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LOCAL ENVIRONMENT AROUND Sn IN HYDROUS GLASSES: INFLUENCE OF REDOX AND MELT STRUCTURE

François Farges (farges@univ-mlv.fr)¹ & Robert Linnen (rlinnen@sciborg.uwaterloo.ca)²

¹ Labo des Géomatériaux, Université de Marne la Vallée, 5 Blvd Descartes, Champs S/Marne, 77454 Marne la Vallée cedex 2, FRANCE

² Dept. of Earth Sciences, University of Waterloo, WATERLOO, N2L 3G1, Ontario, Canada

In order to better understand the effect of melt structure (peralkalinity, water, pressure) on the transport mechanisms of Sn in granitic melts, we undertook x-ray absorption fine structure (XAFS) experiments at the Sn K-edge in a variety of crystalline model compounds and glasses. The Sn-bearing models investigated included two cassiterites (SnO₂, from Bolivia and Malaysia), eakerite, various perovskite-based polymorphs (SnSrO₃, CaSnO₃ and CdSnO₂) as well as SnO, SnCl₂ and metallic Sn. The glasses studied are all water-saturated. Three glass samples were quenched from an haplogranitic melt (ASI series): peralkaline (Al/(Na+K)=0.6), metaluminous (1.0) and peraluminous (1.2). The tin contents of the ASI 0.6, ASI 1.0 and ASI 1.2 samples are 0.95, 0.1 and 0.19% SnO₂, respectively, with predicted proportions of Sn(IV) of 90%, 10% and 20%, respectively. The SQ series was synthesized under the same conditions but at ~FMQ+1.1, whereas the third series (AL) was synthesized at CRPG (Nancy, France) at ~FMQ+2.4. The tin contents of the AL 0.6, AL 1.0 and AL 1.2 compositions are 1.04%, 420 ppm and 520 ppm SnO₂, respectively, with predicted proportions of Sn(IV) of >90%, 30% and 50% Sn(IV), respectively. Finally, the GB glasses were synthesized under conditions that were "in-between" Al and SQ series. The SnO₂ contents of the 0.6, 1.0 and 1.2 glasses are: 1.0%, 0.6% and 0.6% SnO₂, respectively. X-ray absorption fine structure (XAFS) spectra were collected (293 K) at the Stanford Synchrotron Radiation Laboratory (Stanford, USA) using spectrometer 4-1 at the Sn K-edge (~30 keV), using a Si(220) double crystal monochromator, a Stern-Held-type fluorescence detector filled with Xe. Most glasses show Sn K-edge XAFS spectra that resemble to those collected in eakerite, a calcium-tin silicate in, which Sn(IV)O₆⁸⁻ octahedra share corners (<Sn-O-Si> 150°) with SiO₄⁴⁻ tetrahedra. However, the most reduced glasses show significant contributions arising from weakly bounded Sn(II)O_n complexes. From the obtained spectroscopic data, we will try to correlate the structural information to the geochemical properties of Sn.

A HIGH-P EXPERIMENTAL STUDY OF METASOMATIC PROCESSES AT METABAUXITE-MARBLE CONTACTS INDUCED BY DIASPORE DEHYDRATION

Anne Feenstra (feenstra@gfz-potsdam.de) & Bernd Wunder (wunder@gfz-potsdam.de)

GeoForschungsZentrum Potsdam, Division 4, Telegrafenberg, D-14473 Potsdam, Germany

During prograde greenschist/eclogite-facies metamorphism, bauxites undergo a pronounced dehydration related to the breakdown of their major phase diasporite (α-AlOOH) into corundum (α-Al₂O₃) and water. In an average karstbauxite, such as occurring on the island of Naxos (Greece), 6-8 wt% H₂O is released during this phase transition (Feenstra, 1985;

Urai & Feenstra, 2001). We studied experimentally the karst-bauxite dehydration in a piston-cylinder press (up to 40 kbar) using natural fine-grained diasporite dominated by diasporite and Ti-hematite and containing minor rutile, muscovite and paragonite. To mimic nature we embedded the diasporite in either dolomite or calcite marble (Feenstra & Wunder, in press). Overstepping the diasporite-corundum reaction by 40-120°C during 4-7 days resulted in complete transformation of diasporite into corundite. A high-porosity zone containing corundum and various silicates invariably developed along the bauxitic side of the lithologic contact. It results from the solid volume decreases associated with the diasporite-corundum dehydration (-28%) as well as additional decarbonation reactions. At P * 24 kbar, chloritoid, muscovite, paragonite and biotite occur in the porous contact zone; in the 30 and 40 kbar runs, staurolite, Fe-Ca-Mg garnet, and muscovite (using calcite marble) or biotite (using dolomite marble) formed. Petrologic and mineral chemistry data indicate that Si and alkalis have been transported out of the metabauxite towards the contact, whereas Ca and Mg now included in garnet and Mg in biotite and staurolite, have been derived by local breakdown of carbonate. Reactions leading to the mineralogy in the metasomatic zone will be discussed. Mineral chemistry and element (Fe-Mg) partitioning in the metabauxitic (Al-excess) system will be compared with data reported in the literature.

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DETERMINATION OF THE REACTION KINETICS AND REACTION MECHANISMS OF CALCIUM-SILICATE-HYDRATES BY MEANS OF IN-SITU NEUTRON DIFFRACTION

Karl Thomas Fehr (fehr@petrol.min.uni-muenchen.de)¹, Siegfried Zürn (zuern@petrol.min.uni-muenchen.de), Michael Huber (huber@petrol.min.uni-muenchen.de) & Thomas Hansen (hansen@ill.fr)²

¹ Institute of Mineralogy, Petrology & Geochemistry, Theresienstr. 41, 80333 Munich, Germany

² Institute Laue-Langevin, 6, rue Jules Horowitz, BP 156 - 38042 Grenoble Cedex 9, France

Calcium-Silicate-Hydrates (CSH-phases) are formed during the hydrothermal treatment (autoclaving) of ground quartz sand, quicklime and water to produce steam cured building materials. 1.13 nm tobermorite is the predominant CSH-phase in aerated autoclaved concrete with semi-crystalline CSH I and CSH II as minor components. The major aim of our investigations was to determine in-situ reaction mechanism and kinetics of the formation of 1.13 nm tobermorite. Neutron diffraction has the capacity to collect data of the reaction progress in-situ. An autoclave cell has been designed (Fehr et al., 2002) for performing time-resolved neutron diffraction analyses (1 minute) of the dynamic processes during the hydrothermal reactions. Experiments were conducted at 190 to 210°C under saturation pressure and within a time-range of 6 hours. In the experiments the amount of quartz decreases with time. The fraction of poorly crystallized CSH-phases rises to a maximum of 36 wt% in 31/2 hours and decreases with the time by continuous crystallisation of 1.13 nm tobermorite. Tobermorite is not formed initially but by the reaction of poorly crystallized CSH-

phases with quartz. The precursor CSH-phases are more Ca-rich and vary in their Ca/Si in the range of 1.1 to 1.3, characteristic for poorly crystalline phase C-S-H (I) displaying no constant Ca/Si due to its disordered structure. The primarily crystallized tobermorite display (hk0)-reflections only, implying the existence of ab-planes. With increasing time the ab-planes of 1.13 nm tobermorite are forming stacks along the c-axis, indicated by the existence of a (002)-reflection. The mechanism of the reaction can be described by the reaction conversion of quartz according to Chan et al. (1978). In this early stage of the hydrothermal hardening process the reaction is determined by the solution of quartz. The reaction kinetics can be described according to an Avrami equation and the reaction rate can be calculated to $k = 0.1017(52)$ at 190°C.

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EXPERIMENTS ON THE PETROGENESIS OF PLAGIOGRANITES BY PARTIAL MELTING OF OCEANIC GABBROS

**Sandrin Feig (sandrin.feig@gmx.de)¹,
Jürgen Koepke¹, Francois Holtz¹ &
Jonathan Snow (jesnow@mpch-mainz.mpg.de)²**

¹ Institut fuer Mineralogie, Uni Hannover, Welfengarten 1, 30167 Hannover, Germany

² Max-Planck-Institut fuer Chemie, Postfach 3060, 55020 Mainz, Germany

Within the gabbroic section of the oceanic crust occur small amounts of so-called plagiogranites. One model of their generation is the partial melting of pre-existing gabbros within high temperature shear zones (e.g., Flagler and Spry, 1991). In this study, the mechanism of generation of SiO₂-rich melts by partial melting in the oceanic crust is investigated by systematic partial melting experiments on oceanic gabbros (at 0.2 GPa, temperatures of 900°C to 1100°C, oxygen fugacity of ~NNO). Starting material were 3 oceanic gabbros drilled at the ODP Legs 176 (Southwest Indian Ridge) and 153 (Mid-Atlantic-Ridge). Since many plagiogranites contain amphibole as mafic phase indicating a high water activity, the partial melting experiments were carried out under water-saturated conditions. Performing partial melting experiments on natural rocks is problematic due to un-reacted crystals of the starting material (Johannes and Koepke, 2001). Therefore, the powdered starting material was classified into charges of different grain sizes using the Atterberg method (<2µm, 2-10µm and >10µm) which were used for the partial melting experiments. Best results were obtained using the grain size 2-10 µm. Chemical analyses of this charge showed that the composition is the same as that of the bulk rock indicating that no chemical fractionation due to the Atterberg separation occurred. The experiments were performed in internally heated pressure vessels (IHPV) equipped with a hydrogen membrane for controlling the oxygen fugacity and a rapid-quench system which is used to prevent the formation of quench crystals. A problem is the Fe-loss by diffusion into the capsule material at high temperatures. To prevent this we used gold as capsule material up to temperatures of 1020°C where Fe-loss was negligible. For experiments at higher temperatures we used AuPd-capsules pre-saturated in Fe. First results are shown.

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PETROLOGIC AND FLUID INCLUSION STUDY OF AN OH-RICH TOPAZ-BEARING KYANITE QUARTZITE FROM SULU UHP TERRANE, EASTERN CHINA

**Simona Ferrando (ferrando@dsmp.unito.it)¹, Maria Luce Frezzotti (frezzottiml@unisi.it)²,
Augusta Alberico (augusta@dsmp.unito.it)¹ &
Roberto Compagnoni (compagn@dsmp.unito.it)¹**

¹ Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, Via Valperga Caluso, 35, I-10125 Torino, Italy

² Dipartimento di Scienze della Terra, Università di Siena, Via Laterina, 8, I-53100 Siena, Italy

OH-rich topaz in kyanite quartzites has been recently reported by Zhang and Liou (1999) at Hushan, in the ultrahigh-pressure (UHPM) Sulu orogen, China. Quartzites consist of quartz/(coesite), kyanite, topaz, barite, accessory rutile, a Fe-sulphide, zircon and apatite, and retrograde paragonite. A microprobe and crystallographic study (Alberico et al., 2002) indicates that topaz has a high OH-content ($X_{OH} = 0.31$), similar to that of a topaz ($X_{OH} = 0.29$) synthesized by Wunder et al. (1999) at $T = 800^\circ\text{C}$, $P = 1.57$ GPa.

OH-rich topaz clearly overgrows kyanite; it includes rutile, zircon and abundant aqueo-carbonic fluid inclusions. Fluid inclusions have a clear primary (in the sense of Roedder, 1984) distribution, are relatively small (5-8 µm across), and have rounded or negative crystal shapes. The CO₂ phase constitutes from 10 to 30% of the inclusion total volume. Microthermometry indicates that T_{HCO_2} ranges between 17.7 and 30°C. This corresponds to water dominated H₂O-CO₂ mixtures ($X_{H_2O} = 0.96$) and to a total H₂O-CO₂ fluid density of about 0.98 g/cm³. Assuming a peak temperature of 800 ± 80°C, estimated from the associated coesite-eclogites (Zhang et al., 2000), the calculated fluid isochores correspond to high-pressure conditions of 1.6 - 1.7 GPa, and similar to the values obtained from experimental studies (Wunder et al., 1999).

Present results suggest that influx of water-dominated fluids occurred in kyanite quartzites and was responsible for the crystallization of OH-rich topaz. Although microstructural relationships indicate that topaz developed later than the UHPM peak assemblage, water-rich fluid movements must have occurred at $P \geq 16$ GPa, i.e. during an early stage of the decompression history.

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A NEW TYPE OF NANO-EXSOLUTION IN UHP PHENGITE FROM THE DORA-MAIRA MASSIF, WESTERN ALPS, ITALY

Cristiano Ferraris (ferraris@unisi.it)¹,
Daniele Castelli (castelli@dsmp.unito.it)² &
Bruno Lombardo (lombardo@dsmp.unito.it)³

¹ Dipartimento di Scienze della Terra, Via Laterina 8, I-53100 Siena, Italy

² Dipartimento di Scienze Mineralogiche e Petrologiche and C.N.R., Istituto di Geoscienze e Georisorse - Sezione di Torino, Via Valperga Caluso 35, I-10125 Torino, Italy

³ C.N.R., Istituto di Geoscienze e Georisorse - Sezione di Torino, Via Valperga Caluso 35, I-10125 Torino, Italy

Transmission and Analytical Electron Microscopy investigations of phengite from an impure marble of the ultra-high pressure (UHP) Brossasco-Isasca Unit (Dora-Maira Massif, western Alps) reveal a complex nano-structure. Diffraction patterns taken along [010] show that this phengite is a highly ordered 3T polytype. However, a close inspection of the diffraction spots reveals that, for some classes of crystallographic indexes, four diffuse and weak satellite spots surround a central strong spot in the shape of an X. At higher angles only two diffuse satellite spots are visible. In bright-field images, areas of mottled contrast clearly cross the phengite lamellae that represent the matrix sample. The areas of mottled contrast are about 20 nm wide and *ca.* 40° inclined on the (001) of the phengite matrix. The Si content in the matrix phengite (3.47 to 3.51 a.p.f.u.) is higher than that of the exsolved phengite domains which show 3.39-3.42 Si a.p.f.u. The Fe/Mg ratio is 0.20-0.26 in the matrix and 0.43-0.47 in the exsolved areas.

As the presence of both the satellite spots and the spatially ordered mottled contrast is indicative of an exsolution process within the ordered matrix (Ferraris et al., 2001), the above effects are due to the presence of areas of exsolved phengite which differs from the matrix phengite by small differences in the β angle and in both the octahedral and tetrahedral cation content.

To our knowledge, this exsolution process in UHP phengite has never been described before and is different from that described for UHP Fe-free phengite by Ferraris et al. (2000), in which no mottled contrast was noted. The higher content of Fe and the lower content of Si in the exsolved areas suggest that the exsolution has been triggered by some instability of the octahedral iron in a highly Si-rich phengite during decompression.

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NEAR-SOLIDUS PHASE RELATIONSHIPS IN METAPELITES TO 1 GPa

Fabio Ferri (fabio.ferri@unimi.it)¹, **Stefano Poli** (stefano.poli@unimi.it)¹ & **Daniel Vielzeuf** (d.vielzeuf@opgc.univ-bpclermont.fr)

¹ Dipartimento Scienze della Terra, Università di Milano, via Botticelli, 23, 20133 Milano, Italy

² Laboratoire Magmas et Volcans, Université Blaise Pascal - CNRS, rue Kessler, 5, 63038 Clermont Ferrand, France

The transition from amphibolite to granulite facies conditions in metasediments at intermediate pressure is still poorly defined and contradictions persist in currently available petrogenetic grids.

Phase relationships in metapelites are investigated on four synthetic compositions in the model system CaO-K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O. Experiments were carried out in a piston cylinder apparatus at pressures and temperatures up to 1.0 GPa and to 730°C, and in an internally heated pressure vessel at 0.8 GPa at temperatures up to 730°C. In order to monitor the effect of H₂O saturation and fluid speciation, three different charges were loaded for each bulk composition, two at fluid saturated conditions and fO₂ buffered either by graphite or by NNO and one with H₂O added as Al(OH)₃ at graphite oxygen buffer conditions. Experiments were characterized by XRD, BSE images and EMPA. All assemblages contain quartz and anorthite. Garnet + staurolite + biotite \pm orthoamphibole \pm muscovite are stable at 650°C and 700°C. At 700°C and 1.0 GPa, cordierite is also present whereas at 620°C and 0.8 GPa only staurolite-biotite pair is stable. Orthoamphibole is of gedrite type containing 2.0 a.p.f.u. (23 O) of Al at 650°C and 2.5 a.p.f.u. at 700°C. Garnet has grossular and pyrope fractions of 0.1 and 0.2 respectively all over the pressure-temperature range. The Al content in biotite decreases with temperature from 1.8 a.p.f.u. (11 O) at 620°C to 1.5 a.p.f.u. at 700°C. On the basis of phase relations experimentally determined by Poli & Schmidt (2002) and by Vielzeuf & Schmidt (2001), and of natural occurrences of amphibole bearing assemblages in metasediments (Hudson & Harte, 1985), Schreinemaker's rules are used to unravel our new data, considering that Mg/(Mg+Fe) increases in the order:

staurolite \leq garnet $<$ orthoamphibole $<$ biotite $<$ cordierite.

At higher temperatures, orthoamphibole may be directly involved in the production of melt through fluid present or fluid absent melting reactions.

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CRYSTAL CHEMISTRY OF TETRAHEDRITES REVISITED: CONSIDERATIONS ON SIGNIFICANT GEOCHEMICAL OUTPUTS

Ondina Figueiredo (crysmin@clix.pt)¹ & Jorge Ferreira (jorge.ferreira@igm.pt)²

¹ Crystallography and Mineralogy Centre, Al. Afonso Henriques, 41-4°, 1000-123 Lisboa, Portugal

² Geological and Mining Institute, Lab, Rua da Amieira, 4466-956 S. Mamede de Infesta, Portugal

The crystal chemistry of tetrahedrites - important silver ores - has been repeatedly object of contributions (e.g., Johnson et al., 1988), being well established that its tetrahedral M-S framework (M=Cu,Fe,Hg,Zn...) can be related to that of silicates in sodalite. Tetrahedrite crystal structure may otherwise be described as a cubic closest packing of S anions where a cluster of four tetrahedrally arranged vacancies is replaced by a single S atom and where half of the available tetrahedral interstices are filled up. The extra S-atom provides pyramidal and triangular coordinations respectively to four Sb/As/Te and six Cu/Ag ions hosted in former tetrahedral sites assuming a non-lacunar closest packing. Such structural relationship may provide a clue for understanding the morphotropic domain of tetrahedrites and their geochemical behaviour - that is, the set of chemical elements in the periodic table that may occupy each one of the available structural positions. Furthermore, deviations from stoichiometry in tetrahedrite solid solutions and compositiona variations (Foit and Ulbricht, 2001) so far considered anomalous may be explained by taking into account other ideally available sites within the original non-lacunar cubic closest packing. This refreshed crystal chemical insight also emphasizes the important role played by spectroscopic studies (e.g., Patrick et al., 1993) and solid state physics concepts (like the Brioullin-zone model, Johnson and Jeanloz, 1983) as contributions for a comprehensive interpretation of tetrahedrite behaviour in geochemical sulphide differentiation. A prospective approach to significant contributions of X-ray absorption spectroscopies to the mineral chemistry of complex sulphides will be mentioned.

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THE SOLUBILITY OF NATURAL WOLLASTONITE IN PURE WATER UP TO 5 GPa AND 800°C: AN EXPERIMENTAL INVESTIGATION

Thomas Fockenberg (thomas.fockenberg@ruhr-uni-bochum.de) & Gross Juliane

Institut fuer Geologie, Mineralogie und Geophysik, Ruhr-Universitaet Bochum, D-44780 Bochum, Germany

The solubility of natural wollastonite (Ca₃[Si₃O₉] (specimen from Kropfmühl, Bayerischer Wald, Germany) in bi-distilled water was determined in piston-cylinder presses. Wollastonite single crystals were emplaced in cold sealed gold capsules together with large amounts of water (weights: wollastonite < 10 mg; water: 90-130 mg). During the pressurisation phase of

the runs negligible water losses occurred which were taken into account by the determination of the solubility by the method of weight losses of the crystals.

Weight losses of less than 0.5 wt.-% were determined at 1 GPa; at higher pressures of 1.5 and 2 GPa these losses occurred to be between 0.4 and 1 wt.-% and 0.6 - 2.6 wt.-%, respectively. A positive correlation between solubility and run pressure or temperature was observed. Surprisingly at 5 GPa the solubility was almost independent of the run temperatures. When plotted in a log m_{woll} versus run pressure diagram the fitted curves for each temperature exhibit a decrease in solubility at these high pressures. As these P-T conditions lie well within the stability field of the high-pressure polymorph wollastonite-II with a Si₃O₉-ring structure, a drastically different behaviour in the solubility can be deduced.

The wollastonite single crystals are mostly translucent at the end of the runs as the starting material; traces of quenched material on the surfaces were sometimes absorbed. Depending on the rate of solution the edges of the crystals are more or less rounded. The quenched phase forms either whisker crystals with lengths up to 100 µm or very small spherical nodules. Semi-quantitative chemical analyses performed at an SEM showed that this material is rather homogeneous with an average composition close to that of wollastonite indicating that this mineral solutes congruently.

A RESTRICTED ROLE FOR ECLOGITES IN ARCHEAN SUBDUCTION

Stephen Foley (sfoley@uni-greifswald.de)¹, Stephan Buhre² & Dorrit Jacob¹

¹ Geological Sciences, Universität Greifswald, Jahnstrasse 17a, Greifswald, Germany

² Institut für Mineralogie, Universität Frankfurt, Senckenberganlage 28, 60054 Frankfurt-am-Main, Germany

The bulk oceanic crust has probably changed in composition from komatiitic in the early Archean through picritic in the late Archean, to basaltic in the Phanerozoic. However, the only experiments investigating metamorphic reactions during subduction have considered modern MORB. Our experiments on Gorgona and Belingwe komatiites show that all metamorphic products are plagioclase-free and that the incoming of garnet lies at higher pressures than for MORB. Any MgO-rich parts of the Archean ocean crust will transform to types of pyroxenite or lherzolite. These rocks would neither undergo a sudden increase in density during subduction, nor would they partially melt to continental crust-like compositions.

On a cooling Earth, the MgO-content of the bulk oceanic crust decreases with time, so that the garnet-in curve moves to progressively lower pressures and higher temperatures. In contrast, the subduction geotherm moves to higher pressures and lower temperatures, so that the two curves converge with time. The metamorphic and melting behaviour during subduction depends critically on the degree of magmatic differentiation at the mid-ocean ridge. Although the oceanic plateau model for Archean ocean crust predicts abundant basalts and gabbros, these would cause the production of abundant SiO₂-rich melts, which does not agree with most crustal abundance curves for the early Archean. Furthermore, the Zr/Sm and Nb/Ta ratios of the bulk continental crust cannot be explained by melting of eclogite, but correspond instead to melting of

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garnet amphibolite. It may be more likely that partial melting of the oceanic crust as eclogite was volumetrically unimportant in the early Archean, and that the melting of garnet amphibolite first became prevalent in the late Archean. This corresponds to the increase in continental crustal mass between 3.2 and 2.5 Ga, and agrees with the evidence in eclogite xenoliths of this age for them having partially melted in the amphibolite facies.

LOW STRAIN RATE EXPERIMENTAL DEFORMATION OF SMALL GRAINS OF OMPHACITE DURING ITS RETROMORPHIC DESTABILIZATION

Frédéric Foucard (foucard@cict.fr), Olivier Jaoul (jaoul@cict.fr) & Jannick Ingrin (ingrin@cict.fr)
LMTG-UMR5563, 39 allées Jules Guesde, 31000 Toulouse, France

In order to better constrain the rheological behaviour of eclogites we performed creep experiments for months on omphacite polycrystals outside its stability field. Deformation experiments were realized at room pressure in a dead load apparatus especially developed for very low strain rates, at relatively low temperatures so as to reduce destabilization of omphacite. Synthetic iron-free omphacite glass (Jd50-Di50) was prepared from elementary oxides and subsequently sintered and recrystallized in a piston-cylinder at 1000°C and 2 GPa for about 6 days. Samples were recovered free of crack. X-ray and electron microprobe prove specimens to be homogeneous omphacite. Grain size is about 4 ± 2 μm (TEM). We checked that deformation did not induce dynamic recrystallization. Experimental deformation rates on $2\times 2\times 5$ mm³ blocks were 10^{10} to 10^{-6} s⁻¹, for T = 800-1000°C and axial compressive stresses 100-350 MPa. Data from 6 samples show two different domains. 1) At $T \leq 900^\circ\text{C}$: a deformation mechanism with low activation energy $E = 300 \pm 100$ kJ.mol⁻¹. This regime is sensitive to the experimental duration, thus probably to the rate of destabilisation. It disappears after $\leq 1\%$ total deformation in a material that has remained omphacite to 90% or more. Diffusion creep with a such low activation energy (Coble mechanism) is a good candidate for small grain omphacite before it significantly destabilizes. This first behaviour is followed (after $\geq 1\%$ total deformation) by a second mechanism at same T but with lower strain rates. E is about 500 kJ.mol⁻¹ and the stress exponent close to 1. Diffusion creep along grain boundary made of destabilized omphacite could be invoked. 2) At $T \geq 900^\circ\text{C}$, we find $E = 750$ kJ.mol⁻¹ and stress exponent between 2 and 3. This behaviour is identical to what is observed in a fully destabilized omphacite sample, and has same E as pure diopside.

WATER DIFFUSION IN A TRACHYTIC MELT

Carmela Freda (freda@ingv.it)¹, Don R. Baker², Claudia Romano³ & Piergiorgio Scarlato¹

¹ Istituto Nazionale di Geofisica e Vulcanologia, Via di Vigna Murata, 605 - 00143 - Roma, Italy

² Department of Earth and Planetary Sciences, McGill University, 3450 University Street - Montreal H3A 2A7, Canada

³ Dipartimento di Scienze Geologiche, Università degli Studi di Roma Tre, Largo San Leonardo Murialdo, 1 - 00146 - Roma, Italy

The important role played by volatile diffusion in bubble growth dynamics makes knowledge of H₂O and CO₂ diffusivity essential to model volatile exsolution from magmas. Previous experimental studies devoted to volatile diffusion determination used almost exclusively rhyolitic melts. However, some extremely dangerous volcanoes belong to the potassic alkaline series (e.g., Vesuvius and Phlegrean Fields, in Italy). As part of a project devoted to the study of potassic magmas' properties, we determined the water diffusivity in a trachytic composition from the Agnano-Monte Spina explosive eruption. This eruption was the highest magnitude event at the Phlegrean Fields during the last 5000 years and is considered the upper limit for the next explosive episode expected in the area.

Water diffusion experiments were run in a piston cylinder at P=1 GPa, different temperatures (from 1100 to 1400°C), and durations (from 0 to 1800 s), using the diffusion couple technique. The H₂O concentration profiles were measured by FTIR. Water diffusivities at different temperatures and water concentrations were calculated following the Boltzmann-Matano technique.

In the investigated range of temperatures and water concentrations the diffusivity of water in potassic melts can be described by Arrhenius equations that can be generalized for the calculation of water diffusion at concentrations between 0.25 and 2 wt% as follows: $D_{\text{water}} = \exp(-11.924 - 1.003 \ln C) \exp(-(\exp(11.836 - 0.139 \ln C))/RT)$, where C is the water concentration in wt%, R equals 8.3145 (J K⁻¹ mol⁻¹) and T is the temperature in Kelvin.

Our results demonstrate that water diffusion in trachytic melts is higher than in haplogranite and lower than in basalt. In addition, the activation energies for water diffusivity in trachyte and basalt are comparable, and higher than that in haplogranite. However, water diffusion coefficients in all melts appear to converge at lower (900-1000°C) temperatures and strongly diverge at higher ones (1400°C).

EMPG IX

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THE EFFECT OF fO_2 ON THE DIFFERENTIATION OF LIP-BASALTS FROM THE KERGUELEN ARCHIPELAGO. AN EXPERIMENTAL STUDY

Marcus Freise (m.freise@mineralogie.uni-hannover.de)¹, Francois Holtz (fholtz@mineralogie.uni-hannover.de), Jürgen Koepke (koepke@mineralogie.uni-hannover.de) & Dimitri Damasceno (ddamasce@ulb.ac.be)²

¹ Institut für Mineralogie, Universität Hannover, Welfengarten 1, D-30167 Hannover, Germany

² Department of Earth Environmental Sciences (DSTE), CP 160/02, Université Libre de Bruxelles, Avenue F.D. Roosevelt 50, B-1050 Brussels, Belgium

Phase relations of a alkali basalt from the "large igneous province" Kerguelen Plateau have been investigated experimentally to understand the effect of fO_2 on the differentiation path of LIP-basalts. The starting rock sample (OB93-190) from the Mt. Crozier (Damasceno et al., 1999) show the typical geochemical signature of the Kerguelen plume (Weis et al., 1993). OB93-190 is an alkali basalt with ~ 4.4% phenocrysts of pl+cpx+ol, relatively low alkali contents ($Na_2O+K_2O = 4.36$) and it is one of the most Mg-rich samples ($MgO = 5.79$ wt.%) of the whole area. The comparison of the natural phenocryst assemblage with the experimental products are used to constrain the differentiation and pre-eruptive conditions of this magma.

Equilibrium crystallisation experiments were performed for 1 day, $P = 500$ MPa, $T = 950 - 1150^\circ\text{C}$ using dry glasses, water and $Ag_2C_2O_4$ (source for CO_2) as starting materials. Various X_{H_2O} were used to change the water activity during the experiments. The experiments were conducted in an Internally-heated-pressure-vessel (IHPV) equipped with a rapid-quench system and Shaw-membrane technique used to control the oxygen fugacity during the experiments.

We show that the experimental phase assemblage for OB93-190 obtained at oxidizing conditions ($\log fO_2 = NNO+3.7$) reproduces the compositions of the natural minerals. At this fO_2 the observed phase assemblage was: magnetite, clinopyroxene, ilmenite, amphibole, plagioclase and olivine (minerals given in the order of appearance with decreasing T from 1150°C to 950°C at 500 MPa for 3 wt.% water in the melt). The oxygen fugacity calculated for ilmenite/magnetite pairs (QUILF) of the natural rock is around $NNO+3$ and therefore in agreement with the oxygen fugacity estimated by the phase compositions of the experimental phases. In contrast to experiments on MORB, amphibole found to be stable down to low water contents of the melt (2 to 3 wt.% H_2O).

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THERMOBAROMETRY OF GLAUCOPHANE ECLOGITES FROM THE MAKSYUTOV COMPLEX (SOUTH URALS)

Anton Frenkel (fanton@uiggm.nsc.ru), Nina Volkova (nvolkova@uiggm.nsc.ru) & Andrei Korsakov (korsakov@uiggm.nsc.ru)
Institute of Mineralogy and Petrography of SB RAS, Pr.Koptyuga, 3, Novosibirsk, 630090, Russia

In the Maksyutov Complex eclogites occur as boudins within sheared micaceous schists. We carried out a detailed sampling of a one boudin of 1.4 m in thick. The boudin is characterised by alternation of glaucophane eclogites (Grt + Gln + Omp + Phe + Ep + Rt \pm Bar) and garnet glaucophanites (Grt + Gln + Phe + Ep + Rt \pm Bar \pm Omp). Whole-rock compositions widely vary across the boudin extension, with the two rock groups differing in CaO/MgO ratio: (I)MgO = 9.5 ± 2.3 wt.%, CaO = 6.0 ± 1.1 wt.%; (II)MgO = 6.7 ± 1.4 wt.%, CaO = 8.2 ± 2.6 wt.%. A distinct connection between chemical and modal composition of the studied rocks is not observed.

Comparison of chemical compositions of minerals from the distinguished rock clusters has not revealed any sharp distinctions between them. Only compositions of garnet cores exhibit some differences. The P-T calculations are based on the combination of the garnet-clinopyroxene geothermometer (Ellis,Green,1979): $600-700^\circ$ (cores), $640-790^\circ$ (rims); the garnet-phengite geothermometer (Green,Hellman,1982): $550-700^\circ$; garnet-clinopyroxene-phengite geobarometer (Waters,Martin,1993): 15-23 kbar. Attempts at calculating the P-T conditions with using of the THERMOCALC program led to the comparable results.

Despite the data scatter, some conclusions can be made:

1) The garnet-clinopyroxene temperatures show steadily higher values for garnet rims in comparison with garnet cores, indicating progressive metamorphism during growing of garnet grains.

2) The temperature estimates of the peak metamorphism as indicated by the garnet rims are $640-790^\circ$ (Ellis,Green,1979), but the temperatures estimated using garnet-phengite geothermometer are systematically lower.

3) It is evident that the pressure estimates obtained by garnet-omphacite-phengite geobarometer differ appreciably. The possible explanations for this unrealistic pressure scatter is considered to be a partial lack of equilibration of eclogites during their multistage metamorphic history due to a rather short duration of metamorphic processes and contact interaction of rocks of different composition at different diffusion coefficients of chemical components in coexistent minerals. Financial support was given by the Russian Foundation for Basic Research (N 00-05-65203 and 01-05-65093) and Fund by Director of UIGGM.

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EMPG IX

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HIGH-PRESSURE STUDY OF CHONDRODITE, $Mg_5(SiO_4)_2(OH/OD,F)_2$: STRUCTURE, O-D...F/O GEOMETRY AND COMPRESSIBILITY

Alexandra Friedrich (friedrich@kristall.erdw.ethz.ch)¹, George A. Lager², Martin Kunz³, Peter Ulmer¹ & William G. Marshall⁴

¹ Department of Earth Sciences, ETH Zurich, CH-8092 Zurich, Switzerland

² Department of Geography and Geosciences, University of Louisville, Kentucky, USA

³ Department of Earth Sciences, University of Basel, CH-4056 Basel, Switzerland

⁴ ISIS, Rutherford-Appleton Laboratory, Didcot, UK

Chondrodite is a dense hydrous magnesium silicate that could transport water into the Earth's interior. As F-incorporation extends the thermal stability of chondrodite (Stalder and Ulmer, 2001), we examined the influence of the OH \leftrightarrow F substitution on the high-pressure crystal-chemical behaviour.

The compressional and high-pressure structural behaviour of chondrodite ($X_{OH} = 0.42$) and its deuterated analogue were investigated using single-crystal X-ray (diamond-anvil cell, quartz internal pressure standard, $P_{max} = 9.6$ GPa) and powder neutron (Paris-Edinburgh cell, SME gasket, $P_{max} = 7.04$ GPa) diffraction methods.

The compressibility data ($K_{0,T} = 117.0(4)$ GPa; $K_T = 5.59(11)$) suggest a slight softening of the chondrodite structure with OH incorporation, which is consistent with the unit-cell volume increase associated with the substitution of the larger OH ion for F. The largest differences with pressure occur in the M2 octahedron. Cation-cation repulsion moves the M2 cation off-center. Hence, M2-O2 and M2-O3 are the longest bonds and most easily compressed, which is consistent with the large compressibility parallel to the *b* axis. This is also reflected by a kinking between corner-sharing Si tetrahedra and M2 octahedra. Small changes in the O-D...F/O geometry reveal several trends with pressure. The donor-acceptor distances decrease and the covalent O-D distance decreases slightly at the highest pressure obtained. The strong hydrogen bond strengthens, as indicated by an increase of the O-D...F angle and a slight decrease of the D...F hydrogen bond. The positive shifts of Raman O-H stretching frequencies with pressure (Lin et al., 1999) may be related to the shortening of the O-D bond length. The weak hydrogen bond, however, weakens with pressure, as expressed by the increase of the O-D...O1 angle and a minimal increase of the D...O1 hydrogen bond. These changes can be interpreted in terms of a rotation of the O-D vector into the cavity surrounding the D atom.

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MEASUREMENT OF FERROUS AND FERRIC IRON CONTENT IN BIOTITE Mg-Fe SOLID SOLUTION

Noboru Furukawa (furukawa@earth.s.chiba-u.ac.jp)
1-33 Yayoi-cho, Inage-ku, Chiba-shi, Japan

In order to obtain the oxygen fugacity controlled by anthracene ($C_{14}H_{10}$), Fe^{2+} and Fe^{3+} composition in biotite Mg-Fe solid solution was measured. Standard cold-seal autoclaves and internal-heated pressure vessel were used. Experiments were performed at 100 MPa, 600°C. Oxygen fugacity were controlled by QFI, WI, NNO, HM and anthracene. The content of Fe^{2+} was examined by colorimetry measurement with o-Phenanthroline. The ratio of Fe^{2+} and total Fe in biotite were 0.9 in QFI and 0.7 in NNO buffer. These result agrees with ferrous and ferric ratio in annite (Rebbert et al., 1995). In the case of the oxygen fugacity controlled by anthracene revealed that ferrous and ferric Iron ratio was nearly 0.7. The value of Fe^{2+}/Fe^{3+} was constant up to $X_{Mg} = Mg/(Mg+Fe)$ in biotite ≤ 0.8 , but $X_{Mg} > 0.8$, Fe^{2+}/Fe^{3+} ratio was decrease with increasing of Mg content. This tendency can be seen in natural biotite.

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CRYSTALLIZATION OF Fe-LAYER ALUMINOSILICATES FROM HETEROGENEOUS NUCLEATION ON 'SILICA GARDEN' SUBSTRATES

Luis Gago-Duport (duport@uvigo.es)¹, Susana Fernandez-Bastero (sbastero@uvigo.es)¹, Pilar Villar (pilar.villar@uca.es)², Tatiana García (tatianag@uvigo.es)¹, Anton Velo (avelo@uvigo.es)¹ & Alberto Santos (alberto.santos@uca.es)³

¹ Dept. Geociencias Marinas, Universidad de Vigo, 36200 Vigo, Spain

² Dept. Ciencia de los Materiales, Universidad de Cádiz, 11510 Pto. Real. Cádiz, Spain

³ Dept Cristalografía y Mineralogía, Universidad de Cádiz, 11510 Pto. Real Cádiz

The "silica garden", are well known tubular microstructures formed by dissolution of crystals from metal salts in aqueous solution of sodium metasilicate. Although the process is known for long time, only recently has been the subject of a precise structural characterization. (Collins et al, 1998, 1999). These studies shown that the silica garden are framework aluminosilicates with 6-coordinate-Al and a variable degree of Si substitution by 4-coordinate-Al. In addition a great variety, from domain to hierarchical, microstructures have been reported.

In this work the initial stages of the Fe-layer silicates formation by heterogeneous nucleation at the internal surfaces of this tubular microstructures were firstly investigated. Secondly, both, the structural and compositional aspects of the obtained crystals, were characterized and compared with those of natural Fe-Layer silicate minerals.

Low-temperature syntheses experiments were performed by the precipitation Fe-Al-Mg salts during the silica garden formation under reducing conditions and basic pH-s. Soluble salts containing Fe^{2+} , Mg^{2+} , K^+ , Al^{+3} , were employed. In order