma(F_o) ]\) is based on Pb-S like slabs of four-octahedra thickness and appears topologically identical to that of ramdohrite, Pb₆Sb₁₁Ag₃S₂₄ (Makovicky & Mumme, 1983). The main difference is related to the atomic species occupying the different structural sites. In detail, in menchettiite: (i) the M₁ site appears occupied by a mixture of Pb and Mn whereas it is fully occupied by Sb in ramdohrite; (ii) the M₅ site is dominated by Sb whereas it is fully occupied by Pb in ramdohrite; (iii) M₉ is fully occupied by Mn whereas it is Sb⁰.₅₀Ag⁰.₅₀ in ramdohrite; and (iv) variable amounts of As are hosted in M₂, M₇ and M₁₀ which are fully occupied by Sb in ramdohrite. The geometrical parameters of the coordination polyhedra change accordingly.

Menchettiite can be classified among the Sb-rich members of the lillianite homeotypic series which are described with the general formula \( \text{Ag}_x\text{Pb}_{3-2x}\text{Mn}_{x}\text{Sb}_{2+x}\text{S}_6 \) (Moëlo, Y. et al., 2008). Besides the heterovalent substitution \( 2\text{Pb}^{²⁺} \rightarrow \text{Ag}^{⁺} + \text{Sb}^{³⁺} \) taken into consideration by the above formula, however, two isovalent substitutions relate menchettiite to the others lillianite homeotypes, \( \text{i.e. M}^{²⁺} \rightarrow \text{Pb}^{²⁺} \) (also working in uchucchacuaite; Moëlo et al., 1984) and \( \text{As}^{³⁺} \rightarrow \text{Sb}^{³⁺} \). Thus, the general formula of menchettiite can be written as follows: \( \text{Ag}_x\text{Pb}_{3-2x}\text{Mn}_{x}\text{Sb}_{2+x}\text{As}_x\text{S}_6 \) with \( x = 0.5, y = 0.8 \) and \( z = 1.0. \) This formalism makes evident the close similarity of the new mineral with uchucchacuaite \( (x = 0.5, y = 0.5, z = 0.0) \), the only member of the series to have the same ratio between metallic and semi-metallic elements. In its appearance and physical properties menchettiite is indeed quite similar to uchucchacuaite; as expected on the basis of its higher Mn/Pb and As/Sb ratios, however, menchettiite exhibits a reflectivity lower than that of uchucchacuaite.

ASBESTOS AND OTHER FIBROUS MINERALS CONTAINED IN THE GIMIGLIANO-MOUNT REVENTINO UNIT (CALABRIA, S-ITALY)

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The study concerns the investigation of asbestos and other fibrous minerals carrying out on 32 natural rock samples collected in the metaophiolite sequence belonging to the Gimigliano-Mount Reventino Unit (GMRU).

The GMRU consists of serpentinites, metabasalts, metagabbros/metadolerites with a sedimentary cover made up of marble alternating with calcites and quartzites. Ophicalcites are found in close association with serpentinites and show brecciated fabric.

Owing to possible presence of asbestos and other fibrous minerals in these kinds of lithologies, the aim of this investigation is to evaluate their presence and in detail to characterize them. Previous studies are not detailed and above all referred to quarries, because some of these lithologies are quarrying for using as building and ornamental stones and road bed. Besides in these rocks, road yards have often opened.

The univocal distinction among asbestos and other fibrous minerals is very important in so-called “green rocks” as regulated by the Italian law (DM 14/06/1996) which demands the asbestos presence identification and quantification. Besides the Italian law (DM 18/03/2003) established to make a map of the asbestos presence in Italian outcropping rocks. Moreover, the interaction between natural water and serpentinitic rocks can also cause in former an enrichment in heavy metals in particular Cr which is potentially dangerous for human health.

To reach the target a detailed characterization of the main lithologies (serpentinites, metabasites) are being conducting by MOLP, XRPD, SEM/EDS, TEM/EDS, TG/DSC, XRF and micro-Raman investigations.

The most abundant minerals in serpentinitic rocks are serpentine minerals, chloride and clay minerals. Serpentinites show pseudomorphic mesh texture and bastite replacing olivine and pyroxene respectively with some rare relics of these silicates. Intergrowths of fibrous chrysotile with bastite are frequently recovered. TEM/EDS investigations show that serpentine minerals are represented by chrysotile, asbestiform and massive antigorite, fibrous polygonal serpentine, fibrous proto-chrysotile, asbestos tremolite-actinolite and lizardite as main phases. Metabasites consist of amphiboles (dominated by asbestos tremolite-actinolite), epidote, albite, muscovite, chlorite, titanite, calcite, magnetite and nimite. These new knowledges 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 presence, iii) to provide data for compulsory Italian mapping.
MANGANOQUADRATITE, AgMnAsS₃, A NEW MANGANESE BEARING SULFOSALT FROM UCHUCCHACUA POLYMETALLIC DEPOSIT, LIMA DEPARTMENT, PERU

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A new manganese bearing sulfosalt was found at the Nivel 890, Uchucchacua polymetallic deposit, Lima Department, Peru, that is the same type locality for three other Mn-bearing sulfosalts, i.e. uchucchacuaite (Moëlo et al., 1984), benavidesite (Oudin et al., 1982), and the just approved menchettiite (Bindi et al., 2001). Associated minerals are Mn-rich calcite, alabandite, Mn-rich sphalerite, proustite, pyrite, argentotennantite, stannite and other unnamed minerals of the system Pb-Ag-Sb-Mn-As-S. Electron microprobe data, lead to the following empirical formula: (Ag₀.⁹⁵Cu₀.⁰⁵)(Mn₀.⁹₆Pb₀.⁰⁴)(As₀.⁸⁷Sb₀.¹₄)S₂.⁹⁹. Single-crystal X-ray data were collected with a CCD diffractometer, using MoKα radiation. Unit-cell parameters (a₁ = a₂ = 5.4496(5), c = 32.949(1) Å; α = β = γ = 90°) and analysis of intensity data indicated the Laue group 4/mmm and E-statistic strongly indicated the structure to be centrosymmetric. However, systematic absences gave contradictory information and first attempts to solve the structure by a standard way (Patterson and direct methods) were unsuccessful.

Due to the strong subcell aₘₜ = a, cₘₜ = 1/3 c, a first model of the average structure was obtained by refining a chalcopyrite-like model (I₄₂d). The obtained atom coordinates were then transformed for a 3-fold unit-cell and the model slowly achieved convergence in the P1 space group (R₁ = 0.093 for 1622 Fo > 4σ(Fo) and 0.15 for all 2939 data). At this stage, an analysis of the structure with the ADDSYM routine of the PLATON program (Speck, 2003) revealed the real symmetry to be P₄₁22; in this space group the structure was refined up R₁ = 0.086 for 907 reflections with Fo > 4σ(Fo) and 0.14 for all 1532 independent data). The structure consists of a stacking sequence along [001] of square-net layers of O atoms (O-O = 2 1/2 a/2 = 3.85 Å) each one shifted of 1/2 a with respect to the adjacent one, with the cations located in the center of the O4 squared nets. In the sequence, one Mn₂S₄ layer is stacked by two AsAgS₄ layers, thus determining the 3-fold translation along [001]. The layers containing Mn²⁺, located at z = 1/8, 3/8, 5/8 and 7/8, are the most regular. Layers containing As³⁺ and Ag⁺ are more irregular, mostly due to the lone-pair bearing As³⁺ cation which is asymmetrically located within the O4 squared nets. Couples of AsAgS₄ layers are interconnected to each other by both As³⁺-S and Ag⁺-S bonds which complete the coordination polyhedra forming AsS₃ and AgS₅ pyramids, respectively. In turn, the sulfur atoms of the AsAgS₄ layers complete the octahedral coordination of Mn²⁺.

Due to the analogy of the chemical formula and the unit cell parameters with those of quadratite (AgCdAsS₃, a = 5.4995(5), c = 33.914(4) Å; Graeser et al., 1998) the new mineral here described was supposed to be the Mn-analogue of quadratite and therefore named manganoquadratite. The crystal structure of quadratite (supposed to crystallize in the I₄₁/amd space group), however, is still unknown and whether these two minerals are strictly isostructural or not remain to be ascertained.

KAZANSKYITE, BaNa$_3$Ti$_2$Nb(Si$_2$O$_7$)$_2$O$_2$(OH)$_2$(H$_2$O)$_4$, A NEW TITANIUM DISILICATE MINERAL WITH THE TS BLOCK FROM KIROVSKII MINE, KOLA PENINSULA, RUSSIA

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Kazanskyite, ideally BaNa$_3$Ti$_2$Nb(Si$_2$O$_7$)$_2$O$_2$(OH)$_2$(H$_2$O)$_4$, triclinic: $P$-1, $a$ 5.4260(9), $b$ 7.135(1), $c$ 25.514(4) Å, $\alpha$ 98.172(4), $\beta$ 90.916(4), $\gamma$ 89.964(3)$^\circ$, $V$ 977.61(5) Å$^3$, $Z$ = 2, is a new representative of titanium disilicate minerals with the TS (titanium silicate) block (Sokolova, 2006). It occurs at Kirovskii mine, Mt. Kukisvumchorr, the Khibiny alkaline massif, Kola Peninsula (Russia), associated to natrolite, barytolamprophyllite, nechelyustovite, hydroxylapatite, belovite-(La), belovite-(Ce), gaidonnayite, nenadkevichite, epididymite, apophyllite-(KF), sphalerite. The crystal structure of kazanskyite is a new structure type and does not have any analogues. It is a combination of a TS block and an I (intermediate) block. The TS block consists of HOH sheets (H = heteropolyhedral, O = octahedral).

The TS block exhibits linkage and stereochemistry typical for Group III (Ti+Nb = 3 a.p.f.u.) of the Ti-disilicate minerals: two H sheets connect to the O sheet such that two (Si$_2$O$_7$) groups link to the trans edges of a Ti octahedron of the O sheet (Sokolova, 2006). In the O sheet, there are four MO sites. The MO(1) and MO(2), MO(3), MO(4) sites are occupied by Ti$_{0.74}$Mn$_{0.26}$ and Na, Na$_{0.77}$Mn$_{0.15}$Ca$_{0.07}$Fe$^{2+}_{0.01}$ respectively. The cation composition of the O sheet is ideally Na$_3$Ti p.f.u. (per formula unit). The TS block has two H sheets, H1 and H2, which differ in coordination number and dominant cation at the MH site, [6]-coordinated Nb and [5]-coordinated Ti, respectively. In the H sheets, there are four Si sites occupied solely by Si and tetrahedrally coordinated by O atoms, with $<d>$ = 1.62 Å. In the H sheet, (Si$_2$O$_7$) groups link to MH polyhedra. The chemical formula of the H sheets is ideally NbTi(Si$_2$O$_7$)$_2$(H$_2$O) and of the TS block is BaNa$_3$Ti$_2$Nb(Si$_2$O$_7$)$_2$O$_2$(OH)$_2$(H$_2$O)$_4$. There are two peripheral sites, AP(1) and AP(2), occupied by Ba$_{0.51}$Sr$_{0.28}$K$_{0.21}$ and Ba$_{0.19}$ respectively.

There are two I blocks: the I1 block is a layer of AP(1) atoms with ideal composition Ba a.p.f.u.; the I2 block consists of AP(2) atoms and H$_2$O groups, ideally (H$_2$O)$_2$. TS blocks and I blocks alternate along [001]. We write the chemical formula of kazanskyite as two TS and two I blocks divided by two: Na$_3$Ti$_2$Nb(Si$_2$O$_7$)$_2$O$_2$(OH)$_2$(H$_2$O) + Ba + (H$_2$O)$_2$ = BaNa$_3$Ti$_2$Nb(Si$_2$O$_7$)$_2$O$_2$(OH)$_2$(H$_2$O)$_4$, $Z$ = 2. The I1 and I2 blocks of kazanskyite are topologically and chemically identical to the I1 and I2 blocks in nechelyustovite (Cámara & Sokolova, 2009). The layer of Ba atoms (I1 block) also occurs in barytolamprophyllite (Sokolova & Cámara, 2008) and bornemanite (Cámara & Sokolova, 2007).

Gruppo Mineralogico Geologico Napoletano (GMGN) is a non-profit organization founded in Naples in 1980 by three mineralogy fans: Massimo Russo, Giovanni Coslovich and Claudio Lombardo (the latter two left the group over time).

Over the years GMGN has built up a remarkable experience in the field, so that it has substantially contributed to a better knowledge of the mineralogy of the Neapolitan area, especially Somma-Vesuvius and Campi Flegrei areas. It has enjoyed the collaboration of several major national and foreign research institutes: universities of Bari, Napoli, Milano, Pisa, Roma, the British Museum of London, and the Muséum National d'Histoire Naturelle of Paris. At the present GMGN cooperates with Istituto Nazionale di Geofisica e Vulcanologia sezione di Napoli, Osservatorio Vesuviano, Dipartimento di Chimica Strutturale e Stereo chimica Inorganica, University of Milano and Associazione Micromineralogica Italiana.

The research carried out by GMGN has led to the discovery of 34 species new at Somma-Vesuvius (one Type Locality: fluoro-potassicrichterite), two now discredited (one Type Locality: caratiite now piypite), two to be reviewed according to the new IMA definitions: pyroclore and betafite, and two in which GMGN has contributed to a better knowledge of the species: euchlorine and quadridavyne. Similarly, for Campi Flegrei GMGN has contributed with 13 species new to the area and one be reviewed according to the new IMA definitions: pyroclore.

In these thirty years of activity GMGN has published a significant number of scientific and specialized articles in the following bulletins: Notiziario del GMGN, GMGN Notizie, GMGN News, Rivista Mineralogica Italiana, MICRO, and on the web. The collaboration with the Associazione Micromineralogica Italiana led to the publication of the book by M. Russo and I. Punzo (2004): “I Minerali del Somma-Vesuvio”, very popular among scientists and collectors, and edited by Associazione Micromineralogica Italiana.

The GMGN meets regularly to discuss topics related to the Campania territory, to organize geological and mineralogical excursions and lectures and to give specialized advices about Campania minerals. More information: www.gmgn.it.
SECONDARY MINERALS FORMED IN ACID MINE DRAINAGE ENVIRONMENT: THE CASE OF LIBIOLA MINE

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The sulphide-ore of the Libiola mine (Sestri Levante, eastern Liguria, Italy) occurs as massive-, stockwork- and disseminated-mineralizations within pillow and brecciated basalts of the northern Apennine ophiolites. They mainly consist of pyrite-chalcopyrite mineralizations with minor sphalerite and pyrrhotite. Gangue minerals are mainly represented by quartz with minor chlorite, magnetite, hematite, carbonate, and serpentine minerals. The Libiola mine represent one of the most important Italian exploited sulphide-ore, already known in the Bronze Age. Nowadays, the mining area is completely abandoned. Underground and superficial waters are mostly Acid Sulfate Waters, due to active Acid Mine Drainage processes triggered by oxidation of pyrite-chalcopyrite mineralizations. Mine wastes are acid generating because they contain high amounts of partially altered sulphide-rich mineralizations.

Secondary minerals directly formed within dumps, streams, and outcropping mineralized bodies through precipitation from contaminated solutions. They are within stream sediments of the creek and stream of the area or on and within waste-rock dumps. In this last setting, they occur as cement waste-rock fragments and as coating on rock surfaces or between the mineralized clasts, where they partially or completely replace both ore and gangue minerals. They are mainly represented by iron oxyhydroxides and oxyhydroxysulphate (such as goethite, ferrihydrites, lepidocrocite, hematite, and schwertmannite), sulphates (such as jarosite, brochantite, gypsum, epsomite, bieberite, bonattite, siderotil, halotrichite, chalcanthite, pickeringite, melanterite, copiapite, hydrowoodwardite, and basaluminite) and Cu-carbonates (such as malachite and azurite). Locally, native copper, chrysocolla, and alunogen are abundant as fracture fillings or as coating and occur in both superficial and underground settings.

The presence of these minerals and the evaluation of their stability fields are of environmental concerns because they can play an important role in attenuating the contaminant load of mine effluents.

The goal of this study is a comprehensive overview of the mineralogy and geochemistry of secondary minerals that formed in the Libiola mine, owing to acquire a detailed mineralogical knowledge about the genesis and the evolution of the authigenic secondary phases. The knowledge about the types of mineral phases allow to understand the short and long-term fate of the ecotoxic metals. All these information are paramount parameters for any predictive models and also to define effective remediation strategies.
Tinaksite from ultralkaline agpaitic Murun massif (Russia) has been investigated. The name reflects its composition: titanium (Ti), sodium (Na), potassium (K) and silicon (Si). Its structure was reported for the first time in 1971 by Petrunina et al. (1971). To the best of author’s knowledge, tinaksite is the only silicate based on \{hB, 2'[\xi']\[[\text{Si}_6\text{O}_{17}(\text{SiO}_2)]\} hybrid anion (Libeau, 1985). The structural model of Tinaksite proposed by Petrunina et al. (1971) was validated and improved by von Bissert (1980), who observed a more regular tetrahedra conformation. The tinaksite investigated by von Bissert (1980) is triclinic with chemical composition: \(\text{Na}_2\text{Ca}_2\text{Ti}\{3\text{Si}_7\text{O}_{19}\}\text{OH}\).

The compound here investigated has chemistry more complex, \((\text{Na}_{0.855}\text{K}_{1.993}\text{Ca}_{2.008}\text{Ti}_{0.792}\text{Mg}_{0.083}\text{Fe}^{3+}_{0.096}\text{Mn}_{0.010}\text{Zr}_{0.027}\text{Sr}_{0.037}\text{Zn}_{0.008}\text{Ni}_{0.007}\text{Cr}_{0.005})\{3\text{Si}_7\text{O}_{19}\}\text{OH}\), compared with Petrunina’s (Petrunina et al., 1971) and von Bissert’s ones (von Bissert, 1980). It has been refined in \(P1\), using the following lattice parameters: \(a = 7.0565(1)\ \text{Å}, b = 10.3750(1)\ \text{Å}, c = 12.1885(2)\ \text{Å}, \alpha = 92.802(1)^\circ, \beta = 90.763(1)^\circ, \gamma = 99.241(1)^\circ\).

In this work, the cation partition derived from SCXRD and EPMA data, is presented. The structure has been anisotropically refined up to an \(R(F) = 0.025\) (for 5238 observed reflections with \(F_o > \sigma(F_o)\)). Tinaksite exhibits straight channels parallel to \([001]\) direction, formed by double chains of silicate. The channels are stretched approximately along \([110]\) direction, with maximum dimension 10.972(2) Å.

The highest peak in the Fourier difference map is related to some structural disorder inside the Ti octahedron. This disorder likely can be ascribed to the entrance of the large K substituting the six-fold coordinated Na atom. As a matter of fact, the replacing of Na for K changes the coordination number of the polyhedron from 6 to 7, which seems to influence the neighbouring Ti atom position.

Another point concerns the K1 and K2 atoms located inside the channels. According to von Bissert (1980), the higher K1 thermal parameter with respect to the K2 one indicates the site filled by K1 is disorder. The structural refinement shows that K1 atom is located over at least three different positions. A charge distribution analysis, performed by means of the Chardi-It software (Nespolo et al., 2001), has returned an ECON number (Hoppe, 1979) of 11 and 9 for the K1 and K2, respectively. The bond distances for the three K atoms, related to K1, show these atoms are not always bonded to the same oxygen atoms. Indeed, K1 can move inside a cage formed by 14 oxygen atoms with a volume of about 90 Å³. This volume results to be much larger even than the one of the ideal twelve-fold coordinated K atom (~ 18 Å³).

CRYSTALCHEMISTRY OF Cr-SPINELS FROM THE SHETLAND OPHIOLITE COMPLEX (SCOTLAND)

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Cr-spinels are typical accessory minerals in a wide variety of ultrabasic rocks such as dunites, harzburgites and lherzolites, occurring in various geological settings and belonging to different depth-zone facies. In the present study, ten Cr-spinel crystals from four localities in the ~ 492 Ma Shetland ophiolite (NW Scotland) have been studied using single-crystal XRD to assess their petrogenesis and cooling history. The mantle section of the Shetland Ophiolite dominantly outcrops on the Isle of Unst and preserves a heavily serpentinized, two kilometer-thick section of layered dunites and harzburgites (Spray & Dunning, 1991; Flinn, 2001). Numerous podiform chromitites (defined as > 60% vol. Cr-spinel) enclosed in dunite lenses are frequently found close to the petrological Moho (Flinn, 2001). Cr-spinel seams are between 10 cm - 1 m in thickness and laterally discontinuous over the scale of several meters. Previous work reveals that the Cr# [Cr/(Cr+Al)] of the seams vary in different chromitite locations; 0.63-0.81, 0.60-0.67, 0.60-0.65, and 0.65-0.67 respectively (Derbyshire et al., unpublished data).

In the study of spinels the most important structural parameters are cell edge and oxygen coordinate. These parameters are influenced both by chemistry and the cooling history inferred by the host rocks. In particular, oxygen coordinate is sensitive of this last “condition” being influenced by the cation-exchange between T and M sites. For single-crystal XRD analyses, synthetic spinels were mounted on an automated KUMA-KM4 (K-geometry) diffractometer, using MoKα radiation monochromatized by a flat graphite crystal. The unit cell (a₀) was determined by 24 equivalent reflections of (12 8 4) or (8 4 4) (about 90° and 50° of 2theta), according to the size of the crystal accurately centred at both sides of 2theta. Data collection was made according to Della Giusta et al. (1996) up to 2theta = 55°. The analyzed Cr-spinels show cell edges and oxygen coordinate parameters ranging from 8.2580 (6) to 8.3134 (6) Å and 0.2623 (1) to 0.2631 (1), respectively.

One of the most peculiar features of the analysed Cr-spinels is that, despite their occurrence in ophiolitic samples, their structural parameters resemble those of Cr-spinels occurring in layered mafic complexes such as the Bushveld (Lenaz et al., 2007) and Stillwater (Lenaz et al., 2011) intrusions, rather than those of Cr-spinels in typical ophiolitic samples (cf. Bosi et al., 2004). In fact, the spinels from ophiolitic complexes usually show similar cell edges, but very different u parameters ranging between 0.2616 (1) and 0.26267 (8), where low values derived by cation vacancies due to Fe²⁺ oxidation to Fe³⁺.

BENTONITES AND BENTONITIZED ROCKS OF MARCHE REGION, CENTRAL ITALY (UMBRO – MARCHEAN APENNINES)

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The presence of bentonites and bentonitized rocks inside the sedimentary sequences of the Umbro - Marchean Apennines (Central Italy) is poorly known, even though several careful studies have been devoted to these rocks owing to their industrial importance. The above rocks form beds, levels or lenses, spanning from Cretaceous to Miocene in age. They are found inside terrains belonging to several lithostratigraphic units, from the Bisciaro Fm until the Laga Fm. Complex lying of bentonitic deposits is the result of several and successive dislocations caused by orogenic pulses. In the Pesaro-Urbino province (northern Marche), under particularly favorable conditions, bentonite levels and/or lenses, 40 to 200 cm thick, originated between marine sediments such as marly limestones and marls. In the past, bentonitic materials have long been known and used as pietre saponarie (soap stones), argille da sbianca (fuller’s earth), or argille smettiche (smectitic clays). In the late century, from the end of 30’s to the whole 70’s, these rocks have been the object of several researches also of regional extent. Afterwards, national and foreign chemical industries provided to open some mines in the most promising sites.

Purity of such bentonitic materials, as well as their excellent suitability for technological uses, pushed excavation further down until a 275 m depth was reached, corresponding to a digging level of the 9th order, in the Lama-Mondaino mine.

Other important mines were located in the Montefotogno - I Pianacci area (where an exploitation of small extent is still carried on), at Montefabbri (Talacchio - Colbordolo), S. Martino (Case Cecchini - Belvedere Fogliense), and S. Maria (Val di Loto - Sassocorvaro), plus minor occurrences.

Mineralogical analyses revealed that the smectitic term is composed mainly by montmorillonite, montmorillonite - beidellite, and rarely by nontronite. Negligible amounts of calcite, quartz, illite, kaolinite, and dolomite are recognized. The genesis of bentonitic rocks has been widely discussed in the past. Nowadays, it is linked to emplacement of volcanic ashes coming from westerly volcanoes. The age, and mainly the chemistry, of such volcanic materials allow to ascribing them to huge eruptive cycles of the Western Sardinia volcanic district.

At the moment, all the bentonite mines are covered by natural vegetation, which obliterated them almost completely.
Recently, strong developments and improvements of high-pressure (HP) experiments at large scale facilities (both synchrotron and neutron facilities) opened new scenarios on the accurate determination of physical properties of minerals at very deep conditions. High-pressure single-crystal X-ray diffraction (SCXRD) synchrotron experiments allow to determine small structural variations with pressure due to increase of the quality of data collection. In HP experiments the angular limitation access to the Ewald sphere, due to the diamond anvil cell, can be partially encompassed by the high intensity of the synchrotron X-ray beam using small samples and multiple mounting into the DAC. At the same time, HP neutron powder diffraction experiments could determine the hydrogen position (and hydrogen bonds evolution) directly both on deuterated and natural materials.

We performed high-pressure single-crystal synchrotron and neutron diffraction experiments on gypsum (CaSO\(_4\) 2H\(_2\)O) to study the HP behavior of this sulphate including the hydrogen bonds. Literature data (Stretton et al., 1997; Huang et al., 2000; Knittle et al., 2001; Comodi et al., 2008) suggested a polymorphic transition at 4 GPa and the structure of the new polymorph, gypsum-II, was recently solved (Nazzareni et al., 2010). SCXRD studies (Comodi et al., 2008; Nazzareni et al., 2010) suggested that water molecules play a key role on the phase transition.

We combined the HP neutron data with single-crystal and powder synchrotron diffraction data measured on gypsum up to 13 GPa at ESRF (Grenoble, France - ID09 and ID27 beamlines). We performed HP neutron powder diffraction up to 10 GPa at ILL (Grenoble- D20 beamline), loading a Paris-Edinburgh cell with NaCl as pressure calibrant and deuterated ethanol/methanol as pressure transmitting medium and the same sample used in previous papers. Powder diffractions were collected with a radio oscillator collimator and each data collection was measured from 3 to 6 hours as P increased. The lattice parameters of gypsum at increasing P were obtained by refining the powder pattern by using the Fullprof software. In the pressure range investigated we recognized two discontinuities in the \(a\) and \(b\) lattice parameters and beta monoclinic angle corresponding to the first phase transition at 4 GPa (already suggested; Comodi et al., 2008; Nazzareni et al., 2010) and a second phase transition at around 7 GPa not clearly defined previously. A very good agreement was found between our XRD data set (SC-XRD in house, synchrotron SC- and powder XRD at ESRF, Grenoble) and the lattice parameters measured by neutron diffraction at D20 (ILL- Grenoble). We used the synchrotron XRD data to constrain the neutron refinement and decrease the refined variables, thus to focus in the H coordinates and occupancies. Single-crystal XRD data (Comodi et al., 2008) showed that the gypsum interlayer, where the water molecules are located, strongly decreases its thickness up to 3.94 GPa. The water molecule shares an oxygen with the Ca-polyhedron and hydrogen atoms (H1 and H2) form, at ambient pressure, weak hydrogen bonds with the oxygen atoms belonging to S- and Ca-polyhedra. Neutron diffraction data suggest that increasing pressure the two hydrogens configuration changes: the coordinates of H1 move slightly from its position at ambient pressure whereas the \(y/b\) coordinate of H2 decrease significantly explaining the different compressibility of the two hydrogen bonds (Comodi et al., 2008). These new hydrogen bond configurations confirm that in the gypsum structure there is an increasing shift of the calcium-sulphate layer along a axis that lead to the phase transition and allow to retain water molecules at high pressure, namely to prevent the free movement of water molecules and should affect the dehydration condition.

MORPHOLOGICAL CHANGE OF CALCITE CRYSTALS GROWN FROM AQUEOUS SOLUTION IN THE PRESENCE OF L- AND D/L–ASPARTIC ACID

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The mechanisms of biologically driven crystal growth are usually limited to the stereochemistry of the adsorption of biologically interesting molecules. Hence, the theoretical approach is confined to the study of the interaction between specific sites of crystal surfaces (substrate) and the isolated molecule (adsorbate). This is, of course, a necessary step to evaluate the adsorption energy of an isolated molecule on a given substrate. Nevertheless, more information is needed to understand the “cooperative effect” when the adsorbate is not made by a randomly distributed molecular population but is localized either in 2D nuclei or in monolayers making epitaxy with the substrate.

The results of the researches we carried out in the last decade clearly show that several morphological changes, already attributed to the random adsorption of impurity on specific crystal surfaces, can be correctly interpreted in the light of 2D epitaxially adsorbed phases. This is the case of the 2D epitaxies of: i)- Li₂CO₃ on calcite growing from Li-doped solutions (Pastero et al., 2004); ii)- SiO₂ (α-quartz) on witherite growing from Na-metasilicate doped solutions (Bittarello et al., 2009); iii)- formamide on NaCl crystals growing from aqueous solutions (Aquilano et al., 2011). Moreover, it has been shown, in i) and iii), that the 2D adsorption is a preliminary step for selective absorption in the growing substrates followed by the formation of “anomalous mixed crystals” in the sense of Johnsen (1903).

In this work, we deal with the changes induced in the morphology of calcite crystals when variable amounts of L- and D/L- aspartic acid are added to the growth solution. It is worth remembering that the mother solution, supersaturated with respect to calcite, is unsaturated with respect to both the impurities we used, in order to verify:
- the occurrence of 2D adsorbed phase on the crystal surfaces;
- the enantioselectivity of the calcite {21.4} scalenohedron surfaces with respect to the L- enantiomer and to the racemic phase of the aspartic acid.

Concerning the theoretical aspects, the Hartman-Perdok analysis (Hartman, 1965) on the <441> zone of calcite has been carried out and the calculation of the surface ($\gamma_{hkl}$) and attachment energies was performed, on both unrelaxed and relaxed surfaces. The flat (F) character of the {10.4} and {11.0} forms and the stepped (S) one of the {01.8} and {21.4} forms contradicts the observed occurrence frequency of natural crystals: {21.4}>{01.8}>{10.4}>{11.0}. A minor reduction of the relaxed ($\gamma_{hkl}$) values of both {01.8} and {21.4} forms, could be sufficient to make the theoretical equilibrium shape of the crystal composed by the {10.4}, {01.2}, {10.0}, {00.1}, {01.8} and {21.4} forms, which explains the richness of the growth morphology of calcite, even if water adsorption is not considered. Our analysis is focused on the {21.4} scalenohedron. Epitaxy models are described: i)- between D and L {21.4} surfaces and the adsorbed 2D layers of polar {010} and {0-10} L-aspartic acid; ii) - between the {10.4} surface and the adsorbed 1D rows and 2D aspartic layers. Hence, the adsorption enantio-specificity is better explained through a “cooperative molecular” approach, instead of searching for the best interaction of a single molecule on specific surface sites.

COMPRESSIBILITY OF PYROXENES AND ITS TEMPERATURE DEPENDENCE:
THE CASES OF DIOPSIDE, JADEITE AND THE ORDERED OMPHACITE,
INVESTIGATED AT THE AB INITIO LEVEL, THROUGH
QUANTUM-MECHANICAL CALCULATIONS

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Recent developments of (i) sophisticated codes for quantum-mechanical calculations on crystalline materials (Dovesi et al., 2009); (ii) effective hybrid HF/DFT Hamiltonians (Wu & Cohen, 2006); (iii) algorithms from the calculation of thermo-elastic properties of crystals (Prencipe et al., 2011) starting from ab initio calculated static equations of state (no zero point and thermal effect included) and frequencies of the vibrational mode, together with the increased availability of computational resources at a relatively low cost, allows for the determination of compressibility of minerals with accuracies and reliabilities which parallels those reachable experimentally, at room temperature. At high temperatures, in general, while the accuracy of the experimentally measured compressibility decreases dramatically, that of the ab initio calculation remains high, so that the theoretical approach can reliably be used to produce data which are crucial for the development of models of the Earth’s interior.

Examples of applications of the whole first principle procedure will be shown with reference to pyroxenes (in particular diopside, jadeite and ordered omphacite). In the case of diopside, the calculated bulk modulus ($K_0$) and its first pressure derivative, at room temperature, are 106 GPa and 5.5 respectively, to be compared with the correspondent experimental values of 107(1) GPa and 5.8 (Boffa Ballaran et al., 2009). The calculated $dK/dT$ is -0.011 GPa/K, and the thermal expansion coefficient at 300 K is $2.12 \times 10^{-5}$ K$^{-1}$.

AB INITIO STUDY OF THE EFFECTS OF IRON IN PERICLASE ON THERMODYNAMIC PROPERTIES

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The thermodynamic properties of periclase and ferropericlase, at pressures and temperatures typical of the Earth’s lower mantle, have been studied through ab initio calculations carried out at the hybrid HF/DFT level. The correlated thermodynamic properties were calculated by following a standard statistical-thermodynamics approach, within the limit of the quasi-harmonic approximation.

The dependence of the calculated parameters by temperature/pressure/composition in iron has been shown, paying particular attention to the effects on bulk modulus and on thermal expansion. About the former, at environmental conditions an adding of 3% of iron in the chemical composition increases the bulk modulus from 160.14 GPa to 167.41 GPa; the same percentage at the P/T deepest lower mantle conditions (135.8 GPa and 4000 K) reduces the bulk modulus from 563 GPa to 558 GPa.

About the thermal expansion, the same percentage in iron at environmental conditions reduces this parameter from 2.79×10^{-5} 1/K to 2.60×10^{-5} 1/K; at the deepest lower mantle conditions the decrease is less pronounced and the coefficient goes from 1.191×10^{-5} 1/K to 1.186×10^{-5} 1/K.
CONTRIBUTION TO THE STANDARDIZATION IN THE ASSESSMENT OF MINERAL COLLECTIONS

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The recovery of the mineralogical heritage by public institutions, in order to enhance the museums, can lead to the purchase of entire private collections or of part of them.

However, in the practice, the evaluation is influenced by factors and “interests” that are not always clearly defined. Instead, the increasing transparency of public administrative acts requires the adequacy of evaluations, with methods that need to be more reproducible and less questionable.

In this work the authors focus on a series of reproducible parameters, which, starting from the values prevailing in the period, tend to make a final assessment more transparent.
Sideronatrite - Na$_2$Fe$_3^+$\((SO_4)_2(OH)\cdot3(H_2O)\) - is a secondary iron-bearing, hydrous sulfate formed during oxidation of pre-existing sulfides. It is a typical sedimentary product in some soils and evaporative deposits. Sideronatrite is formed in acid, sulfate-rich environments, and plays an important role in the acid drainage mobilization of metals and in the monitoring of water quality. The dehydration behavior of sideronatrite from Sierra Gorda (Chile) was investigated by in situ high-T FTIR spectroscopy.

The structural variations induced by thermal treatment were monitored by FTIR using the bending mode of the water molecule around 1650 cm$^{-1}$, the stretching modes around 3500 cm$^{-1}$, and the corresponding combinations modes in the wavenumber region 4000-6000 cm$^{-1}$. A succession of three structural phase transitions has been observed in the range RT - 400°C. In the first and second phase transition (sideronatrite → metasideronatrite I, [Na$_2$Fe$_3^+$\((SO_4)_2(OH)\cdot(H_2O))$] (Venturiti et al., 2010) and metasideronatrite I → metasideronatrite II, [Na$_2$Fe$_3^+$\((SO_4)_2(OH))] two and one interstitial water molecules, coordinated by the Na atoms, are lost respectively, while the backbone of the structure present in sideronatrite, i.e. the [Fe$_3^+$\((SO_4)_2(OH))]$_x$ chain, keeps unchanged.

The loss of OH$^-$ group corner-sharing between two adjacent Fe$_3^+$-octahedra in sideronatrite chain, involves the break down of the [Fe$_3^+$\((SO_4)_2(OH))]$_x$ chain and the subsequent formation of an intermediate amorphous transition phase from which the Na$_3$Fe(SO$_4$)$_3$ compound (Scordari et al., 2011) will form later. Thermogravimetry combined with mass spectroscopy of evolved gases further confirms the observed dehydration and dehydroxylation processes.

THE DUAL BEHAVIOR OF THE B-As$_4$S$_4$ ALTERED BY LIGHT

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The mineral realgar (alpha-As$_4$S$_4$), and the polymorph of high temperature, beta-As$_4$S$_4$ (stable over 252°C) undergo a peculiar process of alteration induced by light. Both the phases alter to pararealgar (Bonazzi et al., 1995), as a result of the exposure to natural or artificial light (Douglass et al., 1992; Bonazzi et al., 1996) and this causes an anisotropic increase of the unit-cell volume (up to 2.6%) of both the polymorphs. During the process of alteration, starting from both realgar and the beta-phase, arsenolite occurs along with a metastable phase, named chi-phase, which is the precursor of pararealgar.

As Bonazzi et al. (2006) shown remarkable work has been done to understand the nature of the transformation and the authors relate the unit-cell expansion to the substitution of As$_4$S$_4$ units by As$_4$S$_5$ uzonite-type molecules according to the reaction $5\text{As}_4\text{S}_4 + 3\text{O}_2 \rightarrow 4\text{As}_4\text{S}_5 + 2\text{As}_2\text{O}_3$ and the following removal of the additional sulfur atom to produce the molecule of pararealgar. Thus, the untied S atom would be ready to enter another realgar molecule and continue the cyclic mechanism. To better understand the role of the oxygen and if the unit-cell expansion of the beta-phase is really due to the presence of uzonite-type molecules, some powdered beta-phase has been altered by the light with and without the presence of the air, XRPD data were collected in transmission geometry, and structural refinements along with quantitative phase analysis were carried out using the Rietveld method. The alteration induced with the presence of the air caused the formation of pararealgar, arsenolite and an amorphous phase, while from the powder not in contact with the air only pararealgar was obtained.

The second part of the experiment was aimed to detect if the two types of pararealgar, so obtained, could transform into the beta-phase through the action of the heat in a closed environment, and within the stability field of realgar. The powder made by pararealgar, arsenolite and amorphous phase yielded crystalline arsenolite and alacranite. Differently, the powder made of only pararealgar turned into the chi-phase, and slowly into the beta-phase only, the unit cell exhibiting a contraction. This points out that the beta-phase altered by the light shows a dual behavior whether or not that occurs with the presence of the air, that is the oxygen. In the first case the transformation is not reversible and follows a mechanism above mentioned, while in the second case the transformation is reversible. With these evidences it is difficult to make the hypothesis that some As$_4$S$_5$ molecules form during the alteration under the light, since neither arsenolite nor amorphous phase occurs, and the whole material turns into pararealgar. It is also difficult to invoke the proposed mechanism to explain both the expansion of the unit cell of the beta-phase and the contraction of the unit cell of the chi-phase. In this case the transformation must be due to a different mechanism, such for instance the direct transformation of the As$_4$S$_4$ molecule, of alpha and beta polymorphs, to that of pararealgar with the simple breaking of the As-As and AsS bonds and the sudden reconstruction.

ABOUT CATION DISTRIBUTION IN DOLOMITE STRUCTURE
BY THEORY AND EXPERIMENTS

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Features and evolution of many geological processes, such as fluid-rock interaction, CO₂ sequestration, fault weakening and dolomite stability under subduction conditions, significantly depend on the physical-chemical properties of dolomite. Our attention was focused on the study of cation distribution over crystallographic sites since it is one of the main factor impacting physics and thermodynamic properties of the mineral. In situ (Hammouda et al., 2011) and ex situ (Reeder & Wenk, 1983) experiments attributed a T range of about 1200-1400 K to the intra-layered-type disordering where Ca and Mg are randomly distributed over cationic sites. Such structures, however, have not been found in nature probably due to the non-quenchability of thermally treated systems (Reeder & Wenk, 1983). However, there is a possibility of domain disorder that could be stable at lower temperatures and is not investigated in sufficient detail. In order to study various types of disorder in dolomite as well as the thermodynamic stability of disordered dolomite structures, we have used both theoretical and experimental approaches. First principle total-energy calculations were performed at the hybrid Hartree-Fock/Density-Functional-Theory level (Pisani, 1996) using a development version of CRYSTAL software (Dovesi et al., 2009). Calculations were carried out by using the WC1LYP Hamiltonian (Wu & Cohen, 2006), which includes a non local exact Hartree-Fock exchange contribution. Different stoichiometric disordered dolomite structures were simulated and they appeared to be due to both intra- and inter-layered-type defects. Starting from theoretically calculated energies, a quantum-statistical calculation approach was used in order to obtain the probability of specific disordered configurations at a given temperature. A very low degree of disorder was observed for temperatures below 750 K. As T increases, a disordered configuration becomes gradually the most stable one. Such observations allowed us to preliminarily state that disorder in the cation distribution in dolomite seems energetically stable at lower temperatures than expected from previous results. In the experimental part, dolomite crystals were thermally treated by using a piston cylinder apparatus under P of 3 GPa and T of about 1270 K, 1370 K and 1470 K. Products were studied by using powder and single crystal X-ray diffraction. The former analysis evidenced an increase of the intensity ratio of 006/015 reflections by increasing T as a marker for disordering (Schultz-Güttler, 1986). Moreover, data refinement showed mixed Ca and Mg cationic site occupancies. It shows that the disorder is produced by the heat treatment. On the contrary, three dimensional refinement by using single crystal X-ray diffraction analysis showed evidences of twinned structures, following the {11-20} twin law, consisting of twin domains with a high internal crystallographic order. So even if the theoretical modeling suggests the intra-layered-type disordering as the main mechanism affecting Ca-Mg distribution in dolomite during heat treatment also at relative low T, single crystal X-ray diffraction suggests presence of highly ordered domains at all temperatures and a localization of disorder to twin boundaries and defects in the structure. We can speculate that the twinning could be driven by either a disordering process during thermal treatment or a re-ordering process during the quench. In situ single crystal X-ray diffraction analysis under HT and HP conditions are in progress at the ESRF synchrotron facility (Grenoble) in order to clarify the kinetic effects.

Sessone disciplinare GEO/07:
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SMALL SCALE HETEROGENEITIES IN MORB MANTLE: INSIGHTS ON PYROXENITE-PERIDOTITE ASSOCIATION FROM EXTERNAL LIGURIDE OPHIOLITES (ITALY)

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The occurrence of mafic layers in peridotites constitutes an important compositional heterogeneity in the mantle, and their role in mantle melting and basalt generation is currently debated (e.g. Hirschmann & Stolper, 1996; Salters & Dick, 2002). Pyroxene-rich lithologies are commonly documented in subcontinental lithospheric mantle, from both tectonically-emplaced ultramafic massifs and mantle xenoliths (e.g. Downes, 2007), and rarely sampled in abyssal peridotites (e.g. Warren et al., 2009). They are mostly interpreted as high-pressure magmatic products and rarely as remnants of recycled oceanic crust. However, the origin and composition of such lithologies, and their potential role in creating small-scale heterogeneities in the MORB mantle remain still poorly constrained. In this study, we present field, chemical and isotopic data on pyroxenites and host peridotites from some peridotite massifs of the External Liguride ophiolitic Units (Northern Apennines, Italy) with the aim to widen the knowledge on the origin of pyroxenites in MORB-type settings and discuss the occurrence and extent of chemical and isotopic heterogeneities in the MORB mantle related to the pyroxenitic component. At this latter purpose, pyroxenites and host peridotites have been accurately sampled from single dm-scale profiles, in order to test whether the existence of lithologic heterogeneities in the mantle in turn reflects the occurrence of isotopic contrasts at the small scale. Pyroxenites occur as cm-thick bands (up to 12 cm) parallel to the tectonite mantle foliation and vary from spinel-bearing websterite to clinopyroxenite. As the host peridotites, they are partially recrystallized at plagioclase-facies conditions. The occurrence of orthopyroxene-rich rim between pyroxenite and peridotite and large poikilitic orthopyroxene in the wall-rock peridotites indicate that host peridotites have interacted with melts related to pyroxenite intrusion. These latters display very heterogeneous whole-rock chemistry, almost covering the entire compositional range defined by worldwide lithospheric pyroxenites (X_Mg = 74-88, Al_2O_3 = 10-17 wt.%, CaO = 7-20 wt.%). The pyroxenite chemistry reflects high-pressure magma segregation of tholeiitic melts dominated by clinopyroxene crystallization. Both mineral and bulk-rock compositions from peridotite-pyroxenite traverses reveal that the host peridotites have been significantly modified in terms of major (e.g. X_Mg, Al_2O_3, CaO) and trace element (e.g. the LREE) composition by the interaction with pyroxenite component. A multi-step, sequential leaching procedure on clinopyroxene separates enables us to remove partial contamination and provides reliable Sr isotope data. The Sr and Nd compositions of clinopyroxenes from pyroxenites and peridotites fall in the typical range of normal MORB (87Sr/86Sr = 0.7023-0.7029; 143Nd/144Nd = 0.5134-0.5128). Internal Sm-Nd isochrons based on plagioclase, clinopyroxene and whole-rock from several pyroxenite samples yield ages ranging from 174 to 183 Ma (with errors between ±11-25) for the low-P mantle exhumation. On a slightly larger spatial scale, isotopic profiles through the pyroxenite-peridotite boundaries indicate cm-scale modification of the wall-rock peridotite, presumably related to emplacement of the pyroxenites. This suggests that deep melt intrusion can locally modify the host peridotites and introduce small scale compositional heterogeneity in a MORB mantle.

BORON ISOTOPE STUDY OF MAGMATIC-HYDROTHERMAL TOURMALINES FROM BIELLA AND TRAVERSELLA PLUTONIC COMPLEXES (PERIADRIATIC IGNEOUS PROVINCE, WESTERN ITALIAN ALPS)

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The Biella pluton is part of an Oligocene volcano-plutonic complex emplaced at shallow crustal levels within the eclogite-facies rocks of the Austroalpine Sesia-Lanzo Zone. It is a composite stock of calc-alkaline to shoshonitic affinity ranging in composition from monzogranite-granodiorite to syenite and monzonite. Volcanic to volcaniclastic sequences coeval to the Biella stock occur as a steeply dipping belt truncated, to the southeast, by the Insubric Lineament; they range in composition from basaltic andesite and andesite of high-K calc-alkaline affinity to trachyandesite and trachydacite of shoshonitic affinity. Palaeomagnetic, geological and petrological data show that both the Oligocene igneous rocks and the Sesia-Lanzo country-rocks suffered a clockwise (towards southeast) tilting, along a NE-SW trending subhorizontal axis, during late Tertiary; as a consequence, along both the Cervo and Sessera valleys crustal sections, from deeper (to the NW) to shallower (to the SE) levels are exposed (Bernardelli et al., 2000; Callegari et al., 2004; with references). The Traversella stock, coeval with the Biella complex, is also intruded in the Sesia-Lanzo Zone and is mostly composed of diorite to quartz-diorite and monzonite of high-K calc-alkaline affinity, with some mafic cumulates showing shoshonitic affinity (Vander Auwera & Andre, 1991, with references). Both plutons record a complex history of magmatic-related fluid circulation that often involves boron-rich fluids as shown by the occurrence of abundant tourmaline. Within and around the Biella pluton tourmaline occurs (Bernardelli et al., 2000; Rossetti et al., 2007): (1) as a late-magmatic phase in aplitic dykes in the monzosyenite and as Pl + Qtz + Tr + Tur orbicules in satellite magmatic bodies; (2) in early Kfs + Qtz + Tur hydrothermal veins; (3) as Tur ± Qtz ± Ru clasts, locally surrounded by Qtz + Tur, embedded by Qtz ± carbonate matrix in brecciated veins and breccias; (4) as very fine-grained tourmalinite (Tur ± Qtz ± Py) clasts in a Qtz + Py + Cpy hydrothermal matrix in brecciated veins; (5) as radial aggregates of cm-long, acicular crystals in the matrix of a large hydrothermal breccia body at roof of the pluton; (6) as a product of metasomatic replacement of phengite and garnet in metapelites from the Sesia-Lanzo Zone in hydrothermal breccias close to the pluton contact. At Traversella, the occurrence of dolomite marble lenses in the host rock favored the development of complex skarn bodies (mined for magnetite: Vander Auwera & Andre, 1991, with references). Tourmaline occurs: (1) as a late-magmatic phase in aplitic dykes crosscutting quartz-diorite; (2) within the skarn bodies (which locally contain abundant boron-bearing phases other than tourmaline: e.g., ludwigite, szalibelyite and low-T, secondary phases, like canavesite). Boron isotopes represent a powerful systematic in tracing the origin of volatile elements in magmatic-hydrothermal systems and the extent of water/rock interactions occurred (e.g. Palmer & Swihart, 1996). In this study, boron isotope compositions of tourmaline from magmatic to hydrothermal/metamorphic settings have been determined. The new boron isotope data coupled with chemical features of tourmalines (Rossetti et al., 2007) provide new constraints on the evolution of fluid chemistry during the magmatic-hydrothermal transition at the interface between pluton and host rocks. Availability of couples of minerals from similar settings in Biella and Traversella intrusions as well as the occurrence of different boron-bearing minerals (tourmaline and ludwigite) allow the discussion of boron isotope fractionation behaviour in a high temperature setting.

TEMPERATURE DEPENDENCE OF YTTRIUM PARTITIONING BETWEEN GARNET AND XENOTIME: AN EXPERIMENTAL STUDY

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Yttrium is a notable trace element particularly compatible with garnet. Lanzirotti (1995) provided evidences that, among major metapelitic minerals, yttrium preferentially partitions into garnet and that the mode of major metapelite phases besides garnet have little effect on its fractionation. On the contrary trace elements are extremely sensitive to changes in accessory mineral assemblage (e.g. Ganguly, 2010).

Xenotime (YPO4) is a common accessory mineral in metapelites and arguments for garnet growth in equilibrium with xenotime are presented in several papers (e.g. Martin, 2009). Pyle & Spear (1999) described a relevant temperature control on the solubility of yttrium in garnet in xenotime-bearing metapelites from New England (USA). On the basis of a strong negative correlation between Y concentration and temperature they derived an empirical calibration to be used as geothermometer. However, no experimental studies do exist to date on the temperature dependence of Y partitioning between garnet and xenotime. In order to unravel this relation, high pressure (up to 2.0 GPa) xenotime - saturated synthesis of garnet have been performed in an end-loaded piston cilynder. The simple model system MgO-FeO-Al2O3-SiO2 has been investigated at temperature between 800 and 1000°C with running compositions falling along the join almandine-pyrope + 5 wt.% YPO4. Gels have been prepared as starting materials using tetraethylorthosilicate (TEOS) as silica source, pure Mg-, Al-, Ca-, Y-nitric solutions, ferric benzoate and ammonium dihydrogen phosphate (NH4H2PO4) digested in deionised water. Gels were fired in a gas-mixing furnace at fO2 conditions approaching the IW (iron-wustite) buffer at 1 atm for 3 hours. The powder was tightly packed into a gold capsule with an internal graphite sleeve to keep the oxygen fugacity low.

Run products were preliminary identified by X-ray powder diffraction, carefully inspected on back-scattered electron images and by X ray element maps, and analysed by electron microprobe and particle-induced X-ray emission (micro-PIXE). The use of the proton microprobe stems from its higher spatial resolution and lower X-ray background with respect to electron microprobe. This allows to measure trace element concentrations down to levels of ~ 1 ppm on a 1 μm beam spot (Fraser, 1990). Preliminary results will be discussed.

Mg-METASOMATISM OF METAGRANITOIDS FROM THE ALPS: GENESIS AND POSSIBLE TECTONIC SCENARIOS

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The genetic process and the possible tectonic scenarios responsible for the origin of continental Mg-metasomatic rocks in the Alps are proposed by integration of field, petrological, geochemical (bulk-rock chemistry and stable isotope compositions) and fluid inclusion data previously reported for Mg-metasomatic rocks derived from post-Variscan granitoids (e.g., whiteschists, leucophyllites).

Despite the heterogeneous data, the large range of peak metamorphic conditions (from the lowermost greenschists-facies to the ultrahigh-pressure medium-temperature eclogite facies) and the distinct time of metasomatism (from rifting to exhumation), some common features have been recognized in all of the continental Mg-metasomatic rocks belonging to the palaeogeographic realms of both Europe and Adria: i) they occur along shear zones within the metagranitoids; ii) they display a simple MgO-Al2O3-SiO3-H2O±K2O-silicate mineralogy; iii) based on major- and trace-element compositions, they can be grouped in four homogeneous Classes, representative for a progressive increase in Mg-metasomatism from the host rock to the centre of the shear zone; iv) from Class 0 (protolith) to Class 3 (Mg-richest rocks) the lithologies show an increase in Mg, Ni, H2O, Fe, Cr, and a decrease in Na, Ca, Sr, P, K, Rb, Si; v) fluid inclusion data, coupled with bulk-rock chemical compositions, indicate that the metasomatic fluid was a Ni-Mg-rich brine, containing also Fe and Cr, and possibly undersaturated in Si; vi) δ18O and δD data are indicative for seawater, locally mixed with meteoric water, as source of the metasomatic fluid.

All the data indicate that the genetic process responsible for the Mg-metasomatic rocks is most likely the same all along the entire range of the Alps. The proposed process assumes highly channelized fluids (derived from ultramafics that has previously interacted with seawater) that infiltrated the continental crust along high strain zones and produced chromatographic fractionation of major and trace elements. Distinct petrological data and timing of metasomatism from each locality suggest at least three possible tectonic scenarios for this genetic process: rift-related ocean-continent transition, oceanic-continental subduction, and continent-continent collision.
APPLICATION OF CATHODOLUMINESCENCE TO THE STUDY OF METAMORPHIC TEXTURES IN UHP CALCITE-DOLomite MARBLES OF THE DORA-MAIRA MASSIF

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Impure calcite-dolomite marbles from the ultra-high pressure (UHP) Brossasco-Isasca Unit (BIU) of the Dora-Maira Massif (Western Alps) are studied under cathodoluminescence (CL), petrographic microscope, and SEM-EDS. Most of the polymetamorphic (Variscan and Alpine) evolution of these marbles has been already reconstructed mainly by silicate minerals, whereas the local variability in microstructure and mineral assemblages of carbonate minerals are still unconstrained.

Under petrographic microscope, the studied impure calcite-dolomite marbles are medium- to coarse-grained, locally with a weak foliation defined by: i) phengite or Mg-chlorite wrapping around both porphyroclastic dolomite and clinopyroxene; ii) alignment of neoblastic clinopyroxene and garnet; iii) silicate-rich layers. Different relative amounts, kinds and compositions of silicate minerals are present. Early mineral assemblages include garnet, clinopyroxene, phengite, olivine, talc, and rutile, and late mineral assemblages include epidote \textit{s.l.}, Ca-amphibole, phlogopite, chlorite, serpentine, talc and titanite. Rare quartz and accessory zircon are also observed.

Dolomite is strongly zoned under CL and SEM, mainly because of variations in Ca, Mg and Fe contents. The locally zoned dolomite core is most likely a Variscan relic which may include garnet, diopside and rare ilmenite. The locally zoned dolomite rim, which partly corrodes the pre-Alpine core, is interpreted as a product of the Alpine metamorphism. In some samples, the outermost rim locally includes Ca-amphibole, phlogopite and titanite. In one sample, late dolomite, in equilibrium with serpentine, partly overgrows olivine.

The rock matrix is constituted by weakly-deformed medium-grained Mg-calcite that partly corrodes dolomite. In rare samples, exsolved dolomite is present within Mg-calcite. CL observations reveal that Mg-calcite is usually zoned with a rim composition variable from sample to sample. Rare, undeformed and fine-grained (Mg-)calcite is locally present at the grain boundaries.

In conclusion, microstructures in carbonates from the BIU marbles are complex such as that shown in the associated silicate minerals. Because in impure marbles both carbonate and silicate minerals record the same growth history under CL, this is a simple but powerful tool to correlate the evolution of the two groups of minerals. Therefore, the use of CL in studies on metacarbonate rocks allows to better constrain their PTX metamorphic conditions because it is suitable for a more detailed evaluation of the equilibrium mineral assemblages.
MINERALOGICAL TRANSFORMATIONS IN SERPENTINITES FROM THE
MT. CAPANNE THERMOMETAMORPHIC AUREOLE (ELBA ISLAND, ITALY)

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The Mt. Capanne intrusion (Elba Island, Italy) induced thermal metamorphic reactions within pseudomorphic lizardite (liz) + chrysotile (chr) serpentinites, giving rise to prograde minerals crystallization. This research is aimed at characterizing the thermally induced mineralogical and micro/nanostructural transformations in serpentinites, showing four main prograde reactions.

The first prograde reaction takes place both in bastites and mesh cores and leads to the formation of antigorite. Antigorite grows in the form of lamellae, longer than 50 µm, with random orientation; it develops at the expense of low-crystallinity liz + chr serpentine. The TEM study showed that antigorite has a highly defective structure with variable superperiodicity, modulation dislocations and polysynthetic twinings.

The second prograde reaction leads to a fine intergrowth of talc and chlorite starting from the low-crystallinity liz + chr serpentine of the bastites. TEM images show that talc within bastites grows in the form of very long and rather thin lamellae (typical thickness of 30-60 nm), which are finely intercalated to low-crystallinity serpentine. Talc is always associated with lesser amount of chlorite. The lamellae of chlorite show a rather variable width, but they are always wider than the talc lamellae. High-resolution images and SAED patterns showed that also chlorite is often affected by structural defects, generally concentrated in specific crystal portions rather than homogeneously distributed.

The third prograde reaction causes the formation of anthophyllite and/or tremolite amphiboles. Prograde amphiboles can nucleate both in bastites and mesh textures. Within bastite, they may grow as tiny acicular crystals with size around 100 µm in length, developing in random orientation, and evolving to a fine-grained interpenetrating felt. Alternatively, they may progressively replace the bastitic serpentine from the outer toward the inner portions, producing a large pseudomorphic single crystal. In mesh textures, amphiboles typically occur as elongated crystals, with an acicular-fibrous habit in random orientation. In some cases anthophyllite and tremolite coexist within meshes. High-resolution TEM images and SAED patterns showed that anthophyllite is typically affected by polytypic disorder with random stacking of anthophyllite, protoanthophyllite and cummingtonite; conversely, tremolite is very ordered and defect-free.

The fourth prograde reaction leads to the formation of forsteritic olivine, replacing mesh serpentine and never occurring within bastites.

TEM observations suggest that all prograde transformations take place through amorphization and subsequent recrystallization processes; low crystallinity sites tend to react easily evolving to higher temperature paragenesis, while high crystallinity sites tend to persist in samples of higher metamorphic grade.

In most cases, the retrograde association (lizardite + chrysotile) tends to transform directly into prograde associations (talc + chlorite, amphibole and olivine). The formation of prograde antigorite in interpenetrating textures, found in a single outcrop, may have been favored by an intense deformation.

Serpentinite outcrops show a variable metamorphic grade. It could be due to the complex sequence of the intrusion emplacement, to a non-uniform movement of hydrothermal fluids and to a variable deformation induced by pluton on the wall rocks.
PETROGRAPHY OF KAOLINIZED RHYOLITES FROM ROCCASTRADA - CENTRAL APENNINES

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Roccastrada rhyolites are pliocenic volcanites of crustal anatectic origin; they represent the most acid product of the Toscan Magmatic Province.

A kaolin deposit, derived from hydrothermal weathering of the Roccastrada rhyolites, formed near Piloni di Torniella (GR, southern Tuscany). The raw material is currently mined for the ceramic industry.

Hydrothermal fluids caused significant changes of the mineralogical and textural properties of the primary rock as well as changes of the bulk rock composition. The deposit is heterogeneous due to different weathering extents of the rhyolites so that lithologies ranging from poorly weathered to strongly weathered rhyolites and kaolin outcrop in the mining area.

The aim of this work is to classify the different materials outcropping in the deposit and to show their location on a map. Samples have been analyzed by XRF, polarised light optical microscope and SEM-EDS techniques so that field observations can be sustained and correlated with laboratory test, in order to show the effects of different extents of weathering on rhyolites at both macroscopic and microscopic scale.

XRF tests show that different lithologies have different bulk rock compositions: as a consequence of kaolinization, Al\textsubscript{2}O\textsubscript{3} contents and LOI values (wt.\%) increase with the weathering extent, while SiO\textsubscript{2}, K\textsubscript{2}O, CaO and Na\textsubscript{2}O (wt.\%) decrease, often giving rise to nearly pure kaolinitic materials of great interest for exploitation. Locally, high S concentration are found, especially in strongly weathered rocks: S is unwelcome in ceramics and the definition of the location of S-enriched materials in the deposit is fundamental during exploitation.

Investigations by optical and electronic microscope show how weathering affects both the texture and the mineralogy of the primary rocks and allows the reconstruction of a weathering sequence: primary plagioclase is substituted by kaolinitic aggregates, amorphous silica and, locally, alunite in poorly weathered rhyolites. In weathered and strongly weathered rocks also glass and alkali-feldspar are substituted by these pseudomorphic assemblages. Biotite can occur either preserved or totally substituted by pseudomorphic aggregates similar to those described above. Weathering of biotite consists of progressive leaching of Fe, Mg and Ti which, due to low mobility in water solutions, form hydroxides and oxides in the neighbouring groundmass.

The extent of weathering and the amount of kaolinite and alunite are extremely variable all over the deposit: hydrothermal fluids with different compositions circulated through the deposit, causing different weathering products to form.
Sapphirine is generally interpreted to be of metamorphic origin in high Mg-Al rocks. Igneous sapphirine, i.e. sapphirine crystallized from melt, is very rare. We examined sapphirine-bearing rocks in the Finero Phlogopite-Peridotite Massif, Western Italian Alps, to investigate a possible igneous origin for sapphirine in a melt modified via melt-peridotite interaction. Sapphirine locally occurs in a melanocratic zone between a leucogabbroic vein and the host peridotite.

The leucogabbroic vein cuts the foliation and lithologic layering of the peridotite massif, which is defined by alternating phlogopite-rich harzburgites and pyroxenites, indicating that its emplacement occurred after the main metasomatic events in the massif. Melanocratic seams are observed on both sides of the leucogabbroic vein. These mainly consist of orthopyroxene and amphibole, and show a marked zoning in modal compositions: an orthopyroxene-rich zone overgrown on the host peridotite side (OPX zone), whereas an amphibole-rich zone occurs on the leucogabbroic vein side (AMPH zone).

Sapphirine precipitated in the AMPH zone as independent interstitial grains (up to 3 mm long), as independent grains within large amphibole grains or as overgrowth on spinel. The amphiboles with sapphirine inclusions can also enclose spinel crystals that do not have sapphirine envelopes. Amphibole in the sapphirine-free melanocratic zone is more abundant in incompatible elements, such as TiO$_2$ and K$_2$O, than that in the gabbroic veins and the OPX zone, excluding the development of diffusion-controlled subsolidus reaction. A pronounced enrichment in Al$_2$O$_3$ of the parent hydrous melts is indicated by the composition of the amphiboles and phlogopites of this study that show higher Al$_2$O$_3$ than those crystallised by basaltic melts.

Mineral assemblages and chemistry in both the melanocratic zone and the host peridotite can be explained by melt-peridotite interactions, which resulted in replacement of peridotite olivine by secondary orthopyroxene in the OPX zone, and by Al$_2$O$_3$, TiO$_2$, FeO enrichments in the host peridotite beyond the recrystallization front. Interactions between peridotite and a hydrous, high Al$_2$O$_3$, orthopyroxene-oversaturated, mafic melt related to the formation of the leucogabbroic vein caused the formation of orthopyroxene at the expense of peridotite olivine. This resulted in high MgO/FeO and high Al$_2$O$_3$/SiO$_2$ ratios in a modified melt, allowing for precipitation of igneous sapphirine.
IRON OXIDATION STATE IN GARNET (MONVISO META-OPIHOLITE, WESTERN ALPS) AS A MONITOR OF DEHYDRATION-REDOX REACTIONS DURING SUBDUCTION: A MICRO-XANES AND ELECTRON MICROPROBE (“FLANK METHOD”) COMPARATIVE STUDY

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Although it is accepted that the mantle wedge above subduction zones is oxidized, the exact processes of relative oxidation are still controversial (e.g. Parkinson & Arculus, 1999). It is widely recognized that oxidized components are transferred to the overlying mantle wedge by fluid phases coming from the subducting slab (e.g. Parkinson & Arculus, 1999; Peslier et al., 2002; Malaspina et al., 2009; Rowe et al., 2009; Hirschmann, 2009); however, the study of the redox reactions occurring at the interface between the subducting slab and the mantle wedge, is often hampered by the difficulties in accurately determining the oxidation state of phase assemblages involved in these redox reactions.

In this contribution we report the results of a micro-XANES study (performed at ESRF ID22) on strongly-zoned garnet crystals from an eclogitic FeTi-oxide gabbro (Monviso meta-ophiolites, western Alps), aimed to the determination of the Fe\(^{3+}/\)Fe variation across the crystals. The studied sample extraordinarily well preserves evidence of its prograde evolution during subduction down to a depth of ca. 80 km (Groppo & Castelli, 2010). Because in the studied garnet the Fe\(^{3+}/\)Fe variations are small and occur on a micrometric scale, the challenge of this study was twofold: (i) the spatial resolution must be of the order of microns, and (ii) the spectral resolution must be as small as possible in order to appreciate the differences in the oxidation state of garnet. The results of the XANES spectra, acquired with a spatial resolution of 1.7 m \times 5.3 m, show that the Fe\(^{3+}/\)Fe ratio decreases from a maximum of 0.14 in the garnet core to a minimum of 0.00 in the garnet rim. These results are in excellent agreement with those previously obtained using the “flank method” at the electron microprobe. Comparing the results obtained with the two techniques, it can be concluded that micro-XANES can be successfully used to estimate Fe\(^{3+}/\)Fe variations in natural garnets at a high spatial resolution (5 m), provided that the differences in Fe\(^{3+}/\)Fe are higher than ca. 5%. The “flank method” is the only method which has demonstrated, so far, to be sensitive to smaller variations (i.e. 5%) of the Fe\(^{3+}/\)Fe ratio in garnet, for Fe > 8 wt.%. The measured Fe\(^{3+}/\)Fe zoning in garnet, combined with the already estimated P-T conditions of its growth, provides qualitative information about the redox equilibria occurring during subduction of the studied FeTi-oxide metagabbro. Dehydration-reodox equilibria involving the breakdown of lawsonite and chlorite (i.e. Qtz+Lws+Chl\(_{\text{as}}\)+Omp\(_{\text{as}}\)+Grt\(_{\text{as}}\) = Grt\(_{\text{ss}}\)+Omp\(_{\text{ss}}\)+H\(_2\)O+O\(_2\)) are responsible for a significant chemical re-equilibration of garnet (and omphacite), resulting in a progressive decrease of its Fe\(^{3+}/\)Fe ratio toward the rim and, consequently, in the release of oxygen. Dehydration-reodox reactions of this type, occurring at least locally during subduction of the oceanic crust, may be likely involved in the oxidation of the mantle wedge.

The determination of the oxidation state of most metasomatised garnet peridotites is a demanding task because a large number of phases incorporate both ferric and ferrous iron (e.g. garnet and clinopyroxene), and may show zonations. Oxygen fugacity in high pressure peridotites is traditionally determined from the Fe\(^{2+}\) and Fe\(^{3+}\) contents of garnet in equilibrium with olivine and orthopyroxene. However, the low Fe\(^{3+}\) contents in orthopyroxene as well as the Fe\(^{3+}\) partitioning into further peridotite mineral phases are often neglected. Previous studies demonstrated that the increase of Fe\(^{3+}\) in garnet with increasing temperature does not depend on the whole-rock Fe\(_2\)O\(_3\), but is rather the consequence of the redistribution of Fe\(^{3+}\) from clinopyroxene into garnet. This implies that the Fe\(^{3+}\) content of all the mineral phases and their possible Fe\(^{3+}\) zonations must be considered to obtain reliable quantifications of the oxidation state of the whole rock.

This study presents new measurements of Fe\(^{3+}\) in garnet, olivine, clino- and orthopyroxene of a mantle-derived garnet peridotite from Donghai County, the southeastern end of the Sulu ultrahigh pressure terrane. These rocks correspond to a slice of supra-subduction lithospheric mantle wedge, tectonically emplaced into the crust. They record a multistage metasomatism by an alkali-rich silicate melt at high temperature, and a subsequent influx of a slab-derived incompatible element and silicate-rich fluid during the Triassic UHP metamorphism. We employed two “unconventional” techniques to measure the Fe\(^{3+}/\Sigma Fe\) content of mineral phases with high spatial resolution: (i) the Flank Method electron microprobe analyses for garnet, performing for the first time quantitative Fe\(_2\)O\(_3\) map analyses on zoned garnets at the University of Milano, and (ii) the electron energy loss spectroscopy (EELS) for garnet, olivine and pyroxenes, at the Bayerisches Geoinstitut.

The results indicate that the pyrope-rich metasomatic garnets present a chemical zoning, with the complementary decrease in Al\(_2\)O\(_3\) from ~26 to ~21 wt.%, relative to the increase of Fe\(_2\)O\(_3\) from ~0.8 to ~2.5 wt.%. Such a trend is likely related to the Fe\(^{3+}\)-Al substitution in the garnet octahedral site, which is sensitive to the garnet oxidation state. Clinopyroxenes are diopсидic in composition, whereas olivine and orthopyroxene have ~92 mol% of forsterite and enstatite, respectively. The EELS measurements show that clinopyroxene contains relatively high Fe\(^{3+}/\Sigma Fe\) ratios and Na contents, ranging from 0.48 to 0.51 and from 0.13 to 0.17 a.p.f.u., respectively. Interestingly, also orthopyroxene may contain Fe\(^{3+}/\Sigma Fe\) up to 0.10 (±0.05), a percentage comparable to that of garnet, with important consequences in the study of redox processes in mantle rocks and in the application of many geothermometers.

Garnet/clinopyroxene and orthopyroxene/clinopyroxene qualitative partitioning indicates a minimum partitioning of Fe\(^{3+}\) from clinopyroxene to garnet. The enrichment in Fe\(^{3+}\) of Ca-clinopyroxene requires the incorporation of a NaFe\(^{3+}\)Si\(_2\)O\(_6\) (aegerine) component, particularly in garnet peridotites where the Al content of clinopyroxene is buffered by its coexistence with garnet. The coupled Na-Fe\(^{3+}\) enrichment of our clinopyroxene likely suggests a corresponding enrichment in the whole rock. The Fe\(^{3+}\) substitution mechanism into clinopyroxene as aegerine component could be therefore favoured by the influx of alkali-rich metasomatic fluid phases. This suggests that a possible net bulk oxidation and the redistribution of Fe\(^{3+}\) between garnet and pyroxenes could depend on additional variables besides temperature and pressure. Such mechanisms open new possibilities to unravel the redox processes occurring in the portion of mantle wedge interfacing the subducting slab, which is a key location where the mantle redox reactions likely occur.
In the Serre massif (southern Calabria, Italy) a Variscan crust section crops out consisting of: i) a middle-to low-grade metamorphic rocks in the upper segment, ii) an about 13 km thick “layer” of granitoids and iii) 7-8 km thick lower crust. The deep crust forms the lower part of the section and includes from the bottom to the top: a) layered metagabbros including meta-peridotites; b) felsic and mafic granulites with interleaved metapelites; c) migmatitic metapelites with interleaved metabasites, rare marbles and felsic orthogneisses.

The aim of this study is to characterize the geochemistry and the evolution of the Neoproterozoic to Early Cambrian basic magmatism represented by metagabbros and metabasites.

The reconstruction of the geodynamic setting in which the basic magmas were emplacement could allow a better understanding of the tectonic evolution of the peri-Gondwana terraines having memory of the West African craton.

The effects of the Hercynian metamorphism have modified the mineralogical assemblage and, in some case, have induced partial melting modifying the original compositions.

Petrographic and geochemical (major and trace elements) analyses have been performed on 20 samples collected at the base of the deep crust in the gabbroic portion. Two groups of basic rocks have been defined on the basis of the petrographic features. The first group characterized by coarse grained and isotropic texture, consists of gabbros and Qtz-gabbro containing Pl+Opx+Cpx+Amph±Qtz±Grt, rare crystals of biotite can be also present. Frequently, amphibolites with green or brown hornblende form thick layers. On the other hand leucocratic portions showing trondhjemitic composition are interspersed within the main gabbroic body. The second group is characterized by a medium grained and anisotropic texture formed by Pl+Opx+Bt+k-feld±Cpx±Qtz±Grt. Peculiar characteristics of this rock-type are the abundance of biotite and the presence of pockets of granitic melts having eutectic composition. In both groups, few porphyroblastic garnet crystals occur including amphibole, pyroxene, plagioclase, ± biotite and ± quartz. Frequently, garnet crystals are rimmed by Opx+Pl+Amph or Amph+Pl symplectitic corona in biotite free-rock types or by Bt+Pl±Qtz symplectitic corona in biotite bearing-rock types.

The two groups of rocks have variable chemical compositions owing to the variability of their components. The former are subalkaline rocks (Na_2O + K_2O = 1.17-4.84%) with a content of K_2O around 0.47%, whereas the latter are alkaline rocks (Na_2O + K_2O = 4.88-6.77%) with a content of K_2O around 3.9%.

The metagabbros show lower Rb, Sr and Nb contents (Rb = 0-12 ppm; Sr = 68-592 ppm; Nb = 0.5-13 ppm) than the Bt-bearing metabasites (Rb = 10-210 ppm; Sr = 389-1044 ppm; Nb = 8-25 ppm).

The contents of the other major elements are quite similar despite varying in a large range (SiO_2 = 41.53-60.38% vs. 45.75-51.16%; Al_2O_3 = 14.71-20.75% vs. 14.72-19.48%; FeO = 6.29-13.99% vs. 8.13-12.54%; MgO = 2.59-9.84% vs. 4.72-7.99%; CaO = 6.82-15.49% vs. 5.73-8.96%) for the presence of cumulitic portions and of differentiated rock type, in addition the Variscan partial melting events complicate the chemical variability. The first data (ACF and A’KF diagrams) indicate a common origin from basic magmas for the two rock types so the alkali enrichment for biotite bearing-rocks can be connected with host rock interaction or due to permeation of melts derived from wall rocks in Variscan times.

Different hypotheses about the origin and evolution of metabasic rocks of the Serre, can be proposed.
EVIDENCES OF MELT-ROCK INTERACTION ON THE PETROGENESIS OF WEHRITES FROM SORKHBAND ULTRAMAFIC COMPLEX, SOUTHERN KERMAN, IRAN: CONSTRAINTS ON MINERAL AND WHOLE ROCK CHEMISTRY

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The Ordovician Sorkhband ultramafic complex lies in the southern Kerman Province of Iran. The wedge shape complex covers an area of more than 100 km² and is divided into lower and upper parts. The former comprises of dunite, podiform chromitite deposits (Faryab mine, largest in Iran), massive and dyke like olivine clinopyroxenite, wehrlite (as bands with width of 0.5-5 m and a few meters long) and olivine websterite dykes. The upper part consist of foliated porphyroclastic diopsidic harzburgite with subordinate lenses and dykes of dunite, massive and dyke like olivine clinopyroxenite and minor orthopyroxenite dykes with no significant chromitite mineralization.

According to petrographical studies, wehrlites show granular textures with variable modal composition which consist mainly of 40-70% olivine (Fo90-91), 20-50% diopsidic clinopyroxene, 1-10% bronzitic orthopyroxene and < 1% chromite (Cr# = 65-67, Mg# = 44-46). Some olivine minerals show evidences of recrystallization as triple junction with other minerals, deformation lamellae along its slip planes, mini kinking and irregular extinction band configurations, whereas clinopyroxene minerals are deformed and often exhibit exsolution lamellae of orthopyroxene.

Mineral chemistry of olivine, clinopyroxene, orthopyroxene, and chromites in wehrlites are similar to olivine clinopyroxenites and reveal a mantle origin for the Sorkhband ultramafic complex. Moreover, chondrite normalized rare-earth element (REE) patterns of wehrlites show flat medium REE (MREE) and heavy REE (HREE) patterns, [(Gd/Yb)N ~ 1], and highly light REE (LREE) depletions similar to olivine clinopyroxenite patterns. Furthermore, platinum group element (PGE) show highly differentiated pattern in wehrlites with a positive slope (similar to olivine clinopyroxenites) and high Pd/Ir ratio (36-59).

According to Nicolas & Prinzhofer (1983), wehrlite may be formed by the passage of a melt through dunite bodies where by the process of impregnation and melt-rock interaction clinopyroxene crystallize in dunite. Such impregnated clinopyroxenites are allotriomorphic and interstitially filled between olivine crystals and due to poikilitic crystallization may contain spinel and olivine inclusions. Other evidences of melt-rock interaction in the Sorkhband ultramafic complex have been reported before (Najafzadeh et al., 2009, 2010).

So, regarding the mineral chemistry; REE, PGE and transition elements (TE) patterns similarity in between wehrlites and olivine clinopyroxenites in the Sorkhband ultramafic complex it can be concluded that wehrlites are most likely formed by interaction of pyroxenite melt with dunites as a result of impregnation and melt-rock interaction.

SUBSOLIDUS PHASE RELATIONS IN K-BEARING PERIDOTITE SATURATED WITH COH FLUIDS

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The mantle wedge overlying a subducting slab in the sub-arc region is fluxed by acqueous fluids originating from the dehydration of the downgoing oceanic lithosphere, previously hydrated, and its sedimentary cover. These fluids, enriched in large ion lithophile, can promote the crystallization of hydrous minerals in mantle-wedge peridotite, especially amphibole and phlogopite. Several authors stressed the importance of carbon, released from the subducting slab (e.g., carbonate-bearing sediments, ophicarbonates), which can modify the composition of the slab-related fluid and thus its capability of transferring masses to the mantle wedge. In particular, COH fluids obviously influence the coexistence of hydrous minerals, carbonates and elemental carbon (graphite/diamond) in the mantle wedge. However, experimental data concerning relatively complex peridotite compositions are restricted to date to the two studies of Olafsson & Eggler (1983) and Wallace & Green (1988), who described subsolidus phase relations that are profoundly mismatching.

We carried out experiments in the system KNCFMAS + COH at P = 1.6-3.2 GPa, T = 900-1050°C, f$_{O_2}$ = NNO, under fluid saturated conditions. The starting bulk composition is that of a spinel lherzolite (~30% olivine (ol) + 5% phlogopite (phl) (cf. Konzett & Ulmer, 1999), which represents a metasomatized peridotite. Seeded gels were loaded in a piston-cylinder apparatus using conventional double capsule technique. GCOH fluids have been generated by addition of 10 wt.% oxalic acid dihydrate and excess graphite. Following thermodynamic modeling, we expect binary H$_2$O-CO$_2$ fluids characterized by intermediate X$_{CO_2}$ and X$(O)$.

Phlogopite is ubiquitous. The stable carbonates are dolomite (dol) at low P (1.6 GPa at 950°C), magnesite (mag) at high-P conditions (2.6 GPa at 900°C). We observe in between a region where both mag and dol are stable. In this region, an increase in T up to 1060°C at 2.6 GPa induces the melting of the system, producing magnesiocarbonatites. Carbonate-out occurs for P < 1.8 GPa and T around 1000°C, leaving an assemblage composed of ol + orthopyroxene (opx) + clinopyroxene (cpx) + garnet (grt) + amphibole (amph) + phl. In this region, melting occurs at 1075°C producing trachyandesite.

Amph stability field extends up to 3 GPa at 900°C and 2.6 GPa at 1040°C. By increasing P, mass-balance calculations suggest that amph-breakdown reaction produces cpx and grt. Despite amph breakdown, the COH fluid phase decreases its abundance with increasing P, because fluid at f$_{H_2}$ NNO changes its composition from X$_{CO_2}$ = 0.65 at 1.6 GPa, 1000°C to X$_{CO_2}$ = 0.1 at 3.2 GPa, 900°C.

Cpx does not occur in equilibrium with amph+dol for P < 2.3. Chemographic analysis suggests that the absence of cpx in dol-bearing, low-P lherzolite is expected at COH-fluid saturation, i.e. at fluid-present conditions. In mag-bearing, high-P lherzolites, ol can be consumed entirely by COH fluids, through the reaction ol + CO$_2$ = en + mag, leaving an assemblage composed of opx+mag+cpx+amph+grt+phl. Indeed, we observe a marked decrease in ol abundance, especially in experiments where both dol+mag occur.

In conclusion, the presented experimental data constrain the mineral assemblages expected at different P-T conditions in mantle-wedge lherzolites fluxed by K-bearing H$_2$O-CO$_2$ fluids. From the slab at around 100 km depth upwards the inner mantle wedge at about 50 km depth, we expect first mag+amph, followed by mag+dol+amph, then dol+amph and finally fluid+amph assemblages.

Sessione disciplinare GEO/08:
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NEW SEISMO-STRATIGRAPHIC DATA ON BURIED VOLCANIC STRUCTURES IN THE SOUTH-EASTERN OFFSHORE OF THE ISCHIA ISLAND (NAPLES BAY, SOUTHERN TYRRHENIAN SEA): IMPLICATIONS FOR THE CAMPANIA VOLCANISM

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Some new seismo-stratigraphic data on buried volcanic structures and Quaternary deposits in the south-eastern offshore of Ischia island (Naples Bay) are here presented. In particular, we focus our presentation on southern continental slope of Ischia island and eastern Ischia offshore, surveyed during the realization of geological maps at the scales 1:25.000 and 1:10.000 (Geological Map n. 464 “Ischia”; Aiello et al., 2009; Explanatory Notes to the Geological Map - Marine Geology, in press). The geological bodies recognized through seismic interpretation are the volcanic seismic units, acoustically transparent, representing the rocky acoustic basement and the systems tracts of the Late Quaternary depositional sequence. The prevailing volcanic activity, which controlled the stratigraphic setting of the Naples Bay, has prevented the application of a classical stratigraphic approach, taking into account the associations of depositional systems and the interstratified volcanic bodies (volcanites and volcanoclastites). The sequence stratigraphic approach permits recognition and mapping of depositional bodies defined as three-dimensional objects, consequently to their relative stratigraphic position. Complementary stratigraphic information about the nature of the individuated depositional bodies and the geological processes controlling their deposition and preservation is furnished. Volcanic deposits resulting from effusive and explosive eruptions extensively crop out in the Ischia Island, constructing volcanic edifices; some of them are still well preserved, other ones are completely dismantled or buried. The main geovolcanologic event is represented by the eruption of the Green Tuff of the Epomeo Mt, conditioning a complex caldering resurgence. It allowed for the gradual uplift and emersion of the calderic rocks with a rate of about 800-1100 m. Corresponding volcanic products crop out along the southern coasts of the island at Mt. Vico, S. Angelo and Scarrupata di Barano. In the Ischia island the occurrence of intrusions, volcanic domes and necks and tabular seismic units makes more complex the sequence stratigraphic approach in the geological interpretation of seismic profiles. The marine sedimentation includes both the contribution of siliciclastic sediments, alluvial or marine in origin and that one of volcanites and volcanoclastites erupted by Ischia and Procida volcanic complexes. While the volcanic bodies are deaf to the acoustic energy, the pyroclastic edifices and/or deposits may be acoustically observed. As a consequence, the seismic stratigraphy offshore the Phlegraean Fields is more complex and difficult to interpret with respect to that one of the eastern sector of the Naples Bay, where sedimentary seismic units prevail, apart from the Dohrn canyon morpho-structural lineament. The subactual terrace of the Maronti offshore, coincident with a progradational wedge deposited during the last 5-6 ky should coincide, in terms of geological times, with the Holocene highstand wedge. This is not confirmed neither by the thickness of the Holocene sequence, anomalously high, due to the high sedimentary rates coming from the Serrara Fontana basin neither by its internal geometries. A geologic section has been constructed along the south-eastern Ischia offshore. It documents the stratigraphic relationships between the volcanic units of the acoustic basement and the Quaternary deposits. The section is located along the volcanic structure of the Ischia Bank through the Ischia Channel. Here it crosses the relic volcanic edifice “Il Pertuso” and arrives up to the continental shelf of Procida Island (Punta Solchiaro).

GEOCHEMISTRY AND STABLE ISOTOPES OF LATE QUATERNARY MARINE SHELL FROM GULF OF S. JORGE (ATLANTIC PATAGONIA):
PALEOCEANOGRAPHIC IMPLICATIONS

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Late Quaternary raised coarse-beaches from the Gulf of S. Jorge (Atlantic Patagonia, Argentina) preserve rich paraautochthonous shell beds potentially useful for the paleoenvironmental reconstructions (Aguirre, 2003). Petrographic, XRD and geochemical analyses (in particular Mn and Fe content and Mn/Sr ratio) along with the comparison of living and fossil shells of the bivalves Prototacha antiqua, Mytilus edulis and Aulacomya atra indicate that fossil shells sufficiently preserved pristine structure. Also, Strontium radiogenic isotope data suggest a well-preserved state since the studied samples have retained their original seawater isotopic signatures. Therefore, their isotopic and geochemical composition can be used as proxy for the reconstruction of the past sea conditions (e.g. Dodd, 1965; Mook, 1971; Klein et al., 1996). The oxygen stable isotopes record suggest significant changes in the Gulf circulation and salinity, possibly related to the shift of the frontal position of the superficial Falkland (Malvinas) and Brasilian currents during time. Trace elements content (Mg, Ba, Sr, U) appears more difficult to be interpreted, particularly for the high variability observed in living specimens. However, high U content on some set of fossil shells is interpreted as evidence of subtle diagenesis and/or adsorbtion of this very mobile element making currently particularly arduous, as well known in literature (Kaufman et al., 1971; 1996), the application of the U/Th dating method.

Paola Basin, in the Eastern Tyrrhenian margin, is an elongate trough bounded by the Calabrian Arc terranes to the east. Its western margin is represented by the Aeolian Volcanic Arc, which separates it from the Tyrrhenian bathyhal plane. The shoreline of the basin is about 150 km long, from Cape Bonifati to Briatico. It represents the submerged part of the Calabrian Coastal range Province, consisting of Mesozoic ophiolites and Paleoozoic basement nappes (phyllite, schist, gneiss and plutonics) thrust over the Triassic to Paleogene Apenninic sedimentary units (dolostone, limestone and clastics) (Amodio-Morelli et al., 1976; Carrara & Zuffa, 1976; Dietrich, 1976). It has been estimated that during Quaternary the uplift rates of the Calabrian Coastal Range have been of 1±0.1 mm/yr (Westaway, 1993); this quick uplift determined high sedimentation rates in the shelf area (Chiocci, 1994). The Paola Basin filling sequence can be divided into two portions: the pre-12 ka is characterized by sandy-turbidites and mass-failure deposits, while in the post 12 ka pelagic and hemipelagic sediments dominated. In the upper portion, at 20 cm of depth, a tephra layer attributed to the 79 AD eruption of Vesuvius has been found. This tephra consists of pumices fragments with stretched and flattened vesicles containing abundant microphenocrysts of leucite and diopside and minor feldspar. Loose crystals of biotite are common. Glass composition is phonolitic with K_2O content higher than 7 wt.%. Compositional and textural studies of the lower sandy-turbidites at 372 cm of depth evidenced the occurrence of a second distinctive sandy-gray crystal-rich bed containing fragments of vesiculated glass and porphyritic, non vesiculated, volcanic clasts. Micromorphoscopic observation by SEM showed that glass fragments are characterized by rounded and sub-rounded outlines with stretched vesicles. Glass has a dacitic-rhyolitic composition and K_2O content around 5 wt.%. The absence of non-volcanic detritus suggests that both tephra layers deposited sin-eruptively. A provenance of the post 12 ka tephra layer from the 79 AD plinian eruption of Vesuvius seems to be confirmed whereas the calcalkaline affinity of the pre 12 ka tephra layer suggests an origin from the Aeolian Arc volcanic system.

LIDAR MONITORING OF VOLCANIC CLOUDS

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The threat to air transportation represented by volcanic ashes has been recognized after the dramatic events of British Airways Flight 9 on 24 June 1982. More recently, the Eyjafjallajökull’s eruption caused substantial disruption to air traffic across Europe. This problem is also present in Italy where the Catania airport undergoes frequent stops due to Etna’s plume. In the last decade the Diagnostics and Metrology Laboratory (UTAPRAD-DIM) of the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) developed the Agile Tuner Lidar for Atmospheric Sensing (ATLAS), mounted on the Environmental Laboratory (ENVILAB) hosted in a small truck.

ATLAS can be decomposed in four subsystems: transmitter, receiver, detector and ADC (Analog-to-Digital Converter). The main parts of the transmitter are a tunable TEA (Transverse Excited Atmospheric) CO₂ laser and an off-axis reflective beam expander consisting of two OFHC (Oxygen-Free High Conductivity) copper mirrors manufactured in our laboratory. The laser is tunable thanks to the agile tuner consisting of a diffraction grating and a scanning mirror actuated by a computer-controlled galvo motor. The receiver is based on a Newton telescope.

A liquid-nitrogen-cooled mercury-cadmium-telluride photodiode, coupled with a pre-amplifier designed to complement it, has been chosen as detector. The ADC is embedded in a PCI (Peripheral Component Interconnect) card mounted in the personal computer that controls the experiment. In this paper, the monitoring capabilities of ATLAS in the frame of air safety will be discussed. ATLAS already characterized the Etna and Stromboli volcanic plumes. At Etna, the extinction coefficient inside the volcanic plume was retrieved, while at Stromboli also water vapor concentration in cross sections of the plume and wind speed at the crater were measured. Water vapor concentration and wind speed were retrieved by differential absorption lidar and correlation technique, respectively. Lidar returns were obtained up to a range of 5 km.

The spatial resolution was 15 m and the temporal resolution was 20 s. By combining these measurements, the water vapor flux in the Stromboli volcano plume was found. To our knowledge, it is the first time that a CO₂ laser-based lidar is used to profile a volcanic plume and a lidar retrieves water vapor concentrations in a volcanic plume.
MODELING VOLCANIC ASH TRANSPORT AND DEPOSITION

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Volcanic ash fallout can be responsible for severe damages to buildings, infrastructures, viability, agriculture, livestock and air traffic. Numerical models are available for the simulation of transport and deposition of volcanic ash emitted during explosive eruptions, allowing short-term forecasts.

Actual models are able to capture the main processes related to the transport of volcanic plumes, including advection by the wind, spreading due to atmospheric turbulence, particles settling and aggregation. Moreover, statistical analysis based on meteorological records, field observations and modeling allows the estimation of the probability of occurrence of different fallout scenarios in a given area, to be used for long-term analysis. In this talk, both methods for forecasting the evolution of volcanic plumes and for producing hazard maps for ash fallout are presented. In the former case, the forecast wind field and other meteorological parameters, coupled with observations and measurements of the volcanic plume or pre-defined eruption scenarios, are used for forecasting the evolution of the concentration of ash in the atmosphere and the thickness of the deposit. In the latter, a large dataset of daily wind velocity averages (typically 10-50 years) is used to simulate the ash dispersal under different wind and volcanic conditions.

The obtained maps show different frequencies of occurrence of ash deposition in different zones and allow the estimation of the probability maps (hazard maps) for volcanic ash fallout. Typically, these procedures start with the reconstruction of the eruption parameters able to reproduce past deposits (total mass, grain size distribution, column height, wind velocity, etc.).

This task is performed through a best fit of the model parameters with field measurements and leads to the definition of one or more eruption scenarios. This procedure needs the simulation of the ash fall deposit under different input and environmental conditions and is typically very time consuming. For this, simplified ash dispersal models were used in the past for best-fits and statistical analysis. The use of powerful computers may circumvent this difficulty.
THE MT. ARCI OBSIDIANS (SARDINIA IS.- ITALY)

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The Mt. Arci obsidian is an important, well known geo-resource, as it has been subjected to an intense exploitation since the Neolithic, i.e. 9,000 to 8,000 years ago. The Mt. Arci volcanic relief lays in the central-western region of Sardinia, almost 16-18 km SE of Oristano. The central part of the igneous body is a N-S trending ridge, more than 25-30 km long and less than 5-6 km wide.

The massif has a thick morphology, reaching 812 m above sea level at Punta Trebinalonga. The Mt. Arci is included in the sheet n° 217 (quadrants I and II) of the 1:100,000 IGM topographical map. It has to be noted that the massif has a strongly asymmetric shape, also due to intense faulting. The succession of the eruptive events that built up the massif is particularly complex, as it covers wide chemical spectrum (salic and femic magmas coexist) and time span (from 18-15 My to 3.5-3 My).

The later igneous activity is thought to have given origin to the obsidians. Field surveys found obsidian occurrences in the eastern sector, next to the Pau village (just renowned for the obsidian, and in the southern sector, mainly along the basal belt of the massif. Obsidians form numerous outcrops, twenty-nine of which were inferred to have a primary origin (Fanti & Lugliè, 2010). Some other occurrences, presently hidden by the morphological arrangement or by the vegetation cover, cannot be excluded.

Generally, obsidian outcrops at the Mt. Arci have little thickness. Nevertheless, some of them (S. Maria Zuarbara-Marrubiu, Rioa Cannas, Perdas Urias, Conca Su’Ollastu, Canale Perdera, Riu Solacera) underwent to extraction of perlite, in which obsidian is frequently included. On the basis of their colors and textures, the obsidians can be subdivided in the following types: monochromatic black and “coda di pavone” (fan-like), reddish, brown, and gray; stratified; breached with heterogeneous polychromous elements; “fiocco di neve” (snowflake-like); “cariate” (decayed) or crenulated. In most of cases, the genesis of the Mt. Arci obsidians can be ascribed to assimilation of preexisting volcanic rocks, like tuffites, ignimbrites, volcanic breaches, by the high-temperature primary magma. The decayed and crenulated obsidians, in particular, were originated from marine deposits rich in remains of siliceous organisms (sponges, echinoderms, etc.), before the relief emerged of at least.

These studies allowed to classify the glassy products into four types: SA, SB1, SB2, and SC, respectively (cf. mainly Tykot, 1992; 1996; after Puxeddu, 1958).

The whole Mt. Arci massif represents the area n° 1 of the Parco Geominerario Storico-Ambientale della Sardegna (Geomineral Historic and Environmental Park of Sardinia), because of its morphological and petrological peculiarities. Moreover, it has been included in the World Heritage list of the UNESCO, owing to the cultural aspects connected with exploitation and use of the obsidian. After all, the obsidian can be considered as the object of the first exploitation activity having a significant economical impact in the history of Europe.
During volcanic activity large quantities of gases and ashes are injected into the troposphere and, in case of major explosive eruptions, into the stratosphere. The injections of considerable amounts of gases (e.g., SO$_2$ and HCl) into the stratosphere may disturb its chemical equilibrium and affect Earth’s climate. In particular, chlorine free radicals, which form by breakdown of gaseous HCl molecules via heterogeneous chemical reactions and photolysis, contributes to the destruction of the ozone layer. However, before reaching the stratosphere a significant fraction of gases may be removed from the eruption column by adsorption onto volcanic ash surface. Thus, experimental investigations of the adsorption process of volcanic gases on ashes at conditions relevant for volcanic plumes become important to estimate the removal of HCl from the atmosphere during eruptive events.

We performed adsorption experiments on a synthetic glass with rhyolitic composition and on natural obsidian collected on Vulcano island (Aeolian Islands, southern Italy). Both synthetic and natural glasses were ground to sub-micrometer sized particles using a planetary mill under dry conditions. The glass powder was stored in a simple volumetric vacuum device, which was purged with pure HCl gas to a desired pressure. Pressure dropping caused by adsorption was recorded by a vacuum gauge until an equilibrium pressure was reached within hours or days. The pressure was increased in six steps from 32 to 932 mbar and from 87 to 957 mbar in the experiments on rhyolitic and obsidian glasses, respectively. The amount of HCl adsorbed on ash surface during each step was then calculated from the recorded pressure drop applying both the ideal gas law and the van-der-Waals equation. Preliminary results from two experimental runs performed at room temperature on rhyolitic and obsidian glasses, respectively, indicate that adsorption on the order of 1.4 mg/m$^2$ and 0.5 mg/m$^2$ occurs even at low partial pressures of HCl.

The amount of adsorbed HCl appears to depend on the glass composition, and increases rapidly in the first two pressure steps ($P \geq 200$ mbar) in both experimental runs. At higher pressures, HCl adsorption on obsidian ashes continues to increase but less rapidly, whereas the adsorption isotherm for the rhyolitic sample reaches a plateau and exhibits a very slight increase at the highest pressure. The forms of the adsorption isotherms provide evidence for both chemical and physical adsorption mechanisms. No significant desorption and a slight desorption are observed in the experiments on rhyolitic and obsidian ashes, respectively. This suggests that the adsorption process of HCl on ash particles is a partially irreversible mechanism that contributes to the removal of volcanic HCl from the atmosphere.
UNRAVELLING RADON EMISSION FROM ROCK DAMAGE MECHANISMS:
NEW LABORATORY INSIGHTS

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Positive radon anomalies are commonly used as a tool to predict dynamic failure in the crust, as stated by the widely-used dilatancy model for earthquake prediction. The model foresees that the formation and propagation of cracks prior to rupture will serve to create new surface area and hence increase radon emanation. However, this simplified picture is not only occasionally contradicted by negative radon anomalies, but sometimes negative anomalies are measured at the seismic source, whilst contemporaneous positive anomalies are recorded at monitoring stations located hundreds of kilometres away. Mysteriously, alternating increases and decreases or no significant variations have also been recorded. Hence, despite early promise, radon emanation does not appear to be a very compelling warning signal and many questions remain unresolved. Although numerous studies have investigated field radon emanation from rocks under natural stress conditions, only few have attempted to experimentally relate rock deformation with radon change. Here we present, for the first time to our knowledge, an original experimental set-up consisting of a new accumulation chamber made of a drypack material, a polyester-aluminum-polyethylene bag, containing the rock specimen and connected in a closed-loop configuration to the RAD 7.

The drypack-chamber is loaded under a uniaxial press, without being damaged during rock deformation. Radon gas concentration emitted from the samples is simultaneously and continuously monitored by the system; therefore, the originality of the experiments consists in a real time monitoring of radon emission changes during the whole process of rock deformation. Additionally, the drypack-chamber is surrounded by a heating belt that allows us to investigate the effect of high temperature conditions (up to 90°C) on radon emission. It needs to be stressed that the radonometer is alpha-spectrometry based and is able to measure simultaneously $^{222}$Rn (radon) and $^{220}$Rn (thoron) activity concentrations. The great advantage of determining thoron is the possibility of recording any activity change in the closed system within the length of a single run cycle (30 minutes), due to the short half-life of $^{220}$Rn (55.6 seconds) that reaches any new equilibrium conditions in about 5 minutes. Results demonstrate that radon exhalation from the rock specimen drastically increases with increasing the experimental temperature. This finding allows us to discriminate low variations in radon emissions when rock samples are uniaxially loaded under the press.

Uniaxial compressive tests performed on highly porous (47%) volcanic tuff from Vico Volcanic District (central Italy) shows that the radon emission decreases with increasing load. Such a variation is proportional to a reduction of porosity associated with the compaction of the tuff sample. When the specimen fails, a drastic increase of emission is verified. Moreover, long-term experiments (in the order of weeks) performed by maintaining a constant load on the tuff specimen show that the deformation increases with time. The radon signal coherently continues to decrease up to the complete closure of pores.

At that point, a further increase of load does not induce any additional compaction and any radon emission change, with a constant exhalation up to the failure. This has strong implications in the field of radon anomalies prior to earthquakes, showing that the seismic event can be preceded by no significant radon anomalies, as already documented in literature. Our experimental investigation sheds light on several apparently contradictory signals recorded by radon monitoring stations near active faults and volcanoes. Results demonstrate that emanation rate is governed by the prevalent deformation mechanism. In terms of seismic and volcanic hazard, the deformation mechanism of rocks under stresses should be carefully considered to properly interpret data from geochemical field monitoring.
MIS 5/6 TRANSITION AND LAST INTERGLACIAL MULTIPROXY ANALYSES FROM ANTRO DEL CORCHIA SPELEOTHEMS (ALPI APAUANE, CENTRAL ITALY)

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The last interglacial is the most obvious analogue for understanding the climate variability of interglacial conditions when human impact was virtually absent (even if orbital configuration was not exactly that of the current interglacial). However, few well radiometrically dated records exist for this period (e.g. Bar-Matthews et al., 2000) worldwide. Corchia cave (Apuan Alps, Central Italy) shows a continuous phase of speleothem growth during the period between ca. 140 to 90 ka allowing a systematic replication of proxy records from several stalagmites. Stable isotopes (carbon and oxygen) on speleothems calcite from 3 different speleothems obtained with high resolution show very consistent variations and the time series (anchored by more than 100 U/Th dates on exceptionally pure calcite, allowing a mean resolution of less than 50 yr) replicate in detail the most obvious climatic phases recorded in GNIP ice core and marine records (Drysdale et al., 2006; 2009), with the main advantage of an independent, radiometrically-supported chronology.

U and Mg trace element records show a consistent anti-correlation, with variation substantially in phase with $\delta^{18}$O time series, supporting the interpretation that changes in oxygen isotopic composition were mostly driven by changes in the amount of precipitation and trace element variations were driven by prior calcite precipitation linked to changes in residence time of the water within the fractures, as also supported by the geochemical data obtained from different water monitored in different parts of the cave (Piccini et al., 2008). Speleothem growth was severely reduced for most of the late marine isotope stage 5 (MIS5) and MIS3 and 2 (as also supported by several drill cores on flowstone), with significant resumption of speleothem growth at ca. 12-13 ka. We suggest that this phase of discontinuous and extremely reduced growth was due to glaciated conditions in the catchment of Corchia cave.

Sessione disciplinare GEO/09:
Georisorse minerarie e applicazioni mineralogico petrografiche per l’Ambiente ed i Beni Culturali

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DIFFERENT FINE POTTERY CLASSES FROM THE ARCHAEOLOGICAL SITE OF “TIMPONE DELLA MOTTA” IN THE SIBARITIDE AREA (CS) - CALABRIA

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In this work, we focus on the archaeometric characterisation of some pottery remains dated to the 8th and early 7th Centuries BC. The examined sherds come from the excavations carried out by the Groningen Institute of Archaeology (GIA) on the acropolis of the Timpone della Motta archaeological site, located near the well-known Greek colony of Sybaris (Calabria, southern Italy).

We focus here on four ceramic classes frequently found in the sanctuary: a) matt-painted pottery (“Undulating band”, “Fringe” and “Messapian” styles); b) Oinotrian-Euboean style; c) colonial ware (hydriskai); d) Sub-Thapsos pottery.

All the sherds were examined by means of an integrated analytical approach, including petrographic, mineralogical, chemical and micro-morphological investigations and also clay sediments from the area around Timpone della Motta, representing the potential raw materials used for local pottery production, were sampled for comparison with the pottery. To establish pottery firing temperatures, firing tests (950°C) on the collected clay samples and on each test thin section and diffractometric analysis were carried out.

The results demonstrated that the groups of Matt-painted (“Undulating band” and “Fringe” styles), Oinotrian-euboean, colonial-ware and Sub-Thapsos pottery from Timpone della Motta are characterised by similar features. Although they are very similar, thin-section observations and the chemical data (such as their higher Fe₂O₃ and MgO contents) did highlight some small differences only between the Colonial-ware and Sub-Thapsos group respect to the other two classes. The “Messapian” matt-painted pottery instead show very different characteristics, compared to the other ceramic groups.

The similarity between the chemical compositions of the matt-painted pottery (local styles) and Oinotrian-euboean ceramics could implies their production with the same raw materials. The local styles matt-painted and Oinotrian-Euboean groups, are compositionally similar to both the Pliocene and alluvial clay sediments outcropping near Timpone della Motta, but the comparison between the fine ceramics and the thin sections of firing tests showed the greater similarity with the Pliocene clay tests. The extensive outcrop of Pliocene clay sediments near the archaeological site may explain the large-scale production of pottery ware in this area testified by the great numbers of matt-painted and Oinotrian-Euboean specimens brought to light during excavations.

The composition of “Messapian” matt-painted pottery is completely different from the collected clayey materials, so very probably, they were not locally produced.

The chemical data for the hydriskoi and Sub-Thapsos showed some small differences with respect to the other two groups and to the local clays. This could suggest that this ceramic type was not locally produced or, alternatively, that Fe- and Mg-enriched clay layers, possibly occurring in Pliocene outcrops nearby the archaeological site, were used to produce this type of pottery; otherwise could be supposed that the amorphous nodules were intentionally added, therefore local production might also be hypothesised for this groups.

As regards technological features, the combined information of XRD data and micro-morphological observations by SEM indicated a rough estimate of firing temperatures. Temperatures higher than 850°C are inferred for almost all examined samples, instead observations allow to estimate a firing temperature higher than 1050°C for the over-fired hydriskai.
Some archaeological investigations, promoted by Regione Autonoma Valle d’Aosta, Assesorato alla Cultura and Servizio Beni Archeologici, have been carried out in 2005, just in front of the Aosta Cathedral. The excavation revealed the workshop and the kiln where architectural earthenware, used for the Cathedral façade decoration, was produced and fired.

The construction of the new Cathedral façade was started in the second half of XV Century and finished in 1526. The polychrome earthenware Renaissance Apostle statues are located in the arch entrance, which is decorated with flowers tiles.

Flower tile sherds, clay mixtures, raw clay bricks and firing scraps have been found in the excavation. These findings suggest that only the tiles for the Cathedral decoration were fired in the kiln, as scraps from the sculptures weren’t excavated and the small size of the kiln suggests that the statues were made in another workshop. Evidences from the clay materials suggest two possible provenances: a local deposit, probably known by Romans, and/or a deposit in the Eporediese (Ivrea region).

In this work the manufacture process and the firing conditions are reconstructed through the petrographical and mineralogical study of the archaeological findings. Thin sections of tile sherds have been studied to determine their textures and components. Moreover firing tests have been run on mixtures obtained using the original clay materials from the excavation in order to locate the clay provenance area and to compare them with the actual tiles and to reconstruct the technological features of the craftsmen.

The observation under polarizing light optical microscope allows to correlate the clay mixtures with the scraps. The yellowish clay found in the excavation has been fired at 850°C and compared with three tiles fragments found in the same spot. The fired yellow clay mixture is texturally characterized by alternating bands consisting of layers, with a high temper percentage content, and layers with high percentage of matrix. The same texture is observed in the tile sherds from the excavation, supporting that tiles were produced using these raw materials.

Future development of this work is the examination of the clays, tiles, scarps and mixture firing tests by Scanning Electron Microscopy (SEM) and X-Ray Fluorescence.
ARCHAEOMETRICAL ANALYSES OF EARLY EGYPTIAN GLASS

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In this work a series of glass fragments of Egyptian unguentaria were characterized from the chemical and physical point of view. The studied samples were produced in the first period of the Egyptian glass production, during the new Kingdom of Egypt. The glass production in Egypt started under Thumosis III kingdom and reached its maximum during the kingdom of Amenhotep III (XVIII dynasty, 1390-1352 BC) and Amenhotep IV/Akhenaton (XVIII dynasty, 1352-1338 BC). In this period, different glass shapes and typologies appeared with a large variety of decorations and colours. The aim of this work is to compare these samples, never analysed before, with the data relative to coeval Egyptian productions in order to identify a common origin.

The analysed fragments pertain to six vessels (amphoriskoi and krateriskoi) coming from Thebes area and stored at the Egyptian Museum of Turin (Italy) after the excavation carried out at the Valley of the Queens. All these vessels, are blue with yellow, white and turquoise decorations and produced with the core forming technique.

The chemical analyses of major and minor elements were performed by Electron Microprobe (EMPA). The nature of the opacifying and colouring agents was determined by X-ray powder diffraction. Since only micro volumes were sampled from the artefacts (less than 1 mm³), the diffraction experiments were carried out using a single crystal diffractometer equipped with a CCD camera.

The chemical data show that all the samples contain high levels of Na₂O. However, along with a number of glass containing rather high levels of both MgO and K₂O - thus classified as plant ash based glass - some show rather low levels of K₂O along with high MgO amount. Most of these low-potassium high-magnesium samples are Al-rich Co-bearing blue glass: this seems to indicate the possible coloration with Co-bearing alum. This is also consistent with the high level of MnO present in these samples.

These data suggest the use of two different kinds of flux for the production of these glass: an organic source (for the production of most of yellow, white and turquoise items and an inorganic one leading to lower levels of K and Mg-) used for the production of the Co-bearing samples.

Yellow opaque decorations are rich in Pb and Sb, while only Sb is present in the white and light blue ones. This is consistent with the results of the X-ray powder diffraction analyses, that confirmed the presence of lead antimonates in the yellow decorations and of calcium antimonates in white and light blue ones. No crystalline phases were detected in dark blue, black and violet bulk glass.
AN INTEGRATED APPROACH FOR THE CHEMICAL CHARACTERIZATION OF GLASS MOSAIC TESSERAE FROM THE ROMAN “VILLA DEI QUINTILI” (ROME, ITALY)

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Variously coloured vitreous mosaic tesserae have been brought to light during the numerous archaeological excavations of the Roman site “Villa dei Quintili” (Rome, Italy). The architectonic complex, dating back to the 2nd Century AD, is considered to be one of the largest in the roman suburb, extending between the Appia Antica and the Appia Nuova.

The mosaic tesserae studied here have been taken out from the thermal area of the villa, in the southwest wall of Calidarium, embedded in the bedding mortars.

A double analytical approach has been used in order to obtain a complete chemical characterization of all examined tesserae. Specifically, analyses by scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS) have been carried out for the determination of major elements, whereas laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for trace elements, including REE.

Data obtained highlight that all tesserae mainly consist of SiO₂ (55-72 wt.%), Na₂O (8-20 wt.%) and CaO (5-7 wt.%), and subordinate amounts of K₂O and MgO. For this, they can be defined as soda-lime-silica glasses. The concentration of alkali indicates that samples have been produced using natron as flux.

The high Sb₂O₃ content in all samples is imputable to the deliberate addition of antimony to the batch as a decolourant, while Cu and Cr, also present, were probably used as colorant substances.
TRANSPORT AMPHORAE FROM A REPUBLICAN SHIPWRECK DISCOVERED NEAR PONZA (PONTINE ISLANDS, ITALY):
NEW PETROGRAPHIC AND CHEMICAL DATA TO TRACE THE TRADE ROUTE

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This work deals with the petrographic and chemical study of Dressel 1 amphorae from the cargo of a shipwreck discovered in the “Secca dei mattoni” shallows, between the islands of Ponza and Palmarola (Italy).

The presence of this shipwreck has been firstly signalled in 1986 by some skin-divers of the Archaeological Superintendence of Latium. This was followed with an immediate inspection and some emergency recovery.

The ship, resting on the sea bed at a depth of thirty metres, had two differentiated cargos made up of Brindisi amphorae, in the lower layer, and Dressel 1 and Lamboglia 2 types (the most frequent), in the upper layer. The entire cargo would seem to form a well determined typology, already known thanks to the discovery of other wrecks, above all along the Iberian Peninsula and the French coast of the Mediterranean. Everything seems to coincide with a very precise trade route along which wine and ceramics were carried from Southern Italy (probably with departure from he Apulian coasts, due to the layout of the cargo, with a stop over in Campania, probably at Pozzuoli, where she took on board the Dressel 1 and the Lamboglia 2 items) as far as Gaul or Spain, in the chronological period between the end of the 2nd Century and the early part of the 1st Century BC.

The research carried out on Dressel 1 amphorae aims to confirm or reject the hypothesis of a production of such a ceramic type in the Campanian area. With this aim, mineralogical-petrographic (POM and SEM-EDS) and geochemical investigations (XRF) have been performed.

Microscopic observations highlighted homogeneous textural and compositional features for all examined Dressel 1 amphorae, thus suggesting a common provenance area. This hypothesis was also confirmed by XRF results, since the bulk chemical composition of all artefacts resulted to be quite similar. In addition, in order to obtain more precise information on their production area, punctual microchemical analyses have been performed on single crystals of clinopyroxene (largely represented among the volcanic temper occurring within the pastes), according to a volcanic inclusions based approach for provenance studies, recently proposed by Barone et al. (2010). The data obtained have been then compared with compositions of clinopyroxenes occurring within volcanic rocks from different South Italian magmatic provinces. The data are still being processed, even if the first observations seem to indicate a magmatic affinity between the ceramic clinopyroxenes and those from volcanic rocks of the Campanian area, thus confirming the provenance area hypothesized for the examined artefacts.

A MULTIANALYTICAL APPROACH FOR THE STUDY OF HISTORICAL MORTARS FROM THE ROMAN “VILLA DEI QUINTILI” (ROME, ITALY)

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The present contribution focuses on the study of historical mortars taken from the Roman archaeological site “Villa dei Quintili”, dating back to the 2nd Century AD. It’s one of the largest architectonic complexes in the south-eastern part of Rome, extending between the Appia Antica and the Appia Nuova.

The complex was in use until the 6th Century. After that, it gradually decayed and in 1986 became property of the State.

The study regarded several types of mortars, taken out from different edifices within the monumental complex, such as the thermal area (Calidarium and Frigidarium), the Viridarium, some residential areas and the Nymphaeum.

All samples underwent an integrated analytical program including: a) a mineralogical-petrographic characterization through polarizing optical microscopy (POM), which allowed to define the nature and grain size of binder and aggregate and the ratio between the two components; b) the study of hydraulic properties through mineralogical investigations (XRD and FTIR), aiming to the identification of CSH phases, and microchemical analyses (SEM-EDS) in order to get compositional profiles along the reaction rims between binder and aggregate; c) punctual analyses by SEM-EDS and La-ICP-MS of lumps as well as of clinopyroxene crystals and pozzolana fragments, abundantly occurring among the aggregate fraction.

Investigations have been carried out with the aim to discriminate diverse types of binder, to possibly identify different construction phases within the architectural complex and to restrict the source area of the raw materials used for the preparation of mortars. For the latter purpose, the obtained results have been also compared with literature data referring to the chemical composition of clinopyroxenes occurring within volcanic rocks from the Roman magmatic province and pozzolana samples from the Alban Hills area, thus allowing to better constrain the provenance area.
SILVER, LEAD AND COPPER METALLURGY IN THE COLLINE METALLIFERE DISTRICT (TUSCANY) IN THE MEDIEVAL PERIOD: PRELIMINARY RESULTS FROM AN ARCHAEOMETALLURGICAL SURVEY IN THE MONTIERI AREA

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Tuscany has been for centuries one of the most important mining regions of Italy. Among the many districts, the “Colline Metallifere” hosts a number of base and precious metal deposits which fed a long-living mining and metallurgical industry, possibly dating back to the onset of the Etruscan domination (IX-VIII Century BC). The whole district is now included within the “Technological and Archaeological Park of the Colline Metallifere”, established in 2002. Base and precious metal deposits of the Colline Metallifere district are mostly constituted by Cu-Pb-Zn(Ag) vein bodies associated with late-Apenninic tectonic lineaments and emplaced by magmatic-meteoric hydrothermal fluids in the late stages of the Apenninic orogeny (Lattanzi et al., 1994). Ore mineralogy includes mainly chalcopyrite, galena, tetrahedrite, pyrite and sphalerite. The former three minerals are the most important silver-carriers, particularly the Ag-rich variety of tetrahedrite (Tanelli, 1983). The ancient town of Montieri played a major role in the exploitation and metallurgical treatment of base and precious metal ores (mainly Pb, Ag and Cu) at least since the X-XI Century AD, when the castle of Montieri and its mines came into possession of the Bishop of Volterra (Bruttini & Grassi, 2010). According to some scholars, the first issues of the mint of Volterra, known as “old Volterrani” and consisting of an imitation of coins (“lucenses”) minted at Lucca in the 12th-13th Century, were coined just at Montieri, possibly in the Palazzo delle Fonderie, a still-standing old edifice in the centre of the town. In order to better ascertain type and evolution of smelting and metalworking industry at Montieri, a cooperation project was established between the Dip.to Scienze della Terra (Univ. of Florence) and the Dip.to di Archeologia e Storia delle Arti (Univ. of Siena). We started to analyze several kinds of archaeometallurgical material unearthed during recent excavations in the Palazzo delle Fonderie at Montieri (slags), at the nearby S. Niccolò Rectory (slags) and Montemassi Castle (coins). The otherwise scanty traces of metallurgical activity found during excavations at Le Fonderie are referable to metalworking activity for lead, copper and iron; the employed ore charges were presumably constituted by sulfidic ore assemblages. Nothing can be said about the possibility that the edifice actually served as a mint in the Middle Age. From the Montemassi Castle we analyzed for textural, chemical and Pb-isotope composition four coins (“denari”), two typical “lucenses” (minted at Lucca) and two showing somehow distinctive stylistic features, which could be ascribed to a different mint (i.e. “old Volterrani” coined at Montieri?). Based on their mineralogical, textural, chemical and Pb-isotope composition, the two pairs of currencies appeared similar to each other. All the coins are made of a Cu (85 wt.%) - Ag (15 wt.%) alloy and show evidence of intentional surface silvering through the blanching method. The similarity between the four coins does not necessary imply, however, that all of them have been produced in the same mint. Pb-isotope compositions of all coins fall within the compositional field of polymetallic sulfide deposits of southern Tuscany and far apart from the corresponding field of the Apuan Alps district (cf. Lattanzi et al., 1997), another important base and precious metal district of northern Tuscany, very close to the town of Lucca. This seems to indicate that, independently from where coins were minted, metals for coinage came from southern Tuscany, and possibly from the Colline Metallifere.

MONITORING OF COLOR CHANGE AT BUILDING SURFACES: POTENTIALITIES FOR EVALUATING POLLUTION IMPACT ON CULTURAL HERITAGE

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The majority of the monuments and archaeological sites constituting our Cultural Heritage is located in urban areas. Thus buildings and remains of cultural/artistic interest undergo the impact of different climate and pollution parameters, which act synergistically, but at the same time need to be addressed separately. It is important to consider local-scale variations of the urban environment, such as changes in pollutants, temperature and relative humidity cycles, wind field, urban heat island effect, etc. In conservation field, nowadays one of the most important challenge is to understand the impact caused by environmental changes on Cultural Heritage.

The available scenarios of multi-pollutants trends in Europe indicate a shift in modern urban atmospheres from and SO₂ dominated situation to a multi-pollutant situation, linked to the driven role played by traffic in determining the overall pollution in urban centres. In view of the proven overwhelming influence of mobile combustion sources in determining the future urban atmosphere, “modern” soiling on built heritage will be likely to contain primarily organic carbon (OC). This will imply a change in composition of damage layers, which will presumably assume a yellow-brown coloration.

The EC TeACH project (Technologies and tools to prioritize assessment and diagnosis of air pollution impact on immovable and movable Cultural Heritage) sets out to understand the different types of damage on Cultural Heritage that can be expected in the future, due to changes in pollutants, both in terms of typology and concentration.

To accomplish this goal, from the technological point of view the project aims to develop a non invasive device for the continuous monitoring of the damage caused on monuments located outdoor by changing pollution impact, based on the change of colour of the architectural surface. A prototype is currently under testing at 5 monuments located in urban sites in Europe and one in the Mediterranean area, characterized by different environmental and climate conditions: Cologne Cathedral (Germany), S. Maria del Fiore Cathedral in Florence (Italy), the National Gallery in Oslo (Norway), the Arriaga Theatre in Bilbao (Spain), the National Museum in Cracow (Poland), the historic walls of Salè (Morocco). At each target site samples of surface deposits and damage layers have been collected and analysed by:

- Ion chromatography to measure soluble ions, including water soluble organic anions (e.g. formate, acetate and oxalate).
- Chemical-thermal methodology for carbon fraction speciation and measurement, including organic and elemental carbon (OC and EC).
- Colorimetric analyses directly at the building surface for blackening/colour change characterisation using a portable spectrophotometer.

Results achieved within this still running project on the composition of damage layers will be presented and discussed. Elaboration of carbon fractions data will be linked in particular to colorimetric parameters (L*, a*, b*), with the aim of exploring the application of monitoring of color change of architectural surfaces as potential strategy for preventive conservation.
RELATIONSHIP BETWEEN EXCHANGEABLE LEAD AND TEMPERATURE TREATMENT IN A Pb-CLINOPTILOLITE

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The technological characterization of a Pb-clinoptilolite can contribute to the evaluation of the problems presented by zeolite-based exchangers used to treat lead contaminated wastewaters, since the zeolite itself become a potential source of pollution. Thermal treatments could represent a way to achieve the inactivation of exhausted Pb-exchangers. Heating can affects the structure and, consequently, the properties of a zeolite, so a thorough study of the heating effects on Pb-clinoptilolite has been started. This work shows the relationship between temperature treatment and exchangeable lead in a Pb-clinoptilolite.

A Sardinian epiclastite, containing 66% of clinoptilolite (along with glass, feldspars, quartz, opal-CT and biotite), was processed through autogenous comminution followed by dry and wet sieving, obtaining a powder 125-64 μm in size with 87% of zeolite grade (Siemens D5000 diffractometer; Rietveld QXRPD, Topas 4.2 software). This material was split in two aliquots (BZ and CZ) conducted in Pb-form in different times. Initially, these were contacted with a 1 M NaCH₃COO solution (10 cycles, 2 h each; solid/liquid = 30 g/l; T = 65°C; continuous stirring). The Na-forms (BZ2 and CZ2) were then brought to Pb-forms (BZ3 and CZ3) by 3 further exchange cycles in a 0.5 M Pb(CH₃COO)₂ solution (2 h/cycle; solid/liquid = 30 g/l; T = 65°C; continuous stirring). Lead release from Pb-clinoptilolite was tested at 20°C in 0.5 M KCH₃COO (BZ3) and NaCH₃COO (CZ3) solutions (10 cycles, 2 h each; solid/liquid = 30 g/l; continuous stirring). The results were compared with the lead releases, measured in the same solutions and conditions, from different aliquots of BZ3 and CZ3 previously heated for 2 h at 200, 300, 400, 500, 600, 700, 800, and 900°C. White solutions and eluates resulting from all exchange processes were analyzed by AAS.

Chemical analyses showed that both BZ3 and CZ3 substantially contain Pb-clinoptilolite end-members. With respect to their initial Pb²⁺ contents, lead releases from unheated materials were incomplete: 47% in K- and 54% in Na-solution. Regardless of the solution used, heated powders presented the same decreasing relationship between percentage of lead released vs. temperature treatment. Heating up to 400°C brought to a weak decrease of exchanged Pb²⁺ (≈ 43% at 400°C), that became pronounced from 500 (≈ 35%) to 700°C (< 2%). Materials heated at temperature ≥ 800°C did not evidence lead release.

Acknowledgments

A. Brundu acknowledges the financial support of Regione Autonoma della Sardegna PO Sardegna FSE 2007-2013, L.R. 7/2007 “Promozione della ricerca scientifica e dell’innovazione tecnologica in Sardegna”.
INFLUENCE OF RAW MATERIALS ON THE QUALITY OF TRADITIONAL LIME BINDERS

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This contribution presents the preliminary results of a research project named Calci DOC, included in the activities of Forum Italiano Calce. The aim of this project is to realise a database of the raw materials used in the Italian regions for the production of traditional lime. The project was born in Tuscany with the collection of different stones that from Middle Age up to the last century have been utilized for the production of lime and natural hydraulic lime. The project has two purposes: from one side to identify the carbonate rocks, usually outcropping in the neighbourhood of the furnaces, and to fit them into the geology of each region. On the other side we want to assess the relationship among the chemical, mineralogical and physical properties of these carbonate materials and the type and quality of lime that was produced.

Concerning Tuscany, pure Apuan calcitic marbles with different microstructures, pure limestones, marly limestones and other carbonate lithotypes have been utilised in the past centuries and were considered within this study. A standardised processing of the carbonatic stone materials was followed: burning temperature, burning time, slaking, aging of the lime putty, time of setting of the lime putty.

All samples were preliminarily characterised from the chemical (X-ray fluorescence), mineralogical (X-ray diffraction, thermogravimetric analyses TGA), petrographical and physical (optical microscopy and porosimetry techniques) point of view. The colorimetric coordinates expressed in CIElab system were measured with a Minolta colorimeter on the rock samples and on the hardened binder samples. After the setting of the lime putties, during carbonation, at time intervals, mineralogical controls (XRD) and SEM EDS morphological observations on polished and fractured surfaces were performed. The hardness of the binder samples was measured with a Drilling Resistance Measurement System (DRMS). The obtained drilling resistance was put in relation to the compressive strength of material.

In particular for the Alberese marly limestone, the stone used in the Florentine area for the production of lime, the role of structure, porosity and difference amount of clay minerals in controlling the development of calcium silico aluminat e, has been investigated. A comparison with the characteristics of the marly limestone from the Chartreuse Massif used in France for the production of the Roman cement (or Prompt Natural Cement) is proposed.
CHROMATIC ALTERATION OF FLORENTINE SANDSTONES: ONLY A NATURAL PHENOMENON?

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The stone materials mainly used in Florentine architecture are two sandstones: Pietraforte, mostly used during the Middle Ages as building structures and during the Renaissance as facing, and Pietra Serena used for ornamental purposes. The first one is found in abundance in the hills at south of the city, whereas Pietra Serena is outcropping out in the hills near Fiesole (north of the city).

Pietraforte is a sandstone belonging to the turbiditic formation present in the allochthonous complex of the External Liguridi superposed on the Tuscan Series; Pietra Serena, instead, belongs to the sandstones of the Macigno Formation which consists of beds of turbiditic sandstones separated by pelitic levels which are the finest components of single turbidity current.

Petrographically, Pietraforte is a fine-grained lithic sandstone made in the same proportion by silicatic grains (quartz, feldspars and magmatic fragments) and carbonatic grains (dolostones). The grains are bounded by a mainly calcitic matrix that makes the rock particularly strong. Pietra Serena can be defined as a medium coarse-grained greywacke made by quartz, feldspars, micas, fragments of metamorphic and magmatic rocks. The matrix is quite abundant and is made by illite, kaolinite and chlorite-vermiculite (present only in some outcropping areas).

It is well known that the processes of decay of the sandstones are related to the type of matrix, the amount of cement, the kind of clay minerals present and to the distribution of porosity, which lead to water infiltrations, resulting in swelling and peeling.

The sandstones have a bluish-grey color in fresh cut, but is easily oxidized acquiring an ochraceous - reddish brown color on buildings. Such changes in color, appear to be due in part to the oxidation of iron, proceeding very quickly from the surface to the inside, without cohesion decrease. Indeed the chromatic changes not necessarily implies a deterioration of characteristics of the material, but they often seem to represents a natural patina acquired with the time. However, in some cases the thickness of oxidized layer and its hardness could also be the result of treatments performed in the past.

In Florence, several monuments and buildings are affected by such phenomenon, in particular it possible to note an intense and diffuse reddish coloring on bell tower of Valdese Church entirely constituted by Pietra Serena sandstone, in the exterior columns of the Church Santissima Annunziata and in the historical building of Santa Croce square etc.

About the origin of the color change, the hypothesis most reliable is a natural decay of stone, due to iron oxidation. On the other hand the presence of an intense and homogeneous distribution of the red color could be due to the application of conservative treatments, as a possible consequence of a recent restoration.

This study intends to verify the real and more probable causes of this frequent chromatic alteration and the processes which determine it.
THE VOLCANIC TUFFS IN HISTORICAL BUILDINGS: VULNERABILITY AND INTERPRETATION OF WEATHERING PHENOMENA

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The volcaniclastic rocks are undoubtedly an outstanding material widely employed in historic buildings of some relevant cities in southern Italy. In particular, the Neapolitan Yellow Tuff and Campanian Ignimbrite (the yellow facies, with prevailing zeolites and the gray facies, almost exclusively constituted by feldspars), have been extensively used in the architecture of the city of Naples and of Campania region, both as a building material and as ornamental stone when used facciavista.

These materials definitely represent an historical-Cultural Heritage which deserves appropriate protection; however, any conservative operation cannot disregard a deep knowledge of the lithotypes as well as the environment in which they are used as building material.

As a rule, the correct understanding of all the technical features (origin, formation mechanisms, mineralogical and chemical features, geomechanical properties, accurate interpretation of the weathering phenomena, etc.) represents a prerequisite necessary to plan the appropriate restoration and/or preservation interventions, including the use of consolidating and waterproofing products.

The present work aims at evaluating the influence of some parameters such as temperature, humidity and crystallization of soluble salts on some physical features of the stone. On this account, some new parameters have been measured so far, such as the dimensional changes induced by increasing heating and by water saturation. Tests carried out on high zeolite-bearing rocks (TGN; ICgi), showed sensible shrinkages under increasing temperatures, likely due to dehydration of these hydrous phases, and a likewise significant volume increase after water immersion (swelling test). By contrast, feldspar-bearing rocks (ICgr) evidenced slight or no variation of these parameters under the same experimental conditions.

A possible explanation to this unusual behavior should be that the zeolitized rocks subjected to changes in temperature or humidity, undergo deformations that may lead to loss of cohesion of the constituent elements and thus to the decay of the physical properties of the rock; moreover, the combination of two effects such as water that penetrates the pores and the dimensional changes upon heating may represent the main weathering agent (Weiss et al., 2004; Benavente et al., 2008). Artificial ageing tests (wet-dry and freeze-thaw) providing cyclic variations in temperature and humidity also highlighted the different behaviour of the two zeolite facies (TGN and ICgi) if compared to the ICgr. To better understand the decay mechanisms of volcanoclastic materials, soluble salts crystallization tests were also carried out. Actually, salt crystallization definitely represents a major cause of physical deterioration of macroporous materials exposed to marine aerosol. This test enabled to appreciate the substantial different behavior of the investigated rocks. In particular, TGN quickly achieved a substantial deterioration (total disintegration) of the specimens already after few treatment cycles.

Another relevant aspect of this research is that the changes of many petrophysical parameters (water absorption by capillarity or by total immersion, ultrasonic velocity, uniaxial compressive strength, etc.) induced by accelerated ageing tests are not to be linked to the absolute porosity values of the different materials (these values are almost similar for the three investigated lithotypes), but mainly to the different porous system and a different pore size distribution.

A composite boudin is exposed in the antigorite serpentinite of Vallone Bulè, within the Basal Serpentinite Unit of the Monviso massif (Piemont zone of calcschists with meta-ophiolites). The boudin consists of a quartz-jadeite rock core and a jadeitite rim, very similar to the lithologies used by prehistoric men to make stone axeheads (e.g. Ricq-de Bouard & Fedele, 1993; Compagnoni et al., 1996).

In spite of their different bulk-rock compositions, both core and rim show the same trace and REE patterns suggesting a common protolith. The quartz-jadeite rock exhibits a major, trace and REE composition consistent with that of oceanic plagiogranite, most likely a dyke cutting across upper mantle peridotites, later hydrated to serpentinites (e.g. Castelli & Lombardo, 2007, with references). Conversely, the jadeitite, which consists mainly of zoned jadeite crystals progressively enriched in the diopside component from core to rim, is significantly depleted in Si but enriched in Mg and Ca with respect to the quartz-jadeite rock. The trace and REE similarities and the ubiquitous presence of small zircons suggest that the jadeitite derives from an original plagiogranite - the present quartz-jadeite rock - through a metasomatic process involving a significant desilication and Mg- and Ca-enrichment connected to the peridotite serpentinization. The process, responsible for the transformation of the plagiogranite into a jadeitite, should have occurred during prograde Alpine high-pressure (eclogite-facies) metamorphism, since the first Na-pyroxene formed is a jadeite, corroded and partly replaced during the metasomatic process by a progressively more omphacitic pyroxene.

Because similar rocks - mostly jadeitites, but even meta-plagiogranites - are reported from other localities from the Western and Maritime Alps, it is likely that the raw materials of most jadeitites used to make stone axeheads, which are spread all over the Western Europe, have a similar genesis and derive from the Western Alps as long since suggested (Damour, 1881).

PRELIMINARY MINERO-PETROGRAPHICAL ANALYSES OF STONES AND MORTARS IN A ROMAN BRIDGE (THE “PONT’EZZU” OF ILLORAI-SARDINIA)

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The preliminary results of archaeometrical investigations performed on the building materials of the Pont’Ezzu Roman bridge of Illorai (Sardinia), with the aim of a future restoration, are reported.

The monument, built in Roman times is characterized by an original portion consisting of squared ashlars (about 70×30×30 cm) and a portion rebuilt in medieval times, located at the top of the bridge, which consists of shapeless blocks of about 30 cm in diameter. Minero-petrographical analyses carried out in optical microscopy (OM) evidenced that the ashlars are made of a welded ignimbrite, rhyolitic in composition, with eutaxitic texture and xenoliths mainly of metamorphic origin. The irregular blocks instead are made with different lithotypes representative of several rocks outcropping nearby where, beyond tertiary ignimbrites, Silurian marble, granites and metavolcanic rocks are the most suitable for artifact building. Ashlars interstices are also filled with three different mortars, apparently of different ages.

In order to support restoration, a detailed evaluation of alteration processes has been carried out. Macroscopic analyses evidenced lichens, white crusts and, in some ashlars of the basal portion, alveolization and scaling (Normal 1 /88).

As for the crusts, they are more evident on the arcades, particularly in the volts, where they completely coat the masonries. Such crusts are made of calcium carbonate and in places assume the consistency of true concretions reaching thicknesses of 2 cm. Taking into account their relevance, it is necessary to assume a source of calcium carbonate different from the pyroclastite ashlars. At the current state of observations, stones (e.g. marbles) employed in the restoration of the summital portion as well as lime mortars could be hypothesized as the principal source of calcium carbonate. Moreover, SEM observations on sampled crusts permitted to better appreciate the different coating films and EDS analyses do not evidenced the presence of nitrogen, typical of biological crusts (e.g. due to birds dropping).

Finally, optical microscopy analysis of the mortars have shown different characteristics among the three different types. These concern the nature of the binder and aggregate as well the binder/aggregate relationships. From this characterization, that is in progress, the age and the composition of the mortars, as possible Ca source for the concretions, is expected.
Campania is known as one of the Italian regions with the largest number of archaeological sites, and pottery was widespread in the whole region since prehistoric times, with many workshops operating in the territory.

Aim of this research is to achieve new data on raw materials for ceramics (clay and additives) from Campania region (Italy), with particular attention to those most likely exploited for archaeological pottery. Samples were chosen taking into account their proximity to the ancient archaeological sites and to the ancient ways of communication; further information was gathered through the personal communication of potters that still today are using local clays. Minero-petrological and physical investigations on ceramic raw materials are valuable tools to better define the provenance of pottery and the technological potential of clays. Clayey raw materials from Campania region mainly consist of basinal sediments; the others are represented by alluvial sediments and strongly weathered pyroclastics.

From a chemical point of view basinal and alluvial sediments can be distinguished in calcareous (CaO > 6%) and non-calcareous (CaO < 6%); pyroclastics are only non-calcareous, a parameter strongly influencing the technological features of ceramic products. Because of their good thermal shock resistance, non-calcareous clays are more suitable for cooking ware, whereas calcareous clays are generally used to produce common ware or pottery for liquid storage, due to their higher sintering degree achieved at relatively low firing temperatures.

A moderate to high plasticity characterizes both basinal and alluvial sediments, due to the abundance of different clay mineral phases (e.g. illite-smectite, kaolinite, chlorite) and finer fraction; kaolinite/halloysite bearing weathered pyroclastics show worse plastic features and a higher abundance of coarser fraction. Liquid and plastic limits as well as shrinkage are other physical features that strongly affect the technological attitude, such as moldability of clayey raw materials whereas grain size distribution influences the physical-mechanical properties of ceramic products. For this reason ancient potters used to modify the grain size of clays either depurating or adding temper. For example, temper improves the toughness of pottery, enhancing the thermal shock resistance of cooking wares or the impact resistance of amphorae. Sands of the Bay of Naples coastline were analyzed for comparison with the additive observed in the ceramic findings of this area. Those tempers reflect the petrographic composition of the volcano-sedimentary neighboring lithologies, thus they can be used as provenance tracers for the Bay of Naples pottery.

Two different clayey samples from the Bay of Naples area were chosen to make ceramic replicas fired at different temperatures, in order to simulate the technological process as is assumed to be made originally. A calcareous clay from the Island of Ischia (historically known as production center and raw materials supplier) was mixed with different proportions of temper from Campi Flegrei to reproduce the main features of common wares (e.g., fine ware, table ware, amphorae, bricks); a non-calcareous weathered pyroclastic from Sorrento was used to simulate the characteristics of cooking ware. Petrophysical investigation showed that higher strength and lower water absorptions were achieved at relatively low firing temperatures (850°C) for the calcareous ceramics of Ischia. Temper addition improves the mechanical stress resistance, due to the formation of a secondary pore system (discontinuities at the ceramic matrix/temper grains interface), which dissipates the mechanical energy. Such a feature is particularly suitable for the production of objects such as amphorae. Pottery made with weathered pyroclastics show better refractory features, which make these materials appropriate for the production of cooking ware.
GEOCHEMICAL CHARACTERIZATION ON GLASS FROM PIAZZA BOVIO, NAPOLI (ITALY)

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The archaeological excavation of Piazza Bovio in Naples, has yielded a large deposit, characterized by exceptional findings related to the production of a glass workshop built on site or nearby, around the mid to late sixth Century AD. The workshop features, coupled with the presence of numerous broken glass for recycling and glass scraps, lead to identify the area, as part of a secondary workshop.

Samples of residues of glass melting activities, selected finished objects and glass scraps, dated to VI Century AD and IX-X Century AD, were analysed by SEM/EDS associated to LA-ICP-MS analysis. The study aims to highlight the technological and compositional differences of the studied glass fragments and to verify the hypothesis of a secondary production in Naples, using raw materials from Levant area, which seems to continue until the eighth century in the southern Italy.

The composition of sixth century glass fragments of Piazza Bovio, indicates the use of natron-based glass and supports the hypothesis of the technological, cultural and commercial continuity in the glass production from the Roman to early medieval period.

The analysis carried out on the medieval finished vessels, dated to the IX-X Century, demonstrate the widespread recourse of recycled soda-lime cullet and/or glass tesserae, rather than the direct use of sand and natron or plant ash. The plant ash technology that becomes apparent in glass compositions, in both the Islamic world and the West after the ninth century, probably in Naples was a limited process.

The comparison of the Piazza Bovio glass fragments with Medieval glass of the Italian area (Mirti et al., 2000; Silvestri et al., 2005) revealed a compositional similarity that probably, confirms the existence of few workshops for primary glass production in the Mediterranean Area.

SANT'IMBENIA AMPHORAE FROM NURAGIC SANT’IMBENIA VILLAGE (ALGERO, SS): ARCHAEOOMETRIC INVESTIGATIONS AND COMPARISON WITH LOCAL RAW MATERIALS

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The Nuragic village of Sant’Imbenia is located in North-West Sardinia (Alghero, SS). It was inhabited from approximately the XIV to VII Century BC by natives and, during the last period of life, also by foreign people. It is obvious that as well as goods and raw materials they exchanged ideas, knowledge and technologies.

The aim of the work is identify the trades and contacts of this settlement through the provenance of clays and the technology of ceramic.

Particularly, the study takes into account the results of the archaeometric analyses of the so-called Sant’Imbenia Amphorae found in the Village during the excavations carried out in 1990 and 2008. Sant’Imbenia Amphorae, in fact, are considered “an open question” by the archaeologists either for production area or chronology.

80 selected ceramic samples were studied by X-ray fluorescence, X-ray powder diffraction and optical microscopy to analyze their chemical, mineralogical and textural features and compare clays with local raw materials.

Analytical results reveal that the amphorae are characterized by two different typologies. The first, more abundant, is compatible with a local production which results relevant and specialized, the second suggest an import from different sites.
THE NEAPOLITAN YELLOW TUFF PETROPHYSICAL PARAMETERS:
EXPERIMENTAL INVESTIGATIONS ABOUT RECOVERY AND
CONSERVATION OF A MACROPOROUS BUILDING STONE

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Cultural Heritage represented by buildings, monuments and archaeological finds must be considered an
asset of inestimable value as outlines the historical and cultural evolution of a country. The use of the stone as
building and decoration material has ancient origin and Italy offers several example of stone used over the
centuries in sculpture, decoration, building pavement, etc.

The Neapolitan Yellow Tuff (NYT) is the oldest building material in the Naples area and the most
represented in monuments and buildings of its historical centre. In some case tuff is coated by plaster but in the
case of monumental buildings it was frequently used facciavista.

NYT is the most important volcanic product in the Neapolitan area. The factor which promoted the use of
NYT for building is the local availability but also its physical and mechanical properties. However its
mineralogical composition with the abundant presence of zeolites (> 50%) and the high porosity make it
extremely vulnerable to deterioration caused by weathering.

The interest in the protection of building made up of NYT is increased by its utilization in important
monument such as the gothic churches (S. Chiara, S. Domenico Maggiore), Castel dell’Ovo and Castel Sant’Elmo. In this monuments the risk for deterioration is increase by sea-salt aerosol. In the recent years the
awareness of having an architectural heritage, rich but “fragile”, has produced a greater effort to preserve the
stone and/or improve resistance to weathering. In fact during the past intervention, replacing damaged blocks
was a cheap solution thanks to good availability of NYT; at this time the closure of many quarries requires the
preservation of this stone.

More recently however many efforts have been made to search products able to consolidate and stabilize
weathered material and to reduce stone decay, without isolating it from the environment but protecting it from
the causes of degradation.

The aim of this research is the testing two commercial product: an anti-hygro, a protective product which
reduces the swelling ability of clay and zeolitic minerals and a polymeric consolidant (ethyl silicate) applied to
the NYT. Moreover in order to better evaluate the mechanisms of stone consolidation, it was selected, for
comparison, a porous sedimentary rock, Pietra di Vicenza, with a pore radii distribution similar to TGN.

The two stones were saturated by immersion under laboratory conditions. The specimens were divided
into test group: untreated, treated with consolidant and tretated with antyhigro and consolidant.

Investigations were conducted before and after consolidation and included mineralogical and petrographic
analyses (XRD, XRF, SEM), and physical and mechanical determinations (porosity, pore radii distribution,
capillary water uptake, water absorption, ultrasonic wave velocity measurements, compressive strength,
colorimetric measurements). The consolidated samples were subjected to ageing tests, weathering simulations
such as wet-dry and freeze-thaw cycles, salt crystallization tests and salt spray. This has made for measuring the
effectiveness of consolidation and to study the changes in stone properties.

The products modify the physical properties of consolidated tuff and change the behaviour of weathering:
all the treated samples show a decrease in porosity and water absorption, a color variations and an increase in
durability against weathering.
The Trepca mine, whose full name was in past Trepca Stari Trg and has now been changed to Trepca Stan Terg, is one of the most famous mineral localities in the world, but also the most valuable mining site of former Yugoslavia, that produced lead, zinc, silver and minor cadmium and bismuth. The mine underwent in the nineties of last century a rapid decline in production and suffered a forced closure due to the Kosovo war in 1999. The mine is located in the Vardar Zone of the Dinarides Alpine Belt and is related to the intrusion of Tertiary post-tectonic magmas into a sequence of Paleozoic basement and Mesozoic sedimentary cover and ophiolite nappes. The Trepca ore deposit consists of a series of manto orebodies and mineralized skarns within the sedimentary pile. The main orebodies are intercalated between thick marblized limestones at the bottom and thick schists at the top. The distribution of mineralization was controlled by a trachite and dacite volcanic chimney surrounded by an explosion breccia. Deposit formation is due to a hydrothermal plume of magmatic origin mineralizing carbonate host rocks, similar to the Kipushi model (Feraud et al., 2007).

Mineralogical paragenesis of Trepca Mine is extremely rich, with more than 60 different mineral species reported. Several of these minerals form valuable aggregates of bright metallic sulphides and well grown crystals of quartz, dolomite, calcite and rhodocrosite of collector interest. Moreover tens of specific studies were devoted to particularly interesting phases such as phosphates (e.g. childrenite, crandallite and ludlamite) and sulphides (e.g. galena, bourononite and cosalite).

Mining at Trepca is documented since the late Middle Ages when the most valuable metal extracted was silver. Mining continued under Turkish rule, but after 17th Century declined rapidly till closure in the 19th Century. Modern mining at Trepca was begun in 1930 by the British owned Trepca Mine Ltd at the site of the open pit Middle Ages mine and went on in underground. During the following 60 years Trepca Mine, together with other nearby mines, was the most important mining district of Yugoslavia and one of the largest in the world for lead-zinc production, with a total production of about 3 millions tons of lead and 2 millions tons of zinc. Decline, that had already begun in the ‘70s, accelerated under Serbian rule in the ‘90s and culminated with closure of the mine during the Kosovo war of 1998-99. The two smelters were destroyed and the mine completely flooded.

Trepca Stan Terg Mine was reopened thanks to the efforts of the mine management and workers in 2005 with a production, in its first year, of 15.000 ton of lead-zinc ore. Since then production has increased each year, reaching 128.000 tons in 2010. Resources are still huge and could be enlarged by further exploration as the ore bodies have not yet been bounded. Assessed resources total about 40 millions tons at 4.02% Pb, 3.25% Zn and 76 g/t Ag. Future development plans comprise: new exploration in the Trepca mineralized belt, increase of production from known resources, construction of a new flotation plant, a standard procedure for control of mine production and, eventually, construction of lead and zinc foundries at Mitrovicë Industrial Park.

A preliminary agreement between University of Milan, University of Pristina and Mine management led to a visit of the mine in April 2011. During a short survey of the exploitation front at level XI, 640 m below surface, several samples of collector interest were taken. The preliminary agreement is being improved in order to open Trepca Mine to scientific study, comprising collection and study of mineralogical samples, geological interpretation of ore deposit and characterization of huge tailing dumps.

MAGNETIC SEPARATION TESTS ON A BRAUINITE-RICH MANGANESE ORE, ESKISEHIR, TURKEY

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Turkey is an important manganese ore producer and exploration for new manganese deposits is ongoing. One of the prospected areas is the melange zone of the Eskisehir ophiolite. Some samples from the Taycilar deposits, located in the Eskisehir ophiolite melange, were used in this study to assess the feasibility of magnetic enrichment of manganese ore.

The Eskisehir ophiolite is located in the western part of the Izmir-Ankara-Erzincan Suture Zone (IAESZ) that crosses Turkey from the west (Izmir area) to the east (border with Georgia) (Uysal et al., 2009). Manganese deposits within the IAESZ are classified by Ozturk (1997) as radiolarian chert-hosted deposits. They are related to Neo-Tethyan suture and form the epi-ophiolitic sediment succession together with associated radiolarite, radiolarian chert, siliceous shale and brown claystone. The deposits show high Mn, Si variable and low Al contents. The most important of these deposits is the Cayirli Mn deposit in central Anatolia. The Taycilar deposit has never been mined and the local geology is not well known due to paucity of outcrops and absence of investigation. Mn-rich rocks are mainly strongly deformed braunite-rich quartzites, with NW-SE trend of layering. As a whole the Taycilar deposit belongs to the IAESZ Mn deposits but it is characterized by a strong metamorphic overprint that changed its mineralogy and texture.

Mineralogy and texture of the Taycilar deposit show conditions that can favour magnetic enrichment of ore at relatively fine grainsize, providing the opportunity to produce a high grade final product.

Magnetic properties of Mn ore have been assessed in magnetic prospecting (Bhimasankaram & Rao, 1957). Braunite shows a paramagnetic behaviour that is strongly affected by incorporation of elements, like Mg and Fe, substituting Mn. In addition the Taycilar deposit shows a metamorphic re-crystallization with grainsize increase that allows good separation of Mn-rich phases and quartz at relatively fine grainsize of crushed ore.

For the experiment samples, about 25 kg each, were taken from two outcrops (ESK1 and ESK2) and mixed in equal proportion. Ore was crushed at grain size < 4 mm.

Magnetic separation tests were carried out with a Permroll dry magnetic separator at University of Eskisehir, using constant roll speed and magnetic field.

First test, on the whole sample, crushed at < 4 mm, shows that separation of a Mn-rich sand is possible with a high metal recovery. Efficiency is higher for the finest fraction (< 1 mm), with an MnO content increase from 15 to 30 wt.% at a very high metal recovery of more than 96 wt.%. For coarser grainizes, without any change of setting, metal recovery decreases due to stronger effect of gravity (78 wt.% at > 2 mm) but MnO enrichment increases up to 35 wt.%.

A second test was carried out dividing beforehand the feeding sand in three grainsize classes, in order to study the effect of sorting on separation. Results show that metal recovery does not change meaningfully and hence previous separation of feeding sand in different grainsize classes is useless.

In conclusion tests show that braunite-rich metamorphic manganese deposits can be successfully enriched magnetically, with a metal recovery that is inversely correlated to grainsize. Minimum grainsize is hence chosen on the basis of crushing costs and market demand.

The present study focuses on the provenance of volcanic stones (andesites) sampled in the archaeological site of Kyme (Turkey), the major city of the Aeolia was founded in the middle of the XI Century BC by populations coming from the North of Greece. The work is part of a wider project aims to supply the first compositional data on the stone materials of Kyme. However, despite the archaeological importance of Kyme, there are few archaeometric studies on this city (Ciminale, 2003; Miriello et al., 2011).

Previous and preliminary studies have suggested that the provenance of volcanic blocks could be from the Burunçuk quarry (La Marca, 2006) located near the ancient city of Larisa (a few kilometers from the archaeological site of Kyme). In this work were performed new and exhaustive compositional analysis, comparing the composition of the stones from the Burunçuk quarry with that of archaeological samples. The samples were studied by chemical (SEM-EDS, XRF), mineralogical (XRPD) and petrographic (polarised optical microscopy) analysis. The comparison between the archaeological samples and the quarry materials definitively confirmed the provenance from the Burunçuk quarry.

The Balmuccia peridotite massif is one of the subcontinental mantle peridotite bodies intruded in the mafic-ultramafic Ivrea-Verbano complex in the Western Alps, Northern Italy. The Balmuccia body consists of dominant foliated lherzolites crosscut by several generations of pyroxenite dikes, approximately belonging to an earlier “Cr-diopside suite” and a later “Al-augite suite”. These dike suites are interpreted as mineral segregations from melts which percolated into the lherzolite, refertilized it and caused focused dunitization of the host peridotite. Our study is focused on some thin, cm- to dm-thick pale grey-violet dikes presumably belonging to the late-stage Al-augite suite and intersecting the lherzolite mass at its eastern margin, near the intrusive contact with the Ivrea-Verbano complex. These dikes often show a spotted texture due to the segregation of abundant coarse vitreous black spinel phenocrysts. The mineral assemblage is both Al- and sulphide-rich. The silicate-oxide assemblage includes dominant clinopyroxene (diopside-augite) and blue-green, transparent Al-rich spinel, with minor Ti-rich Na-K pargasite amphibole, Al-bearing orthopyroxene (enstatite), accessory Ti-rich phlogopite and plagioclase and rare olivine (intergrown with spinel droplets). Abundant Fe-Ni-Cu sulphides (pentlandite, phyrrotite, chalcopyrite and bornite) are widely disseminated across the dikes both as mm-sized polyphase nodules interstitial to the silicate-spinel matrix and as tiny, locally extremely abundant drop-like inclusions in spinel. Assemblages containing bornite exclusively occur as inclusions in spinels, which host a redox-dependant equilibrium pentlandite-chalcopyrite-bornite association. The richness in Ni sulphides copes with the scarcity of olivine in this association and is one of the interesting features of these dikes. Another curious feature involves the margins of the dikes. The contacts with the host lherzolite are sharp but not tectonic and are characterized by lateral passage from dike-related undeformed to lherzolite-related, variably foliated assemblages (olivine, ortho- and clino-pyroxenes, fine-grained dark brown spinel and rare amphibole). A visual inspection of the host lherzolite/grey dike contact zones showed a peculiar, progressive change in colour of the spinel from dark brown, in “distal” position, to green transparent near the dike margin. That was the most visible evidence of the interaction between lherzolite and intruding dikes, as an actual reaction zone is not easy to recognize texturally. Analytical transects across these mm- to cm-sized “contact zones” by means of microprobe showed that there may be a cryptic reaction zone. The lherzolite phases do record some changes in major element composition, and in particular spinel, pyroxenes and amphibole show variations in chromium concentration, among others. Across the reaction zones lherzolite spinel vary their Cr content from about 19 wt.% Cr₂O₃ to <1%. They also decrease their Fe²⁺ content whereas Al and Mg are enriched. Clinopyroxene shows a variable “response” to this reaction zone as it shows a tendency to Cr depletion coupled with Ti enrichment and fluctuations in alkalis. Accessory amphibole crystals in lherzolite show a trend of Cr depletion and Ti enrichment as well as a variability in Al and Na contents towards the dike margin. Cr is rather low in lherzolite orthopyroxene, however it shows a tendency to Cr and Mg depletion (and Fe enrichment) towards the dike contact. Olivine tends to be more forsteritic in a distal position. Ongoing and future analytical investigations are aimed to characterize and verify the meaning and the extent of this Cr-depleting Al-enriching and dike-lherzolite metasomatic interaction. Of particular interest is the fate of Cr, one of the economic elements enriched (after mobilization from a source) in relation to metasomatic processes, e.g., dunitization, affecting peridotites.
THE ROCK PAINTINGS FROM NYERO (UGANDA): MINERALOGICAL AND GEOCHEMICAL CHARACTERIZATION OF THE PIGMENTS

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Rock painting samples from the archaeological sites of Nyero, Kakoro and Mukongoro (Teso District, Uganda) were collected in the framework of a collaboration between the Universities of Tuscia and Firenze (Italy) and the National Museum of Uganda. The main goals of this project are those to provide a mineralogical and geochemical characterization of the pigments with which these rock paintings were made. The Nyero rock-paintings sites are consisting of primitive drawings of unknown age, although they are commonly attributed to the Later Iron Age. These paintings are main set on the surfaces of large rounded blocks of Precambrian granites and granodiorites, the latter rising above the surrounding areas of about 30 to 50 m outlining a typical Inselberg landscape related to the long-lasting weathering of such acidic rocks. The rock paintings mainly represent concentric circles, flowers, vegetables, ships and other figures not well defined. Two colors are dominating the Nyero paintings: white or reddish-orange.

The sampling collection was carried out in order to preserve the most significant drawings, consequently, only small flakes or fragments also containing the bedrock were removed. This has posed some difficulties in separating the drawing material and has allowed to collect only small quantities of the pigments. Thus, not destructive mineralogical and geochemical analyses were performed. In particular x-ray diffraction (XRD) and chemical analyses by FT-IR and micro-Raman spectroscopy were carried out.

Preliminary results indicate the presence of different pigments that were used to draw the rock: the reddish-orange color is certainly characterized by iron oxides, while for the white could assume the use of kaolin based. Moreover, several organic compounds were recognized, e.g. calcium oxalates: whewellite [Ca(C₂O₄)·(H₂O)] and weddellite [Ca(C₂O₄)·2(H₂O)], in the pigment samples that were used to date the drawings by ¹⁴C radiometric method with the technique of accelerator mass spectrometry, at CEDAD (Centre of Dating and Diagnosis) of the University of Salento (Italy) and whose analysis is currently in progress.
EXTREME CHROMITE ALTERATION IN ANTANIMBARY CHROMITITES
FROM THE MAEVATANANA BELT,
TSARATANANA SHEET (NORTHERN MADAGASCAR)

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The Maevatanana Belt, located in the north-central Madagascar, is the westernmost of three belts (Andriamena, Beforona and Maevatanana) belonging to the Tsaratanana Sheet. This tectonic unit, individuated by Collins (2006), is composed of mafic gneisses, tonalites, chromite-bearing ultramafic rocks and meta-pelites, some of which were metamorphosed to ultra-high temperatures at 2.5 Ga (Goncalves et al., 2004).

Chromitites were found close to the village of Antanimbary in the northern part of Maevatanana Belt, but unlike nearby chromitites, hosted within ultramafic bodies of Andriamena belt, they have never been studied.

Seven separate chromitite lenses, forming a 3 km long, NE to SW trending, alignment, outcrop close to the Ikopa river bank. They are included within a metamorphic unit, known in literature as orthoamphibolite, composed of sodic plagioclase, hornblenditic amphibole and minor biotite and quartz.

All chromitites are massive with more than 70 and up to 90 modal % chromite and have a cumulus texture where the cumulus phase is always chromite with intercumulus silicates. Chromite grains, completely altered in ferritchromite, ranging from 0.5 to 0.1 mm in size, are euhedral, with fractured cores and porous rims, and enclosed in an anhedral silicate gangue. The most common silicate mineral is chlorite, whose composition falls in the fields of sheridanite and clinochlore and shows detectable Cr₂O₃ contents (1-2 wt.%), which are anyway low if compared to kammererite usually associated to ferritchromite. Tremolitic to actinolitic amphibole and orthopyroxene also occur, often in intergrowth. Serpentine and titanite are present as accessory silicate phases. Ilmenite, as tiny inclusions in chromite grains, is the most common non silicate gangue mineral, followed by rutile, monazite, magnetite and rarely pyrrhotite.

Chromite crystals (isolated or in aggregates) preserve the original shape even if they are completely altered in ferritchromite. A slight core to rim zonation occurs with broken and porous ferritchromite cores surrounded by a more porous corona showing a stronger alteration. Grains never preserve composition of primary chromite. Generally ferritchromites are very low in Cr₂O₃, never exceeding 43 Cr₂O₃ wt.%. FeO is high, ranging between 29.23 and 32.81 wt.%, calculated Fe₂O₃ is never below 6.60 wt.% and reaches very high values, up to 28 wt.%, in more altered ferritchromite grains. MgO is extremely low, systematically below 2.14 wt.%. Al₂O₃ content is strongly variable, with the lowest and highest limits at 3.33 and 21.96 wt.%.

Ferritchromite composition, plotted in \( X_{\text{Fe}} \) vs. \( X_{\text{Cr}} \) and \( X_{\text{Fe}} \) vs. \( X_{\text{Fe}^{3+}} \) “fried egg diagrams”, shows a best fit with layered mafic-ultramafic intrusions (Barnes & Roeder, 2001), confirmed by composition of chromite alteration rims from Bird River Sill (Ohnenstetter et al., 1986).

Quite constant high values of \( X_{\text{Fe}} \), ranging between 0.89 and 0.94, together with variable \( X_{\text{Cr}} \) evidence that alteration of primary chromite is complete and occurred firstly at reducing conditions with a primary substitution of Fe\(^{2+}\) on Mg. Only after almost complete loss of Mg iron is oxidized to Fe\(^{3+}\) and substitutes for Al and Cr.

PRELIMINARY REPORT ON MINEROGENETIC PROCESSES IN THE TGV T
(SABATINI VOLCANIC DISTRICT)

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Many ignimbritic deposits of Central and Southern Italy are deeply affected by minerogenetic process
leading to the zeolitization of the volcanic products. Zeolitization processes in volcanoclastic formations,
develop by interaction between alkaline solutions and a precursor represented by a volcanic glass. This
interaction mainly depends on the temperature conditions of the deposits, the glass composition, the cationic
content of the interacting solution and its pH (Hall, 1998).

Phillipsite and chabazite are the main zeolites occurring within the volcanoclastic deposits of central-
southern Italy, such as the Neapolitan Yellow Tuff and the Campanian Ignimbrite from Campania region, and
the Orvieto-Bagnoregio Ignimbrite (Tufo rosso a scorie nere), the Sorano formation (Sorano Yellow tuff) from
Vulsini district, the Tufo Giallo della via Tiberina from Sabatini volcanic district and the Lionato tuff from
Albani Hills volcanic complex (Lazium and Toscana regions) (de’ Gennaro et al., 1995).

The present research reports the preliminary results of a detailed mineralogical characterization of the
Tufo Giallo della Via Tiberina (TGV T), Sabatini volcanic district (Nappi & Mattioli, 2003). The main goal of
the study was to correlate the volcanological features (eruptive styles, emplacement mechanism, etc.) with the
post-depositional minerogenetic processes (type of zeolite, areal and stratigraphical variations of authigenic
phases, etc.) in order to propose a suitable minerogenetic model.

The investigated samples come from four quarries (Cannetaccio, Perina, SICAT, Fantini), located close to
Riano (Rome). Optical microscopy (OM) on thin section and scanning electron microscopy (SEM) allowed to
identify the major phases and their relationships. Quantitative mineralogical analyses were performed by X-ray
powder diffraction (XRPD) using RIR-Rietveld (Bish & Post, 1993) methods. Chemical analyses were carried
out by XRF for bulk rocks and by EDS for crystal phases. The main zeolitic phases are chabazite and phillipsite
(total content ranging between 25% and 55%). Analcime, was only occurring in samples from Cannetaccio
quarry. Primary constituents are sanidine, calcite, pyroxene and an amorphous matter.

OM revealed that the occurrence of calcite, identified by XRPD, is related to the calcareous clasts from the
underlying sedimentary basement. Further analyses are in progress to establish whether a carbonatic cement
is present too, linked to post depositional carbonatic water circulation. EDS data shows that chabazite always
display Ca as main extra-framework cation, followed by K, and vice versa for phillipsite. Analcime is probably
related to the alteration of leucite. SEM observations show the presence of low-temperature K-feldspar
(adularia).

UNIDIRECTIONAL SOLIDIFICATION TEXTURES AND MINERALIZATION: 
THE KULE PORPHYRY-MOLYBDENUM SYSTEM (XINJIANG UYGUR, CHINA)

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The Kule valley is located close to the western end of Xinjiang Uygur Autonomous Region, 100 km southeast of Yining. The area belongs to the western sector of the > 2500 km long, east-west trending Tian Shan mountain range. In this part of range (central Tien Shan) the Yili Terrane, a wedge-shaped Precambrian craton, is exposed, and bound by the North and South Tien Shan ranges. Variscan calc-alkaline granite and granodiorite bodies (dated 400-250 Ma) crop out over much of the Yili block, representing a still poorly understood magmatic arc derived from orogenic events on both sides of the block. The Kule area is composed of a suite of magmatic rocks of inferred upper Carboniferous to Permian age. Based on field relations and petrographic features, the following units are recognized:

- Granite Unit, composed of: a) medium-grained, equigranular to porphyritic granite, affected by a pervasive “propylitic” alteration; b) microporphyritic granite, made of plagioclase, K-feldspar and quartz phenocrysts in a micrographic matrix; c) microporphyritic leucocratic granite, showing peculiar (UST) textures which are described below.

- Rhyolite Unit: it is a mixture of rhyolite lava and volcanoclastic rocks with the same composition. It includes massive rhyolite bodies related to emplacement of rhyolitic magma under hypoabissal conditions.

- Tuff Unit: shows the same composition of the Rhyolite Unit, but displays features typical of pyroclastic (to epiclastic) deposition. Its primary bedding shows a NNE-SSW trending subvertical attitude, suggesting (in agreement with other evidences) that the Kule sequence suffered a tilting towards WNW.

- Andesite Unit: intrudes the Tuff Unit and is composed of porphyritic andesite affected by propylitic alteration. Dykes related to the Andesite Unit intrude the Rhyolite Unit. The sequence is affected by veining, alteration and Mo mineralization.

The following main veins types occur (older to younger):
- Qtz-Kfs±Mgt (magnetite) veins: they crosscut the microporphyritic granite and rhyolitic rocks, producing a strong “potassic-type” alteration given by brown Bt+Qtz+Mgt±Kfs;
- Qtz-Ms+Py±Mlb (molybdenite) veins and breccias: crosscutting the microporphyritic granite, rhyolitic rocks and Tuff Unit, they produce a mild to very strong alteration given by the same assemblage.
- Qtz±Chl±Ep±Cc veinlets: they only occur in the medium-grained granite and Andesite Unit, where produce a pervasive Chl-Ep-Ab-Ttn±green Bt (“propylitic”) alteration.

When restored to its primary position, the Kule sequence shows features (e.g., calc-alkaline volcano-plutonic setting; multiple veining and alteration, with a “potassic” core surrounded and in part overprinted by a “phyllitic” envelope; hydrothermal breccias; molybdenite) typical of a (low-F) porphyry-Mo system. The microgranite porphyry, that in the restored setting lies below the potassic core, shows a “layered texture”, given by cm-thick coarse-grained, crenulated quartz-magnetite layers separated by leucocratic granite. Both quartz and magnetite crystals within the layers grow in the same direction, thus representing Unidirectional Solidification Textures, like those firstly recognized in the Henderson porphyry-Mo deposit (Shannon et al., 1982). Peculiar of the Kule microgranite is the occurrence of coarse-grained magnetite within the layers. However, the absence of hydrous magmatic phases in the microgranite (the only mafic mineral being fine-grained magnetite) strongly suggests, as proposed for other UST occurrences, release of (ore) fluid to the time of crystallization and solidification of the apex of a stock. The occurrence of Unidirectional Solidification Textures at the Kule porphyry-Mo system further emphasizes their importance, as features indicative of high primary volatile content and ore fluid release in magmatic-hydrothermal systems.

El Creston is a porphyry-moly deposit with proven and probable mineral reserve of 146,705,000 tonnes grading 0.077% Mo (+Cu±Zn±Ag as byproducts). It is located in the Mexican part of the Basin and Range Province, where a metamorphosed Proterozoic basement, mainly composed of a metagranite body (Creston metagranite) intruded in a sequence of phyllites, quartzites, gneisses and metavolcanics, rests as a roof pendant on the Tertiary Sonoran batholith, which includes several intrusions mostly ranging in composition from granite-granodiorite to quartz monzonite. The deposit is related to the emplacement of porphyry stocks in the basement (particularly, the Creston metagranite). The mineralized system underwent a complex tectonic history, the most relevant structures being low-angle normal faults (dipping N35/30°) with horizontal displacement.

A polyphasic hydrothermal evolution is testified by several types of hydrothermal veins and breccias. The following main veins types have been recognized (older to younger, even if some reversals surely occur): (1) Qtz + Kfs ± Ab ± Mlb (molybdenite) ± Phl (phlogopite) ± Ms ± Py ± Rt veins (QTZ-KF); (2) Qtz + Kfs ± Phl ± Mlb veins (QTZ-PHL); (3) Bt + Mgt veins (BT-MT); (4) Qtz + Ms + Rt + Py ± Sp ± Ccp ± Td-Tn (tetrahedrite-tennantite s.s.) veins (QTZ-MU); (5) Zn-Sd (zincian-siderite) ± Ms ± Sp ± Ccp ± Td-Tn veins (ZN-SID).

Different types of breccia occur, including pre-mineralization intrusive breccias and hydrothermal breccias. Among the 7 alteration facies identified, the most significant are: (1) Qtz + Kfs ± Ab ± Zrn ± Py (KF), connected with the QTZ-KF veins; (2) Bt + Mgt ± Ms ± Zrn ± Ep (MT); (3) Qtz + Mu ± Py ± Ccp ± Rt (MU), related to the QTZ-MU veins.

Apart from an early (relict) albition stage, the KF and (often overprinting) MU are the strongest alteration facies; the envelope of MT alteration around the KF alteration likely represents its slightly lower T equivalent. Mineralization is mostly connected with the KF veins and related alteration. At least locally, however, molybdenite enrichments are found in Py-Ms-bearing assemblages and at the contact between the two alteration facies. Strong enrichments also occur in the quartz (+ Kfs ± Phl) matrix of hydrothermal breccias.

A reconnaissance fluid inclusion study performed in quartz from the QTZ-KF and MU veins led to identification of the following populations:
- L+V+several solid phases (Phl, Ms, Cal, Mgt, Tur, Ccp...): these are the earliest inclusions, only occurring in QTZ-KF veins;
- L+V+several solid phases (Phl, Ms, Cal, Mgt, Tur, Ccp...): these are the most abundant inclusions, connected with the MU alteration;
- L+V+Hl±Hem: rarely occurring in QTZ-MU veins, or QTZ-KF veins with MU overprinting;
- V+L±Ccp: VLC inclusions surely not due to necking are rare.

Often in samples containing the halite-bearing inclusions, they may be coeval with them. A striking feature of the fluid inclusions picture is the paucity of hypersaline inclusions. This observation and microthermometry/Raman preliminary data suggest that in the QTZ-KF veins fluids with low salinity and moderate CO₂ content, of likely magmatic derivation, were trapped above the solvus in the H₂O-NaCl-CO₂ system, thus implying a great depth of formation for the deposit. Also during cooling the fluid remained above the solvus, and only episodically unmixed: cooling and, probably, water-rock reaction, more than fluid immiscibility, played an important role for molybdenite precipitation at El Creston.
ARCHEOMETRIC INVESTIGATION OF RED-FIGURED VASES
OF UNKNOWN PROVENANCE

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Three red-figured vases, kindly provided by the Carabinieri Corps for Protection of Cultural Heritage, Cosenza Unit (Calabria, Italy), were subjected to archeometric investigation.

The primary fine of the study was to establish the definite origin and source area of archaeological artefacts. For this reason the samples were characterized from petrographical, morphological, mineralogical, and chemical viewpoints with the aim of identifying technological features and defining the nature of coatings.

The results obtained highlighted common technological features: fine texture of the ceramic body, and black gloss painted directly on it.

A study of their composition excluded the possibility that they are of Greek production. Inductively coupled plasma mass spectrometry (ICP-MS) data revealed that they come exclusively from the Locride area in Calabria, South Italy.
CHARACTERIZATION OF ARCHAEOLOGICAL MORTARS FROM ISOLA CAPO RIZZUTO CASTLE (CROTONE, ITALY) AND IDENTIFICATION OF CONSTRUCTION PHASES BY COMPOSITIONAL DATA ANALYSIS

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In this work different samples of mortars taken from Aragonese Castle, located in Isola Capo Rizzuto (Crotone, Italy) were analyzed.

It was built in 204 BC and represents one of the most important monuments of Calabria. With the aim of finding a complete characterization of the used mortars, different and complementary analytical techniques were carried out on the samples. In particular samples were studied by optical microscopy and analyzed by SEM-EDS, LA-ICP-MS and XRPD analysis.

The results obtained identified different construction phases involved in building the Aragonese Castle. Precisely, data provide information on several important technological aspects: ratio binder/aggregate, porosity, presence of lumps. In addition, mineralogical and petrographic characteristics of the aggregate were determined and found to be compatible with local geological deposits from the Crotone area.
BIOGENIC AND ABIGENIC HYDROCARBONS AND OROGENIC BELTS

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Oil and associated phenomena can be found preferentially along old fold-belts and margins. A fold belt building model proposed in preceding papers by Scalera (2005, 2007, 2008) can be used to judge if the difficulties encountered by the different biogenic/abiogenic conceptions can be solved. The main characteristics of the model are:

i) The tectonic overpressures (Mancktelow, 1995, 2008), and the higher temperatures at shallower depth in the model of Scalera (2005, 2007, 2008), can bear a relation with the synthesis of biogenic and abiogenic hydrocarbons.

ii) Higher thermal gradients - produced by the isostatic uplift of very deep materials - together with uplifted contents of mantle metals (catalysts) and hydrogen, can favour the occurrence of the conditions leading to the development of the Fischer-Tropsch reaction. iii) The underthrust carbonate slabs can interact at proper high temperature with hydrogen and catalytic metals.

iv) Pressure range can be very wide both because the nonlithostatic overpressures (Mancktelow, 1995, 2008) at the boundary between uplifting material and adjacent stable or underthrust lithosphere and occasionally because the inevitable occurrence of strong earthquakes during the thrust-fold belts building.

v) Laboratory experiments (Martinelli & Plescia, 2005) have ascertained that calcareous-marly rocks to which friction is applied produce an emission of CO$_2$ and methane of inorganic origin.

vi) The compressional state of the gravity-driven nappes, together with the general rifting environment of the proposed model and the aperiodic activation of deep change of phase with extrusion of material below the fold belt, can be facilitating factors in HCs migration towards the surface and its accumulation under impermeable layers.

The lack of reducing conditions in the upper part of the upper mantle to be possible the Fischer-Tropsch reaction (Glasby, 2006), is overcome in this model by the upward isostatic transport of the reducing under-lithospheric mantle environment. The criticism of Kenney that suitable TP conditions to produce HCs can be found only at depth greater than 100 km is overcome by the transport of such conditions toward the surface. In my framework a high-temperature reducing environment of undepleted mantle rises up and come in contact with the relatively cold oxidizing lithospheric environment. In the interposed region of thermal gradient, and of hydraulic gradient due to nonlithostatic overpressures - all at depths not overcoming few tens of km - a continuum of very different physicochemical conditions come in existence.

A number of chemical reaction are then favoured in this sort of tectonic oxidizing-reducing pile, leading to a multiple origin of hydrocarbons. In addition, near to the surface - in the first few tens of kilometres - a considerable amount of fluids (Fyfe, 1978) and of organic biogenic material of various provenance is present in the underthrust sedimentary layers, which can participate in a passive way (contaminant) or active way (transmuting materials, kerogens) to the HCs forming.

In Italy, a comparison of the petroleum and gas fields (data from Pieri, 2001) with the maximum felt intensity (VIII, XI, X and XI MCS degrees) shows a good agreement between the model and the highest seismic energy release. The earthquakes enclose an elongated area of tectonic working in which hydrocarbons can be produced in the depts, and then expelled laterally toward the cold side of the region. The ‘warm side’ can be considered the region where the volcanic rocks are located. On this side oil cannot migrate without being decomposed. More deep geochemical investigations and analyses need in determining the real nature (biogenic or abiogenic or mixing of them) of the Italian hydrocarbons.
PRELIMINARY ARCHAEO METRIC STUDY ON COMMON WARES FROM THE FORUM OF POMPEII, ITALY

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We present the preliminary results of an archaeometric study performed on different pottery classes found in the archaeological site of Pompeii, during the I.E. 1980-81 excavations. The selected ceramic group, coming from the western side of the Forum of Pompeii, is the principal evidence of the commercial and cultural development of the ancient Pompeii town and it is ideal for an archaeological and archaeometric study.

In the following work, we considered the common wares, both cooking wares and plain wares, dated in a large time span between the end of the fourth Century BC and 79 AD. On the basis of the morpho-typological analysis, most of these vessels can be considered of local production, instead an extra-regional provenance is supposed for a small group.

The strong morphological and technological changes in the pottery production is an evidence of a large socio-cultural revolution that characterizes the considered period (IV BC - I AD. In particular from the II Century BC, but especially from the first Century BC, the Campanian town has highlighted the opening of new extra-regional common ware trade, in the Bay of Naples.

Optical microscopy (OM), X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM/EDS) and Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS) were performed on the vessels in order to obtain information regarding provenance and technological change in the ceramic production (firing temperature and raw material source area) during the studied period of time.

Petrographic and chemical characterization verified the archaeological hypothesis about the presence of extra-regional productions. The identification of the provenance areas will provide important information on the complex trade mechanisms in the Bay of Naples.
MICRO-XRF TRACE ELEMENT QUANTIFICATION IN CALCITE: A CONTRIBUTION TO WHITE MARBLE PROVENANCE DETERMINATION

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In the last few decades marble provenance identification has represented a focal concern for archaeometric researches, leading to the creation of extensive databases based on the combined results of different geological and physico-chemical methods. Even though isotope geochemistry seemed to give the most discriminant results, the progressive increasing of the database and the consequent overlapping of the characteristic fields pointed out the need of developing multi-method strategies. The methodological approach presented here combines petrographic and micro-XRF geochemical data acquired on a set of 320 reference samples from 20 different Mediterranean quarrying sites. Main goal of the research was to evaluate the effective discriminant capability of a new micro-analytical approach based on trace element quantification with micro-XRF Eagle III-XPL (Röntgenanalytik Messtechnik GmbH, Germany) non-destructive instrument. Poly-capillary lenses (30 µm) were used to collimate the microbeam at the sample surface. Single spot analyses on calcite grains gave reproducible results and allowed overcoming the problem of the considerable variations of solution-based ICP-MS analyses. Preliminary results on Alpine and Apuan Italian marbles encouraged the creation of a wider database which took advantage of the availability of different collections coming from the University of Turin, Genoa and Florence and from the Regional Museum of Natural Science of Turin. The whole set of samples led to the acquisition of original data and allowed quantitative testing the discriminant power of the chosen variables though different samples of the same quarry and in different quarries of the same district. Moreover, it contributed to the scientific valorization of valuable Cultural Heritage. The choice of the varieties to be included in the database was determined by the historic and economic importance of each specific quarrying site over time. They correspond to the well-known Greek marbles from Aegean Islands and Attica, Turkish islands, Aegean coast and Western Anatolia. Spain was represented by Macael marble, while Italian Apuan varieties were analyzed together with some of the best known Alpine white marbles. Calcite compositional data were acquired optimizing analytical conditions for different energetic intervals and the statistical error was evaluated by amorphous and crystalline standards (NIST SRM 610 - 612, Standard Carrara Marble M43). The referred averages for NIST SRM trace elements standards (SRM 610 - SRM612), were used for µ-XRF calibration. Applying 40 kV, 1 mA, a Ti primary filter (25 µm thick), the statistical intensity error percentage from Mn to Nb was < 5% at 50 ppm nominal concentration (live time of 1000 s) and < 3% at 500 ppm (live time 1000 s). Mg concentration was acquired for 1000 s using 10 kV, 1 mA on unfiltered primary beam. Statistical intensity error, in this case, was below 2% at 500 ppm nominal concentration. Calcite compositional data were cross-checked and critically compared to SEM-EDS, ICP-AES and ICP-MS independent analyses on the same samples. Factor and principal component statistical analysis drove the selection of the experimental variables, taking into account petrographic and geochemical evidences. Continuous variables matched micro-XRF calcite composition, expressed as ppm of the most discriminant minor and trace elements: Mg, Mn, Fe, Zn and Sr. Petrographic parameters as maximum grain size, grain boundary shape, texture and shape of the crystals were considered as categorical variables. Chemometric methods were used for data processing and development of proper grouping procedures. The final cross-validated models were successfully used in different case-studies, including byzantine ancient marble artifacts from Liguria and medieval coat of arms from the Racconigi (CN, Italy) residence of the Royal House of Savoy.
NON-DESTRUCTIVE ANALYSIS OF GLASSES BY MICRO-XRF

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Analysis of glass objects in the field of Cultural Heritage primarily aims at determining chemical composition in order to obtain information on production techniques and geographical provenance. In fact, chemical composition may allow one to shed light on the raw materials used, and in some cases, the provenance of these may be ascertained; all this may provide useful data for a chronological assessment of the studied objects. In order to achieve such information the detection of major, minor and trace elements is strongly recommended.

This paper reports the results of an analytical approach for a non-destructive study of glass finds by the µ-XRF technique, which is suitable for quantitative analysis of small sized solid samples, showing lower limits of detection than electron microprobe analysis.

The Brandani-Rava collection consists of 62 Islamic glass weights from Egypt, mainly belonging to the Fatimid age (952-1170 AD), used as reference weights for coin production. Due to the legends impressed on the samples, that may contribute to their chronological classification, a non-destructive analytical technique had to be used, with the aim of determining whether the samples had been produced by recourse to evaporites or sodic ash as a source for the introduction of the network modifier in the glass batch. Forty four glass weights were analysed in this study; out of these, 37 may be assigned to the Fatimid age thanks to the legend impressed, reporting the name of the caliph ruling at the time of their production, three may be tentatively assigned to the later Mameluk age thanks to the symbol impressed on them, while the last four are of unknown allocation.

Major and minor (Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe), as well as trace elements (Cr, Ni, Cu, Zn, Sr, Zr, Pb) were determined and quantified. The obtained results show that the composition of the analysed samples is consistent with a production based on the use of sodic plant ash, due to the relatively high contents of K₂O and MgO; in addition, the lack of correlation between the contents of Al and Ca, as well as the Sr contents, suggest the use of a non-calcareous sand, in agreement with the use of plant ash. Two opaque samples of late Fatimid age feature a high lead content together with the occurrence of Sn, related to the use of SnO₂ as an opacifier.

In conclusions, micro-XRF proved to be a well suited technique of elemental analysis for the non-destructive study of glass finds. The homogeneous composition of the analysed samples, while confirming the use of ash as a flux in Fatimid age, further suggests that comparable quantities of similar raw materials were employed in the course of several centuries; this further points to a consolidated tradition of glass production, appropriate for obtaining reference coin weights with matching features.
AN APPLICATION OF PORTABLE HYPERSPECTRAL SENSOR TO CULTURAL HERITAGE

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Hyperspectral image analysis (HIA) is a potential tool for obtaining many spectral information in the visible and near infrared region with a series of narrow and contiguous wavelength bands, permitting to discriminate materials on the basis of their different patterns of absorption at specific wavelengths. This technique, widely used for determining the characteristics and properties of soils, air and water in a rapid, simultaneous and non-destructive way, has been recently proposed as a non-invasive method for in situ analyses of artworks (Vettori et al., 2008; Camaiti et al., in press).

A portable high-resolution spectroradiometer (a special kind of spectrometer that can measure radiant energy), ASD FieldSpec FR Pro, is a compact, field portable and precision instrument designed to acquire Visible and Near-Infrared (VNIR: 350-1000 nm) and Short-Wave Infrared (SWIR: 1000-2500 nm) punctual reflectance spectra with a rapid data collection time (about 0.1 s for each spectrum). The ASD-FieldSpec FR Pro spectroradiometer can acquire spectra using the contact reflectance probe employing an artificial internal light source with a spot analysis of about 1.5 cm².

Since the spectral fingerprints of a number of mineralogical phases fall within the spectral range covered by ASD-FieldSpec FR Pro, like calcite and gypsum.

In collaboration with Opificio delle Pietre Dure of Florence, the spectroradiometer has been employed for selecting the best cleaning procedure on a marble column belonging to the Loggia di Baccio D’Agnolo of Florence Cathedral. The column was originally heavily affected by sulphation and the superficial gypsum layer showed a good adhesion to the underlying patina; in this situation a not controlled gypsum removal may cause the damage of the original surface (over cleaning).

Our results on the marble column indicate differences in the cleaning efficacy depending on the methodology adopted. These results point out that portable hyperspectral instruments may be powerful tools for characterizing historical surfaces in a non-destructive and non-invasive way.