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EFFECT OF TETRAHEDRALLY COORDINATED Co^{2+} IN SPINEL AND MELILITE SOLID SOLUTIONS

M. Ardit[1], G. Cruciani[1], M. Dondi[2]

[1] Dipartimento di Scienze della Terra, Università di Ferrara, Via Saragat 1, 44100 Ferrara, Italy

[2] Istituto di Scienza e Tecnologia dei Materiali Ceramici (ISTEC - CNR), Via Granarolo 64, 48018 Faenza, Italy

A fundamental problem in determining the chemical and physical properties of a crystal structure is the precise distribution of atoms in its lattice. While in the early application of X-ray diffraction, the lattice constant as well as the mean atomic bond distances were assumed to linearly scale with the composition of the investigated structures (*i.e.* Vegard law), it is now well known that many solid solutions deviate from the linearity predicted by the Vegard law.

The study of those deviations are of fundamental importance when the intrinsic properties (physical, chemical, mechanical, electric, magnetic, ...) of minerals, compounds, or alloys are considered. Since no single experimental method can determine the average long-range crystal structure and, at the same time, give indication on the local distances between the central ion and its surrounding atoms, the long- *vs.* short-range properties of a crystal structure along a join have to be obtained through the combination of diffraction and spectroscopy techniques. In this work, the structural relaxation around four-fold coordinated Co^{2+} ion along the gahnite ($ZnAl_2O_4$) - Co-aluminate ($CoAl_2O_4$) as well as the hardystonite ($Ca_2ZnSi_2O_7$) - Co-åkermanite ($Ca_2CoSi_2O_7$) solid solutions (*ss*) was investigated by a combined X-ray powder diffraction (XRPD) and electronic absorption spectroscopy (EAS) approach. Monophasic samples were obtained through solid state reaction synthesis. Distinct behaviors of the two structure-types are observed as a function of the cobalt incorporation.

While in the spinel *ss* the Co^{2+} doping induces a linear increase of the unit-cell parameter, the melilite *ss* is characterized by a non-linear variation of the lattice constants, revealing a negative excess volume of mixing due to the single isovalent substitution of Co for Zn in the tetrahedral site. A careful inspection of T–O distances for both spinel- and melilite-type structures highlights the role played by an enhanced covalence degree of Zn–O bonds. The optical spectra are characterized by the occurrence of electronic transitions of Co^{2+} in tetrahedral coordination affected by a strong spin-orbit coupling (plus the lowering of point symmetry in melilites) causing a 3-fold splitting of spin-allowed bands. In agreement with the diffraction data, deconvolution of the optical spectra show a progressive decreasing of the crystal field strength parameter $10Dq$ moving toward the cobalt end-members, meaning that the local cobalt-oxygen bond distance, $<Co–O>^{local}$, increases along the join with the amount of cobalt. In order to achieve a reliable estimation of the local Co–O distance for the spinel *ss*, the tetrahedral distance evolution was recast to eliminate the effects of the inversion degree, although very small (*i.e.* the maximum inversion degree was 0.07, found for the Co-aluminate end member). By this way, a relaxation coefficient as low as $\varepsilon = 0.47$ was obtained, *i.e.* significantly smaller than literature data for other spinel systems. At variance with this latter value, the calculated structural relaxation for the $Ca_2(Zn_{1-x}Co_x)Si_2O_7$ join was $\varepsilon = 0.69$ (far from the Vegard's prediction, *i.e.* $\varepsilon = 0$). This difference is consistent with the largest constraints existing on the spinel structure, based on cubic closest packing, compared to the more flexible layered melilite structure.

MINERALOGICAL AND CHEMICAL EVOLUTION OF OCHREOUS PRECIPITATES FORMED DURING ACID MINE DRAINAGE PROCESSES AT THE ROŞIA MONTANĂ GOLD MINE (ROMANIA)

E. Azzali[1], P. Marescotti[2], C. Carbone[2], E. Dinelli[3], G. Capitani[4], G. Lucchetti[2]

[1] Dipartimento di Geoscienze, Università di Padova, Via Gradenigo 6, 35131 Padova, Italy
[2] Dip.Te.Ris., Università di Genova, Corso Europa 26, 16132 Genova, Italy
[3] Dipartimento di Scienze della Terra, Università di Bologna, Piazza Porta San Donato 1, 40126 Bologna, Italy
[4] Dipartimento di Scienze della Terra "Ardito Desio", Università di Milano, Via Botticelli 23, 20133 Milano, Italy

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 Acid Sulphate Waters (ASW; $pH \leq 3$), containing very high levels of Potentially Toxic Elements (PTE) deriving not only by the sulphide mineralizations but also from host rocks and gangue minerals (such as Zn, Cr, Cu, Ni, As, and Pb) [1].

The studied area is located within the Roşia Montană mining site, which is a hydrothermal gold deposit hosted in andesites and dacites of Neogene age, piercing the prevolcanic sedimentary basement [2]. In this study a mineralogical and geochemical characterization of the ochreous precipitates and associated waters forming within the Roşia river was carried out in order to evaluate the mineralogical variations starting from the lowest adit of the "Sf. Cruci din Orlea" gallery up to the confluence between Roşia and Abrud rivers; the partitioning of PTE between contaminated waters and secondary minerals was also investigated. The mineralogy of the precipitates was determined by means of XRPD, whereas the bulk chemistry by ICP-MS. Some selected samples, representative of the main mineralogical assemblages, were further analyzed by means of transmission electron microscopy (TEM) and microanalysis (EDX). Temperature, pH and Eh were measured *in situ*, whereas the chemical analyses on mine waters were made by means of ICP-OES, AAS and chromatography.

Ochreous precipitates are characterized by high concentrations of PTE (in particular V, Zn, Cd, As, Pb) and consist of a mixture, in variable proportion, of K-jarosite and schwertmannite, which represent the stable secondary minerals along the investigated transect of Roşia river. Moreover a positive correlation between Fe and S with As, V and Pb suggests an effective control of schwertmannite and jarosite on the mobility of specific PTE. Waters flowing from "Sf. Cruci din Orlea" gallery (ASW) are characterized by the lowest pH values (2.7-3.1) and the highest Eh (460-484 mV), SO_4 (688-4800 mg/L) and PTE contents (Zn, Cr, Cu, Ni, Co, Cd). A remarkably different hydrochemistry is evident at the confluence between Roşia and Abrud rivers, being characterized by a significant increase in pH (6.3-7), decrease in Eh ($\approx$ 300 mV), and a general reduction of dissolved SO_4 and metal load.

The results indicate that the role of secondary minerals as "mitigating agents" can be limited because even minor pH-Eh oscillations would cause mineralogical transformations, via dissolution-reprecipitation or solid-state transformation that could lead to trace elements mobilization in the environment. Positive correlation with more stable minerals could suggest a permanent storage within the solid phases.

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H₂O CONTENTS OF GRANITIC MELTS PRODUCED AT THE ONSET OF CRUSTAL ANATEXIS: CONSTRAINTS FROM EXPERIMENTAL RE-MELTING OF *NANOGRANITE INCLUSIONS* IN GARNET FROM RONDA MIGMATITES (S SPAIN)

O. Bartoli[1], B. Cesare[1], A. Acosta-Vigil[2], S. Poli[3], R.J. Bodnar[4]

[1] Dipartimento di Geoscienze, Università di Padova, Via Gradenigo 6, 35131 Padova, Italy
[2] Instituto Andaluz de Ciencias de la Tierra, Consejo Superior de Investigaciones Científicas, Armilla 18100, Granada, Spain
[3] Dipartimento di Scienze della Terra, Università di Milano, Via Botticelli 23, 20133 Milano, Italy
[4] Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA

Crustal anatexis and melt extraction produce S-type granitic magmas in the upper crust and granitic leucosomes in migmatites, promoting the chemical differentiation of the continental crust and affecting its rheology. H₂O plays a significant role during anatexis, constraining melting conditions and reactions, as well as granitic magma production, composition and mobility/viscosity [1]. Despite the significance of crustal anatexis for the evolution of the Earth, to date there are no available methods to directly analyse the chemical composition, including the nature and concentration of the dissolved volatile species, of natural anatectic melts particularly at the onset of crustal anatexis.

Here, using a novel and cutting edge approach in crustal petrology (the study of *nanogranites* in migmatites; [2]) and taking advantage of a new experimental method for their re-melting, we demonstrate that it is possible to directly determine the H₂O content of granitic melts during their formation in the source region, rather than after the magmas have separated from its source.

We use as an example a migmatite from the Betic Cordillera (S Spain). Piston cylinder re-melting experiments led to the complete re-homogenization of *nanogranites* hosted in peritectic garnet at conditions (700 °C, 5 kbar) close to those inferred for anatexis, maintaining the original fluid concentration in the melt. After re-melting and quenching, glasses have been analysed by Raman spectroscopy, providing the primary H₂O content of the earliest melts produced in the migmatites. Our data indicate that S-type granites produced at Ronda are mainly H₂O-undersaturated even at low degree of melting and suggest that peraluminous leucogranitic melts formed at low temperature (~ 700 °C) may not be as wet and of low viscosity as previously considered, implying much greater rock strength and much longer timescales for melt extraction at Ronda and, in general, through the metasedimentary continental crust.

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Sb-RICH ROUTHIERITE FROM MONTE ARSICCIO MINE (APUAN ALPS, TUSCANY, ITALY): OCCURRENCE AND CRYSTAL STRUCTURE

C. Biagioni[1], E. Bonaccorsi[1], Y. Moëlo[2], P. Orlandi[1]

[1] Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 50126 Pisa, Italy
[2] Institut des Matériaux Jean Rouxel, Université de Nantes, 2 rue de la Houssinière, 44322 Nantes, France

Routhierite, $Tl(Cu,Ag)(Hg,Zn)_2(As,Sb)_2S_6$, is a rare sulfosalt first described from Jas Roux (France), in association with pierrotite, stibnite, smithite, sphalerite, realgar, orpiment, pyrite, baryte, and chabournéite [1]. Routhierite was later described from the Hemlo gold deposit, Ontario, Canada [2] and from Vorontsovskoye, Middle Urals, Russia [3]. The crystal structure of routhierite was recently solved using a specimen from the type locality [4].

During the study of the sulfosalt assemblages of the baryte-pyrite-iron oxides ore deposits from Southern Apuan Alps, Tuscany, Italy, routhierite was identified at the Monte Arsiccio mine. It occurs as anhedral grains, up to 1 mm in size, strictly associated with aktashite, baryte, boscardinite, cymrite, protochabournéite, pyrite, realgar, Hg-rich sphalerite, and stibnite, in small veinlets embedded in pyrite-rich dolostones. In this occurrence, routhierite in some cases seems to replace aktashite. More rarely, routhierite was also found in quartz veins, as euhedral crystals, dark red in color, associated with boscardinite. Preliminary identification was achieved through X-ray powder diffraction and qualitative EDS chemical analysis, which shows the presence of Tl, Cu, Ag, As, Sb, and S as the only elements with Z > 9.

The crystal structure of routhierite from Monte Arsiccio was solved in the space group *I-42m*, with *a* 9.9780(5), *c* 11.3764(7) Å. It was refined up to $R_1 = 3.00\%$ for 960 observed reflections. In the crystal structure of routhierite, $(Cu,Ag)S_4$ and HgS_4 tetrahedra share corners to form a framework with channels parallel to **c**. These channels host TlS_6 and $(As,Sb)S_3$ polyhedra, sharing corners and edges with the tetrahedra. All the geometrical features are in agreement with those reported by [4]. The relatively short Tl–Tl distance of 3.33 Å could indicate some Tl–Tl interaction, as proposed by previous authors for routhierite [4] and its Zn analogue, stalderite [5].

The crystal structure study of Italian routhierite points to the formula $Tl(Cu_{0.84}Ag_{0.16})Hg_2(As_{1.28}Sb_{0.72})S_6$, Z = 4. The Sb/(As+Sb)$_{at.}$ ratio is 0.36, to be compared with the value 0.11-0.12 for routhierite from Jas Roux [1]; the highest Sb/(As+Sb)$_{at.}$ ratio was measured on routhierite from Hemlo, giving 0.60 and 0.80 [2], and corresponding to the Sb analogue of routhierite.

The Sb-rich nature of routhierite from Monte Arsiccio mine agrees with the usual richness in antimony of the sulfosalts from the Apuan Alps ore district. Actually, protochabournéite [6] and boscardinite [7], first discovered at this locality, are the Sb-rich member of the chabournéite series and a Tl-Sb homeotype of baumhauerite, respectively. Finally, routhierite is the eighth Hg sulphide described from the baryte-pyrite-iron oxides ore deposits from Apuan Alps.

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GLOBAL-SCALE Sr-Nd ISOTOPIC HETEROGENEITY OBSERVED ON METER SCALE IN NORTHERN APENNINE OPHIOLITIC PERIDOTITES RESULTING FROM PYROXENITE-PERIDOTITE INTERACTION

G. Borghini[1,2], E. Rampone[1], A. Zanetti[3], C. Class[2], A. Cipriani[2,4], A.W. Hofmann[2,5], S.L. Goldstein[2]

[1] DIPTERIS, Università di Genova, Corso Europa 26, 16132 Genova, Italy
[2] Lamont-Doherty Earth Observatory, Columbia University, Palisades NY 10964, USA
[3] Istituto di Geoscienze e Georisorse-CNR, Sezione di Pavia, Via Ferrata 1, 27100 Pavia, Italy
[4] Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Largo S. Eufemia 19, 41100 Modena, Italy
[5] Max Planck Institute for Chemistry, P.O. Box 3060, 55020 Mainz, Germany

Melt-peridotite interaction and melt intrusion are the most important petrologic processes in creating lithological, chemical and isotopic heterogeneities in the lithospheric mantle. Addition of mafic components can significantly increase the compositional variability of the lithospheric mantle, however, the origin and composition of mafic lithologies, and their significance in creating heterogeneities in the lithospheric mantle, remain poorly constrained. Here, we present field, chemical and isotopic data on pyroxenite-peridotite mantle sequences outcropping in the Western External Liguride ophiolitic Units of the Northern Apennines, Italy. These mantle sequences experienced a cold decompressional tectonic evolution [1], partially freezing chemical and isotopic variability inherited from their deep lithospheric origin. This study aims to improve our understanding on the origin of pyroxenites and quantifies the modification of the chemical and isotopic composition of the lithospheric mantle by their emplacement. Pyroxenites (from websterite to clinopyroxenite) occur as cm-thick bands (up to 12 cm) parallel to the spinel-facies tectonite foliation in the host peridotites. In spite of partial subsolidus low-P re-equilibration (spinel- to plagioclase-facies), most of the pyroxenites record chemical features inherited from a primary garnet-bearing assemblage; this indicates that they originated from melt segregation in mantle peridotites at high pressures (> 18 kbar). Orthopyroxene-rich rims developed at the boundaries between pyroxenite and peridotite, along with large poikilitic orthopyroxene in the wall-rock peridotites, indicate that the host peridotites have interacted with melts related to pyroxenite intrusion. Mineral and bulk-rock decimeter-scale pyroxenite-peridotite profiles reveal that the host peridotites have been significantly modified in terms of major (*e.g.* XMg, Al_2O_3, CaO) and trace element (*e.g.* the REE) chemistry. In the longer profile (up to 12 cm from the pyroxenite band), the host peridotites record an increase of LREE/MREE ratio coupled to a progressive increase of the absolute REE contents (in bulk rock and clinopyroxenes), suggesting that a large peridotite volume has been modified by pyroxenite emplacement *via* melt infiltration and melt-rock reaction. Detailed isotopic investigations were performed on clinopyroxenes separated from pyroxenites, host peridotites and pyroxenite-free peridotites (> 1 m from the pyroxenite bands). Sr and Nd isotopic compositions fall within the MORB field ($^{87}Sr/^{86}Sr$ = 0.7023-0.7029; $^{143}Nd/^{144}Nd$ = 0.5134-0.5128). Remarkably, the large range in $^{143}Nd/^{144}Nd$ ratios in the peridotites, which document the isotopic variability with and without pyroxenite emplacement (host peridotite and pyroxenite-free peridotite) on the scale of a few meters, covers almost the entire Nd isotopic variability documented in abyssal peridotites globally (*e.g.* [2, 3, 4]). Our trace element and isotopic profiles indicated that pyroxenite intrusion modified host peridotites, lowering their $^{143}Nd/^{144}Nd$ as a combined effect of the systematic LREE enrichment (*i.e.* Nd/Sm increase) and radioactive decay. Sm/Nd errorchrons defined by pyroxenite and host peridotite yield a small range of ages between 424-452 Ma (errors < ±50 Ma), predating the low-P evolution (178±25 Ma) related to rifting and opening of Jurassic Ligurian Tethys.

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Fe AND Mn SPECIATION IN MULTICOLOURED TOURMALINES

M.R. Cicconi[1], G. Giuli[1], A. Trapananti[2], E. Paris[1]

[1] Scuola di Scienze e Tecnologie - Sez. Geologia, Università di Camerino, Via Gentile III da Varano, 62032 Camerino, Italy
[2] CNR-IOM-OGG Grenoble, c/o ESRF, BP 220, 38043 Grenoble, France

Four multicoloured tourmalines, where the variation of colours occurs in concentric bands, have been analysed by X-ray Absorption Spectroscopy (XAS) at the Fe and Mn K-edge, in order to investigate the oxidation state and the site location of Fe and Mn, with the final purpose of understanding the physico-chemical factors affecting their colour. The natural multicoloured crystals present only Fe and Mn as chromophore elements, but despite the quite simple chemistry, they show a variety of colours including hues of blue, pink, red and green. In zones where Mn is predominant, a pink colour is observed, whereas Fe predominance induces green or blue colours. Interestingly, the presence of Fe and Mn has been recognized also in the colourless areas.

XAS measurements have been collected at beamline GILDA-BM08 of the ESRF. The beam size at the sample was 0.15×1 mm in order to be able to selectively measure the different coloured zones of the crystals. A 13-elements high-purity Ge detector allowed to collect the fluorescence spectra through a cross section of each of the samples. Detection of the Mn $K\alpha$ and Fe $K\beta$ X-ray emission lines allowed to selectively collect profiles of Mn and Fe abundances across the studied crystals. Pre-edge peak (PE) analysis shows that Mn and Fe are dominantly divalent in all the measured samples. PE integrated intensities are compatible with the location of Mn and Fe in the octahedral sites. Preliminary theoretical XANES calculations also agree with the octahedral coordination of Mn and Fe. For these samples, the change in colour appears related to the variation in the relative abundance of Mn and Fe rather than to variations of their oxidation states.

HIGH TEMPERATURE REACTIONS OF SERPENTINE GROUP MINERALS

C. Giacobbe, A. Viani, A.F. Gualtieri

Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Largo S. Eufemia 19, 41100 Modena, Italy

The thermal transformation, stability field, and reaction kinetics of serpentine minerals (antigorite, chrysotile, and lizardite) have been studied to draw a comprehensive model for their dehydroxylation and recrystallization reactions. Despite the huge amount of work devoted to the temperature-induced dehydroxylation and recrystallization reactions of serpentine minerals in air at ambient pressure, several issues are still open to debate: the nature and stability of amorphous dehydroxylate phases, the nature and stability field of talc- and chlorite-like phases possibly appearing during the reaction path, possible topotactic relationships between the serpentine and newly formed phases forsterite and enstatite, the nature of the pyroxene phase, and a comprehensive model based on kinetic parameters is still missing. Combined studies with a multi-technique approach have permitted to consider these aspects which have been taken into account, analyzed and clarified.

In situ X-ray powder diffraction (XRPD) and kinetic studies were combined with transmission electron microscopy (TEM) observations to describe the mechanisms of dehydroxylation and later high-temperature crystallization. During dehydroxylation, a metastable transition phase with a characteristic peak around 9 Å was observed in antigorite and, to a minor extent, in lizardite. Rietveld refinements confirmed that the 9 Å phase actually possesses a talc-like structure. The appearance of this phase is controlled by structure and kinetic factors. It was found that the three serpentine polymorphs decompose at different temperatures. Chrysotile is stable up to 750 °C, lizardite up to 775 °C and antigorite decomposes at 800 °C. Talc is observed as metastable phase in antigorite and, to a minor extend, in lizardite. When the heating rate is fast (that is > 30 °C/min), the talc-like phase is not observed. When the heating rate is slower (< 30 °C/min), the talc-like phase is observed. Regardless the rate of heating, talc is never observed in chrysotile indicating both a crystal chemical (thermodynamic) and kinetic control of the reaction. The kinetic parameters and reaction mechanism for lizardite and antigorite dehydroxylation in air at ambient pressure were calculated using the Avrami models and compared to those of chrysotile. For both lizardite and antigorite, the kinetics of dehydroxylation is controlled by diffusion. Apparent activation energy of the reaction in the temperature range 612-708 °C was 221 and 255 kJ/mol for lizardite and antigorite, respectively. The reaction sequences of chrysotile, lizardite, and antigorite leading to the formation of stable high-temperature products (*i.e.*, forsterite and enstatite) are described taking into account previous topotactic and dissolution-recrystallization models.

CONFINEMENT OF DYE MOLECULES IN NANOPORES: STRUCTURAL CHARACTERIZATION OF FLUORENONE IN ZEOLITE L BY SYNCHROTRON X-RAY POWDER DIFFRACTION

L. Gigli[1], G. Vezzalini[1], G. Agostini[2], C. Lamberti[2], R. Arletti[3], E. Fois[4], G. Tabacchi[4], S. Quartieri[5]

[1] Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Largo S. Eufemia 19, 41121 Modena Italy

[2] Dipartimento di Chimica Inorganica, Fisica e dei Materiali – Centro di Eccellenza NIS & INSTM, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

[3] Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy

[4] Dipartimento di Chimica e Scienze Ambientali & INSTM, Università dell'Insubria, Via Lucini 3, 22100 Como, Italy

[5] Dipartimento di Scienze della Terra, Università di Messina, Salita Sperone 31, 98166 Messina – S. Agata, Italy

Zeolite L (LTL framework type) is an appealing and excellent host for the supramolecular organization of different kinds of molecules and complexes. The capacity of this zeolite framework – characterized by monodimensional 12-ring channels – to induce an ordered geometrical arrangement of dye molecules, is used for the design of antenna systems and charge-transfer complexes [1-3]. Relatively few structural information is available about the orientation and alignment of the dye molecules in the zeolite pores [4], hence a detailed structural characterization is of great importance for understanding the functionality of these host-guest systems.

In this study, the neutral dye fluorenone (FL) was inserted – by using gas-phase adsorption under vacuum – into a synthetic potassium zeolite L, previously dehydrated so to assure that water molecules do not block the pathway for molecule entering [5]. Synchrotron X-ray powder diffraction experiments were performed at Gilda beamline (ESRF, Grenoble) on both dehydrated and FL-loaded zeolite L (FL-L). The diffraction data clearly evidenced the embedding of the dye into the channels, as well as the minor presence (7.4%) of fluorenone molecules on the zeolite surface. As a consequence, the structure of FL-L was determined by a two-phases Rietveld refinement in the hexagonal space group $P6/mmm$ [6].

The relevant incorporation of FL into the channels of dehydrated L was confirmed by a significant change of the unit cell parameters: 1.8 FL molecules per unit cell were located near the walls of the large 12-membered ring channel. A strong interaction between FL carbonyl group and the extraframework potassium cation is suggested by the short bond distances, and explains why FL is not displaced by water molecules when FL-L hybrid is re-exposed to the air.

Our experimental results are in agreements with those obtained by molecular dynamics simulations on a less loaded hybrid [4], and explain the high stability under ambient condition of this material.

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TRIOCTAHEDRAL MICAS IN XENOLITHS FROM RECENT VOLCANISM OF THE SOMMA-VESUVIUS (ITALY): CRYSTAL CHEMISTRY AND VOLCANOLOGICAL INFERENCES

M. Lacalamita[1], G. Balassone[2], E. Schingaro[1], F. Scordari[1], A. Mormone[3], M. Piochi[3], C. Petti[4]

[1] Dipartimento di Scienze della Terra e Geoambientali, Università di Bari, Via Orabona 4, 70125 Bari, Italy

[2] Dipartimento di Scienze della Terra, Università "Federico II", Via Mezzocannone 8, 80134 Napoli, Italy

[3] Osservatorio Vesuviano - INGV, Via Diocleziano 328, 80124 Napoli, Italy

[4] Centro Museale "Musei delle Scienze Naturali", Università "Federico II", Via Mezzocannone 8, 80134 Napoli, Italy

A systematic investigation of trioctahedral micas from xenoliths found as ejecta in recent volcanic deposits of the Somma-Vesuvius (Southern Italy) was undertaken to: 1) get the first full crystal chemical characterization of the Vesuvian micas; 2) shed light on the relationship between chemical and structural features of micas and petrogenesis/evolution of their host rocks. Three xenolith types were selected: metamorphic/metasomatic skarns, pyrometamorphic/hydrothermally altered nodules and mafic cumulates. They are associated to three historical eruptions characterized by different magma chemistry and effusive styles: from sub-plinian and most evolved (AD 1631 eruption) to violent strombolian with medium evolution degree (AD 1872 eruption) to vulcanian-effusive, least evolved (AD 1944 eruption) event [1], respectively.

The mica crystals were studied by electron probe microanalysis and single crystal X-ray diffraction, the xenoliths by X-ray fluorescence, inductively-coupled plasma-mass spectrometry, optical microscopy, X-ray powder diffraction, and quantitative energy-dispersive microanalysis.

In a Mg *vs*. Ca (wt.%) diagram, only one xenolith sample falls in the skarn compositional field from the Somma-Vesuvius literature [2-4], some fall close to the skarns and cumulate fields, others plot close to the syenite/foidite/essexite field. A subgroup of the selected ejecta does not fall or approach any of the compositional fields.

The Somma-Vesuvius micas of this study can be chemically gathered in three groups: Mg-, Al-rich, low Ti-bearing, low to moderate F-bearing crystals representative of the 1631 eruption (Group 1); Mg-, F-rich and Ti-, Fe-poor micas from the 1872 eruption (Group 2); Ti- and Fe-rich crystals from the 1944 ejecta (Group 3). All micas belong to the 1M polytype and have crystal chemical features consistent with the above subdivision into three groups. Specifically, Group 1 is characterized by c parameter ~ 10.24 Å, <M-O> (~ 2.072 Å) and <K-O> (~ 3.168 Å) distances; Group 2 has the lowest c lattice parameter of the whole suite (~ 10.14 Å), <M-O> (~ 2.061 Å) and <K-O> (~ 3.136 Å) distances; Group 3 is characterized by c lattice parameter, <M-O> and <K-O> distances varying in the ranges 10.2261(8)-10.2733(2) Å, 2.061-2.073 Å and 3.160-3.172 Å, respectively. Other structural details [5-6] evidence that Group 3 is the most affected by $M^{4+, 3+}$-oxy substitution mechanisms; Group 2 are fluorophlogopites; Group 1 is affected, to variable extent, by both oxy-type and $OH^- \rightarrow F^-$ substitutions.

The variability of micas chemical and structural parameters is consistent with the geological history of their host rocks. Particularly, fluorine and water activities seem significant parameters in controlling the overall micas crystal chemistry.

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ELASTIC BEHAVIOR AND HIGH PRESSURE-INDUCED PHASE TRANSITION IN CHABAZITE: NEW DATA FROM A SAMPLE FROM NOVA SCOTIA

L. Leardini[1], S. Quartieri[1], G. Vezzalini[2], A. Martucci[3], V. Dmitriev[4]

[1] Dipartimento di Scienze della Terra, Università di Messina, Viale Ferdinando Stagno d'Alcontres 31, 98166 Messina S. Agata, Italy

[2] Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Largo S. Eufemia, 19, 41100 Modena, Italy

[3] Dipartimento di Scienze della Terra, Università di Ferrara, Sez. Mineralogia, Petrografia e Geofisica, Via Saragat 1, 44100 Ferrara, Italy

[4] Swiss-Norwegian Beam Lines at ESRF, BP220, 38043 Grenoble Cedex, France

Recently, the high pressure (HP) behavior of a natural chabazite from Vallerano [1] (VALL), and on the synthetic phases SAPO-34 [1] and ALPO-34 [2], was investigated in the frame of a wider project aimed at understanding the role of the framework/extraframework content on the compressibility of CHA-type porous materials.

In this work, further structural information is obtained studying the response to HP of another natural chabazite sample from Nova Scotia (Canada) (NS) (s.g. *R*-3*mR* [3]), characterized by a different chemical composition with respect to VALL. The study was performed by means of *in situ* synchrotron X-ray powder diffraction (XRPD) and silicone oil as non-penetrating P-transmitting medium. XRPD experiments were performed in DAC at the BM01 beamline at ESRF (Grenoble, France) with a fixed $\lambda = 0.7355$ Å. Powder patterns were collected from P_{amb} up to 8.6 GPa and upon decompression. All the features of the P_{amb} pattern and the unit cell parameters are well recovered upon P release. Below 2.1 GPa, *a* and α cell parameters slightly decrease and increase respectively with a resulting volume reduction of 3.6%. Above 2.1 GPa, a transition to a triclinic *P*-1 pseudo-rhombohedral phase is observed.

The rhombohedral to triclinic phase transition is accompanied by an abrupt decrease in the unit cell parameters and in the unit cell volume ($\Delta V = -4.0\%$). Between 2.5 and 5.9 GPa, the triclinic/pseudo-rhombohedral cell parameters decrease regularly and the unit cell volume variation ($\Delta V = -3.0\%$) indicates a lower compressibility with respect to that observed before the transition. In the highest P regime (5.9-7.2 GPa), a further slope change, with an increase in compressibility, is observed. As a whole, ΔV between P_{amb} and 7.2 GPa is -12.6%. The elastic parameters, calculated with a second order BM-EoS, are $V_0 = 826$ (1) Å^3, $K_0 = 54(3)$ GPa and $V_0 = 784(2)$ Å^3, $K_0 = 91(5)$ GPa, for the rhombohedral and triclinic phase, respectively.

Preliminary results from Rietveld refinements up to about 1 GPa, suggest that the deformation mechanism acting in the low-P regime is a cooperative tilting of the tetrahedra belonging to the double 6-ring – resulting in a decrease of its thickness – accompanied by a simultaneous di-trigonalization of the two 6-rings. A similar mechanism was previously observed during compression of levyne [4].

The HP-induced cell volume contraction of NS (12.6 %) is higher than that of VALL (10.3%) in the same P range. This is congruent with the lower content in large extraframework potassium cations of NS, which contribute to sustain the porous structure in VALL.

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RAMAN SPECTROSCOPY IN Ca,Co PYROXENES:
A MODEL FOR STRUCTURE AND COMPOSITION IN SILICATES

L. Mantovani[1], M. Tribaudino[1], D. Bersani[1], P.P. Lottici[1], G.D. Bromiley[2]

[1] Dipartimento di Fisica e Scienze della Terra "M. Melloni", Università di Parma, Via G.P. Usberti 157/A, 43124 Parma, Italy
[2] School of Geosciences, University of Edinburgh, Grant Institute, West Main Road, Edinburgh EH9 3JW, UK

Pyroxenes are among the most abundant major rock-forming minerals. They have a relatively simple structure allowing a wide range of chemical substitutions. The silicate chain provides a simple structural feature to model the effect of deformation in silicates, and the polyhedra that build up the pyroxene structure show different degrees of flexibility, so that the effects of chemical substitution on different cation polyhedra can be ascertained.

One of the most intriguing features in pyroxenes is the substitution of smaller cations onto the M2 polyhedron, which in $C2/c$ pyroxenes generally hosts a larger cation like Na or Ca. An example is given by the series diopside-enstatite ($CaMgSi_2O_6$-$Mg_2Si_2O_6$). Along this series the substitution of Ca by Mg promotes the formation of a miscibility gap (the basis for the two pyroxene thermometry) and, at hypersolvus conditions, gives rise to a phase transition between $C2/c$ and $P2_1/c$ pyroxenes. Raman spectra of the diopside-enstatite series show a one-mode behaviour, and changes in peak positions are related with structural features, like tetrahedral chain kinking angles and average bond lengths [1]. Here we will examine the results of the companion series $CaCoSi_2O_6$-$Co_2Si_2O_6$. In this series the replacement of Ca by Co, with cation radius similar to that of Mg (0.745 vs. 0.72 Å), is expected to result in a similar change structure to the replacement of Ca by Mg, although owing to significantly different masses the effect in Raman spectrum has to be verified.

A series of samples with compositions between $CaCoSi_2O_6$ and $Co_2Si_2O_6$ were synthesized at P = 3 GPa and T = 1200-1350 °C using a piston-cylinder apparatus. Additional synthesis experiments were performed in order to obtain single crystals of composition $Ca_{0.8}Co_{1.2}Si_2O_6$, $Ca_{0.6}Co_{1.4}Si_2O_6$ and $Ca_{0.4}Co_{1.6}Si_2O_6$, which were then studied by single crystal XRD. Raman spectra were obtained from all the samples.

As expected, changes in the atomic structure were close to those found for the Ca-Mg substitution in the M2 site. The Raman spectrum in CaCo pyroxenes is also similar to that of CaMg ones; a significant change in the peak position vs. composition was observed at the composition $Ca_{0.4}Co_{1.6}Si_2O_6$, for peaks between 300 and 500 cm^{-1} and at the composition $Ca_{0.2}Co_{1.8}Si_2O_6$ for the peaks at 660 and 1000 cm^{-1}. These changes were related to the transition from C to P lattice. However, splitting of the 660 cm^{-1} peak previously ascribed to the presence of symmetrically distinct chains in $P2_1/c$ pyroxenes, was not found, as has been note in clinoferrosilite ($Fe_2Si_2O_6$). A comparison of changes of peak position with composition in Raman spectra of CaCo and CaMg pyroxenes also shows a different trend. For instance, the peak at 1010 cm^{-1}, which does not change for Ca-Mg substitution, shifts by as much as 20 cm^{-1} between $CaCoSi_2O_6$ and $Co_2Si_2O_6$. The effect of similar structural changes in chain kinking and polyhedral deformation on Raman peak positions is also different, although qualitatively similar.

This point is discussed in terms of the interplay between the effect of mass and structure changes on the Raman spectra. Careful analysis has yet to be performed to separate the two effects, also taking into account the fact that the modes often involve contributions from several atoms in the structure.

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HP *AB-INITIO* STUDY OF DOLOMITE COMPRESSIBILITY
AS INFLUENCED BY CATION DISORDERING

A. Zucchini[1], P. Comodi[1], S. Nazzareni[1], M. Prencipe[2]

[1] Dipartimento di Scienze della Terra, Università di Perugia, Piazza dell'Università 1, 06123 Perugia, Italy

[2] Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy

Dolomite $[CaMg(CO_3)_2]$ is the most abundant double carbonate in nature. A fully ordered dolomite consists of alternated calcium and magnesium layers separated by carbonate groups (CO_3^{2-}); disordered cationic configurations can arise as Ca and Mg randomly distribute over dolomite crystallographic sites. The stability field of dolomite extends from sedimentary up to high temperature (HT) - high pressure (HP) conditions being the mineral stable at mantle conditions down to approximately 250 km depending on the rate of subduction as well as on the crystallographic characteristics of the mineral, *i.e.* the dolomite stability field is contracted as cation disorder arises in the dolomite structure [1]. However, experiments at HP conditions on the compressional behaviour of disordered dolomite have not been performed since the non-quenchability of disordered crystal structures [2, 3]. Therefore, an *ab initio* study was carried out in order to analyse the baric behaviour of differently ordered dolomites.

Two configurations were used, a fully-ordered dolomite (SC1) and a partially-disordered one (SC4895) characterized by an order parameter [2] $s = 0.5$, as these have been account as the most probable configurations at lower and higher T respectively [4]. Total static energy calculations were performed at the hybrid Hartree-Fock/Density-Functional-Theory level by means of CRYSTAL09 code [5]. Volume cell variations and energy minimization at each optimized geometry were performed. The corresponding P range was approximately 0-13 GPa.

Mean linear compressibility of *a* and *c* axes shows a strong anisotropy (*c/a* compressibility ratio is approximately 3:1). P-V data were fitted by a third order Birch-Murnaghan Equation of State and results were $K_0 = 93.4$ GPa ($K_0' = 4.7$) for the ordered configurations and $K_0 = 92.3$ GPa ($K_0' = 4.4$) for the disordered one. They become $K_0 = 95.9$ GPa and $K_0 = 93.9$ GPa respectively, when K_0' is fixed to 4.

Notwithstanding SC4895 is not a completely-disordered configuration due to computational issues [4], it has a lower bulk modulus with respect to the ordered phase. Thus, cation disordering seems to act in slightly increasing volume compressibility of dolomite.

Our previous studies [4] have shown that an intra-layer type disordering is the most probable driving mechanism for cation distribution in dolomite as T increases. Therefore, we can hereby speculate that the thermal structure of subduction zones, affecting the order/disorder conditions of dolomite, plays a fundamental rule on the compressional behaviour of the mineral during the subduction. This should influence the decarbonation conditions and, in turn, the release of carbon from the slab to the mantle wedge at subduction zones.

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