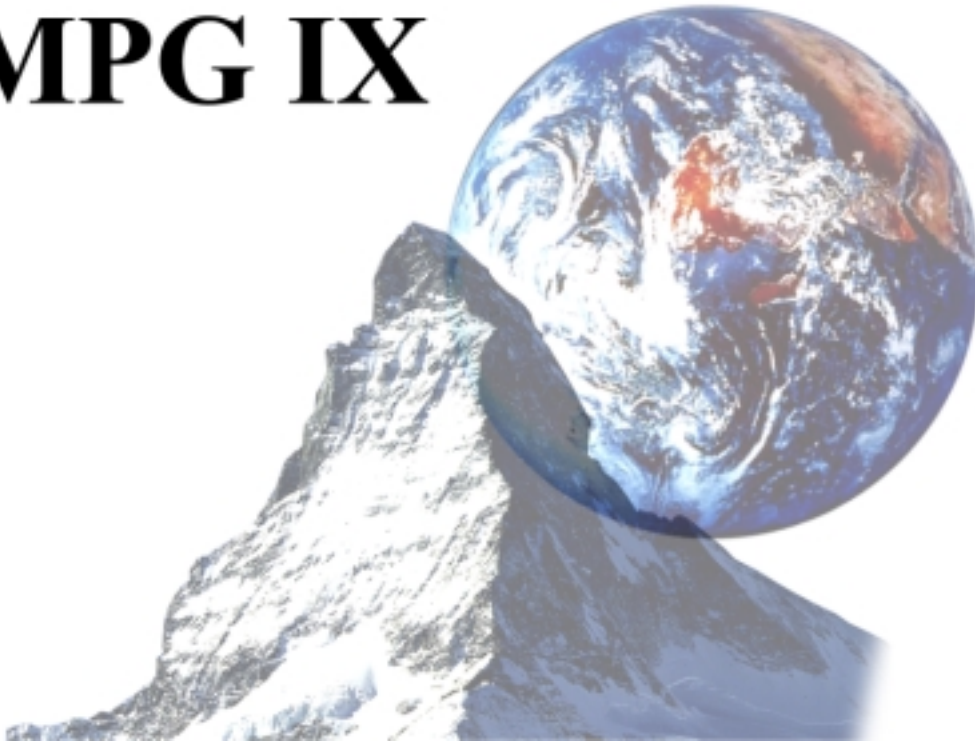


# EMPG IX



## **Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry**

**Zürich, Switzerland, 24 – 27 March 2002**

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### ANALYSIS OF ISOTOPICALLY DOPED REACTION RIMS: A MULTILAYER MOVING BOUNDARY DIFFUSION MODEL

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Milke et al. (2001) produced polycrystalline enstatite reaction rims between forsterite with normal isotope compositions and quartz extremely enriched in <sup>18</sup>O and <sup>29</sup>Si at 1000°C and 1 GPa. Enstatite grew from the original quartz-forsterite interface into both directions. The <sup>29</sup>Si/<sup>28</sup>Si+<sup>29</sup>Si profile is symmetric across the reaction rim. The <sup>18</sup>O/<sup>16</sup>O+<sup>18</sup>O profile is skewed with a shallow gradient in the compartment of the rim which replaced quartz and a steep gradient in the other compartment. Milke et al. (2001) used the formalism of Le Claire (1963) to extract grain boundary diffusion data. This formalism was designed for systems with fixed geometry. This is a severe limitation in the context of rim growth. We suggest a model, where quartz, forsterite and the two compartments of the enstatite rim are treated as distinct media. The rim thickness increases with time, and the geometric effects of forsterite and quartz consumption are taken into account. The four media are coupled through the conditions of mass conservation and isotopic equilibrium between coexisting phases. Oxygen and silicon bulk diffusivities in the enstatite reaction rim derived from our model are:  $D_{Si,En}^{bulk} = 3.4 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$  and  $D_{O,En}^{bulk} = 4.1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$  in the compartment of the reaction rim which replaced forsterite and  $1.9 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$  and  $3.7 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$  in the compartment, which replaced quartz. The silicon diffusivities obtained are approximately equal in the two compartments of the reaction rim. Using  $D^{gb} = D^{bulk} \cdot d \cdot \tau$ , where  $d$  is grain size (2  $\mu\text{m}$ ) this translates to  $D_{Si,En}^{gb} \cdot \delta = 2 \times 10^{-22} \text{ m}^3 \text{ s}^{-1}$ , about two orders of magnitude faster than derived from LeClairs formalism. Oxygen diffusivity was by about one order of magnitude larger in the compartment of the reaction rim which replaced quartz than in the other compartment. The reason for this behavior and for the lack of the same effect in the silicon system is still unclear.

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### THE INFLUENCE OF PRESSURE AND WATER ON TRACE ELEMENT PARTITIONING BETWEEN CLINOPYROXENE, AMPHIBOLE AND BASANITIC MELTS

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Clinopyroxenes and amphiboles crystallized from a basanite by Adam & Green (1994) and Fujinawa & Green (1997) were re-analysed by LAM ICP-MS for Li, Rb, Be, Sr, Ba, B, Ga, Y, Zr, Hf, Nb, Ta, La, Ce, Sm, Ho, Yb, Lu, Th and U. The results

confirm earlier observations of a negative correlation between D values for REE and HFSE and pressure at near constant temperature (1000-1050 °C). Estimated values of  $R_0$  and E for REE are near constant with  $R_0 = 1.030\text{-}1.045 \text{ \AA}$  and  $E = 285\text{-}316 \text{ GPa}$  for both clinopyroxene and amphibole at 0.5 to 2.0 GPa. There is an approximately linear correlation between  $\ln D_0$  for cations in M2<sup>cpx</sup> and M4<sup>amph</sup> sites and  $e^2$  (where  $e$  = formal valency of a particular cation minus the average valency of cations in the same site).  $D_0$  for REE and HFSE are also positively correlated with both Al<sup>iv</sup> in T sites and average cation valencies in M2<sup>cpx</sup> and M4<sup>amph</sup> sites, consistent with an electrostatic control of  $D_0$  inside individual crystallographic sites. However, the changes in Al<sup>iv</sup> and average valency are quite small and seem insufficient to explain the magnitude of the changes in  $D_{REE}$  and  $D_{HFSE}$ . If our data are linked to the findings of Wood & Blundy (1997) it can also be argued that the negative correlations between  $D_{REE}$  and  $D_{HFSE}$  and pressure are due (at least in part) to increased concentrations of H<sub>2</sub>O at higher pressures. By decreasing the  $\Delta G$  of fusion of REE and HFSE components in amphiboles and clinopyroxenes, H<sub>2</sub>O reduces  $D_0$  values, thereby producing a negative correlation between partition coefficients and H<sub>2</sub>O at constant temperature.

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### HIGH-PRESSURE PHASE EQUILIBRIA AMONG GARNET, ILMENITE AND PEROVSKITE IN THE SYSTEM MgSiO<sub>3</sub>-Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>: PHASE TRANSITION EXPERIMENTS AND CALORIMETRY WITH APPLICATION TO MINERALOGY OF THE MANTLE

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Phase equilibria in the system MgSiO<sub>3</sub>-Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> were examined by high pressure experiments and also by calorimetry and thermodynamic calculation in order to investigate phase transitions of majorite garnet in the mantle of relatively low temperature regime such as subducting slabs. The phase transition experiments up to 27 GPa at 1000°C by a multi-anvil apparatus showed that majorite garnet transforms to ilmenite solid solution and subsequently to perovskite solid solution and that ilmenite solid solution is stable in the whole compositional range. Ilmenite of pyrope composition is stable below about 1200°C at about 25-27 GPa. These results are quite different from phase relations at 1600°C in which garnet transforms directly to perovskite and ilmenite solid solution is stable only in composition very close to MgSiO<sub>3</sub>. Calorimetric measurements of enthalpies of ilmenite solid solutions showed an almost linear relationship with composition. Using the measured transition enthalpies, the phase relations in the system were calculated. The calculated phase boundaries confirmed that the stability field of ilmenite solid solution expands rapidly to pyrope-rich composition with decreasing temperature. The above results are applied to phase transitions of majorite garnet in the mantle. Assuming that mantle compo-

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sition is pyrolite and its geotherm is lower by 600°C than that in average mantle, majorite garnet first transforms to ilmenite at depth range of about 620-680 km and further to perovskite at about 710-750 km. The post-spinel transition occurs at about 680 km between the two broad transitions. Calculation of density and seismic velocities based on the phase relations shows that, in subducting slabs near the top of the lower mantle, steep gradients of density and velocities can be observed above and below the sharp discontinuity at 680 km.

### CHARACTERIZATION OF AN OH-RICH TOPAZ OCCURRING IN A KYANITE QUARTZITE FROM SULU UHP TERRANE, EASTERN CHINA

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Pure hydroxyl topaz,  $\text{Al}_2\text{SiO}_4(\text{OH})_2$ , has been synthesized at very high-pressure (Wunder et al., 1993), but usual natural compositions range from pure fluor topaz in rhyolites, to about  $\text{Al}_2\text{SiO}_4\text{F}_{1.4}(\text{OH})_{0.6}$  in hydrothermal deposits (Barton et al., 1982). The OH-richest topaz with  $X_{\text{OH}} = \text{OH}/(\text{OH}+\text{F}) = 0.41$  has been recently reported from a kyanite quartzite from the Sulu UHP terrane in Hushan, Donghai area (Zhang & Liou, 1999). An OH-rich topaz has been collected in the same locality (Ferrando et al., 2002). It shows: good {001} cleavage, weak birefringence, mean refraction index of 1.63 and the lowest  $2V\gamma$  value  $33(2)^\circ$  ever reported for natural topaz, close to  $28(2)^\circ$  determined for pure hydroxyl topaz (Wunder et al., 1993).

X-ray  $\text{MoK}\alpha$  single-crystal diffraction data were collected and the crystal structure was refined in the space group  $Pbnm$  to  $R = 0.023$ . The refined electron content of the F/OH site shows a random substitution between the two ions and  $X_{\text{OH}} \sim 0.5$ . The refined cell parameters are:  $a = 0.4669(8)$  nm,  $b = 0.8849(2)$  nm,  $c = 0.8392(2)$  nm. By using the determinative curves of Ribbe (1982), the measured values of both the edge  $b$  and the volume  $V$  give  $X_{\text{OH}} = 0.31$ . This mean value satisfactorily agrees with the average F content analyzed by WDS electron microprobe. The chemical analyses show zoning in the F content, with  $X_{\text{OH}}$  in the range between 0.21 and 0.39.

The fitting of the  $2V\gamma$  value to the relevant determinative curve of Ribbe (1982) gives  $X_{\text{OH}} = 0.45$  which is significantly higher than the value expected from the chemical analyses. Although this disagreement could be due to the combined effect of chemical zoning and difficulties in  $2V\gamma$  measurement, it could also be interpreted as the effect of different growing P/T conditions, i.e. HP/UHP vs. low-pressure metamorphic condition.

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### SPECTROSCOPIC CHARACTERIZATION OF AN HERCYNITE-BASED PIGMENT

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Two samples of an hercynite-bearing pigment, with and without titanium, were investigated by means of mineralogical techniques (XRD, EMPA, AAS), together with advanced spectroscopies (Mössbauer, EPR) and magnetic measurements (SQUID susceptometer), in order to characterize the overall electronic properties of the bulk material. The two samples are mainly constituted by corundum and contain up to 3.5 wt% hercynite ( $\text{FeAl}_2\text{O}_4$ ). The pigment with Ti shows a strong blue color, whereas the other one shows a pale sky-blue hue. In the Ti-bearing pigment small amounts of Ti are revealed from EMPA analysis of hercynite grains. The Ti valence state has been established as tetravalent on basis of EPR results, which excluded the presence of  $\text{Ti}^{3+}$ . Mössbauer data point to  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios corresponding to 90/10 and 87/13 in the Ti-bearing and Ti-free samples, respectively.  $\text{Fe}^{2+}$  is mainly distributed in tetrahedral coordination (T site of hercynite) and  $\text{Fe}^{3+}$  in the octahedral one (M site of hercynite and/or corundum). The complex EPR spectra of the two samples may be attributed to two different species of  $\text{Fe}^{3+}$ , the first of which presents features practically unchanged in the two samples. The EPR line of this species is due to a distorted Me-vacancies complex, with a very high zero-field splitting anisotropy. The other signal, very narrow and symmetrical, attributed to  $\text{Fe}^{3+}$  in a regular polyhedron coordination, is strongly related to the presence of Ti in the sample. As concerns magnetic investigations, deviations from the expected Curie-Weiss behaviour were detected at temperatures lower than 50 K, thus suggesting the presence of antiferromagnetic interactions. On the basis of the distribution and the interaction between Fe and Ti, revealed by all magnetic and spectroscopic investigations, a charge-transfer mechanism between  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  in hercynite may be invoked, which would account for the coloring properties of this pigment.

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### THE MISCIBILITY OF MELTS IN THE SILICATE-CARBONATE SYSTEMS

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There are many experimental data, which show the immiscibility of silicate and carbonate melts. These data are in contradiction with the structural compatibility of solid silicates and carbonates. They are able to form silicate-carbonate compounds and solid solutions. This is a reason to revise the results of these experiments. The wide miscibility gap was established by Koster Van Groos and P. Willie in the system  $\text{NaAlSi}_3\text{O}_8 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$ . We used the special technics, which allows to divide silicate and carbonate melts in the cardge. Our experiments showed, that there was no immiscibility in the system  $\text{NaAlSi}_3\text{O}_8 - \text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$ . We also revised the experimental data of Freeston and Hamilton (1980), Brooker (1998) etc on the immiscibility of felsitic, nefelinitic, phonolitic melts and carbonate ones. There is an uncorrect graphic interpretation of the experimental data in these papers, because compositions of the melts are shown on the triangle diagram, which has no carbonate top. We recalculated these data and put them on the triangle diagram with tops:  $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2) - \Sigma \text{Me}_x\text{O} - \Sigma \text{Me}_x\text{CO}_3$  and showed that the main part of the carbonate melts represented by carbonate component only and does not contain silicate components. It is obviously that this situation will be able if the carbonates are crystallised from homogeneous melt and is not the liquid, which appears as a result of immiscibility. The cause of mistakes of the experimental data in the silicate-carbonate systems is the confined possibility of the quenching method, when carbonate melt is unable to transform to glass. The project is supported by RFFR, grant 99-05-65408

### COMPRESSION MECHANISMS OF COESITE

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Understanding the thermodynamics of coesite has become increasingly important as it is discovered in more UHP terraines. However, the elastic properties of coesite are very anomalous (Angel et al., 2001). We have now undertaken a single-crystal X-ray diffraction study of coesite to pressures in excess of 8 GPa in order to determine the underlying structural reasons for this behaviour.

The structure of coesite is a three-dimensional framework of corner-linked  $\text{SiO}_4$  tetrahedra similar to that of feldspar (Megaw, 1970). But it is unusual in that it contains a straight Si-O-Si linkage that is the only bridge between two parallel semi-close-packed planes of oxygens. The distance between the two oxygen planes does not change with pressure, although the Si1-O1 distances forming the bridge shorten by 2%, indicating that mutual repulsion of the planes keeps the Si-O1-Si link in tension and thus linear. The major change upon compression involves the rotation of the Si2 tetrahedra about

[001], which increases the torsion angle between two adjacent Si2 tetrahedra along the *c*-axis and closes the "crankshaft" chains of tetrahedra by a shearing motion. These are the structural reasons for the anomalous positive value of one of the off-diagonal components of the elastic compliance tensor,  $s_{23}$ , of coesite and thus the initial softening of the *c*-axis under compression (Angel et al., 2001). The eventual stiffening of the structure, and the anomalous positive value for the second derivative of the bulk modulus of coesite, has no obvious structural cause that we can detect. But it may be related to the rotation mechanism being constrained by repulsion between the two semi-close-packed oxygen layers.

Angel RJ, Moenfelder JL & Shaw CSJ, *Phys. Earth Planet. Int.*, **124**, 71-79, (2001).

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### MODEL INDEPENDENT PHASE EQUILIBRIUM CONSTRAINTS ON FERROSILITE ACTIVITY IN THE BINARY Fe-Mg ORTHOPYROXENE SOLID SOLUTION

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Reversals of orthopyroxene (Opx) composition on the enstatite (En,  $\text{Mg}_2\text{Si}_2\text{O}_6$ )-ferrosilite (Fs,  $\text{Fe}_2\text{Si}_2\text{O}_6$ ) join equilibrated with hematite (Hm), magnetite (Mt) and quartz (Qz) were obtained in piston-cylinder apparatus in the pressure range 10-25 kbar at temperature 800 and 950°C. Double capsule technique with the Hm-Mt external buffer was employed to ensure the presence of both iron oxides in the run products. Starting materials were crystalline mixtures of synthetic Opx with  $X(\text{Fs}) (= \text{Fe}/(\text{Fe}+\text{Mg})) = 0.05$  and 0.45, synthetic Mt, reagent Hm and natural Qz finely ground together in stoichiometric proportion. Run products were carefully examined using optics, SEM, BSE imaging and wavelength dispersive electron microprobe. Despite the differences in the rates of forward and backward reactions  $\text{Fs (in Opx)} + 2\text{Hm} = 2\text{Mt} + 2\text{Qz}$  (1), very tight compositional brackets (less than 0.01  $X(\text{Fs})$ ) were obtained at each P-T. At 800°C midpoints of the compositional brackets are: 0.195/10 kbar, 0.24/15, 0.29/20 and 0.34/25; at 950°C: 0.21/15 kbar, 0.25/20 and 0.295/25 kbar. Activities of Fs, recalculated from these compositions using either Berman and Aranovich (1996) or Holland and Powell (1998) data sets for the pure end-member reaction (1), show negative deviation from ideal mixing. Strongly temperature dependent enthalpy of mixing is required to make these activity values consistent with the configuration entropy of the solid solution deduced from the site occupancy measurements. Simple mixture model with temperature dependent W term, similar to that of Berman and Aranovich (1996), adequately reproduces experimental data.

The work was supported by RFBR grant #00-05-64881

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### THE COMPOSITIONAL EVOLUTION OF DIFFERENTIATED LIQUIDS FROM THE SKAERGAARD LAYERED SERIES AS DETERMINED BY PHASE EQUILIBRIA MODELING

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Based on the COMAGMAT-3.65 crystallization model a set of phase equilibria calculations at  $P=1$  kbar and closed-to-oxygen conditions has been conducted for 65 rocks representing the principle units of the Layered Series of the Skaergaard intrusion. It allowed us to define the range of initial temperatures (1145 to 1085°C) and oxygen fugacities (1-1.5 log units above  $QFM$  to slightly below  $QFM$ ) intrinsic to the original crystal mush from which the rocks from LZa to UZa have been crystallized. In parallel, average major-element compositions of residual (interstitial) liquid were calculated demonstrating a trend of continual enrichment of  $FeO^*$  (up to 18 wt.%) and  $TiO_2$  (up to 5.5 wt.%) with only minor variations in the  $SiO_2$  contents (48 to 50 wt.%). Projection of the compositions onto  $OLIV-CPX-QTZ$  diagram evidences for the most of the Layered Series was crystallized on  $Ol-Pl-Cpx$  cotectic along with oxides. Estimated amounts of interstitial melts trapped in the Skaergaard "cumulates" range around 50 wt.%. Wager's compositions inferred from simple mass-balance were found to lie too far from the  $Ol-Pl-Cpx$  boundary to represent a realistic approximation of the low-pressure Skaergaard magma evolution. The main problem of genetic interpretations of the Skaergaard intrusion is shown to be a strong misbalance (Si, Ti, P) between the parental compositions followed from marginal rocks and the results of phase equilibria calculations and that of the whole differentiated body. One possible explanation is to assume the Skaergaard magma came to the chamber with an amount of crystals ( $Ol+Pl$ ) equilibrated with the calculated parental liquid. However, even if some amount of "hidden" troctolitic material exists, it is problematically that crystallization in a closed system could produce large volumes of rocks so rich in Fe-Ti oxides without complementary more felsic differentiates.

### AN EXPERIMENTAL CALIBRATION OF THE BIOTITE GARNET FELDSPAR QUARTZ GEOBAROMETER

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The biotite-garnet-feldspar-quartz assemblage involves different partial equilibria among which:

- (1)  $2Phl+3An+3Qtz=3Prp+Grs+2Kfs+2H_2O$
- (2)  $2Ann+3An+3Qtz=3Alm+Grs+2Kfs+2H_2O$
- (3)  $Phl+Alm=Ann+Prp$
- (4)  $3Ann+6An=3Sd+6aQz+2Gr+Alm$
- (5)  $3Eas+12An+6Ann=4Gr+2Py+12aQz+9Sd$

The geobarometric properties of equilibria (1) and (2) have been tested using a series of experiments carried out to understand the melting behaviour of metagreywackes (Vielzeuf and Montel, 1994). Thirty experiments in the range 5 to 24 kbar and 800 to 950°C show the coexistence of biotite, garnet, plagi-

clase and quartz. Consistent variations in phase proportions and compositions are observed as a function of pressure increase. In particular, the proportions of biotite and feldspar decrease while the garnet fraction increases. In garnet, the grossular content increases from 1,6% at 5 kbar to 21% at 20 kbar. These changes can be ascribed to the pressure-dependent equilibria (1) and (2). Mineral compositions and thermodynamic modelling using two different data sets (Berman, 1988; Holland and Powell, 1998) allow the calculation of P and T of equilibration. Calculated T, with the Bt-Grt thermometer, differ significantly from the experimental temperatures (errors higher than 75°C in half cases). Assuming a  $H_2O$  activity of  $0.7 \pm 0.2$ , we were also able to calculate pressures. Below 10 kbar, there is a good agreement between calculated and experimental pressures though P are always underestimated by about 1 to 2 kbar. This deviation increases progressively towards high pressures and reaches 5 kbar at P of 20 kbar. The origin of this deviation is not yet understood but cannot be ascribed to the uncertainty on the activity of  $H_2O$  in the fluid phase. Using different starting materials, an intercomparison with the GASP geobarometer is in progress. Nevertheless, these experiments demonstrate that equilibria (1) and (2), and more especially (2), can be used to determine pressures in metasedimentary rocks devoid of aluminum-silicate below 12 kbar.

### NUMERICAL EXPERIMENT ON GARNET CRYSTALLIZATION

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The experimental investigations focus mainly upon phase equilibria and mineral thermodynamics. Study of the mineral growth under metamorphic P-T conditions is restricted by numerous difficulties. Instead numerical modelling can help. We considered the growth of garnet which is quite usual metamorphic mineral and may give us information about metamorphic processes.

The aims of our studies were: (1) the reconstruction of mechanisms and duration of the mineral growth, and (2) the reveal of the prevalent mechanisms producing growth zoning in garnets. We constructed the mathematical models describing both isothermal and nonisothermal crystal growth in closed systems and at fluid flow. Because of lack of experimental data on component distribution between Fe-Mg garnet and aqueous fluid we were compelled to calculate these distribution coefficients.

The numerical experiment displays that:

1. Garnet growth should be preferably surface-limited. This conclusion is confirmed by the morphological features of natural garnets.
2. The time of the garnet growth does not exceed 0.1-0.5 Ma but may be much shorter, depending on fluid supersaturation. It means that mineral growth is close to isothermal. The main crystallization way is desupersaturation.

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3. The prevalent mechanism producing growth zoning is fractionation in the closed system (the Rayleigh fractionation). Nonmonotonic zoning can appear at fluid flow through metamorphic rock.

4. The fractionation can produce both normal and reversed zoning. The normal zoning arises at the growth from the neutral aqueous fluid whereas the crystallization from alkaline fluid should result in reversed zoning.

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### PHASE TRANSFORMATIONS IN $\text{CaCO}_3$ AND $\text{SiO}_2$ UP TO 2.5 GPa FROM ELECTRICAL IMPEDANCE MEASUREMENTS

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The phase transformation in calcite I-IV-V, calcite  $\Leftrightarrow$  aragonite and in  $\text{SiO}_2$  have been characterised by electrical impedance measurements at temperatures 500-1200°C and pressures 0.5 - 2.5 GPa in a piston cylinder apparatus. The bulk conductivity  $\sigma$  has been measured from Argand plots in the frequency range  $10^5 - 10^2$  Hz. The cell represents a coaxial cylindrical capacitor with a geometric factor  $c$ . 6 cm [1]. As a starting material the synthetic polycrystalline powder of  $\text{CaCO}_3$ , natural crystals of calcite (Spain) and of quartz Mont Rose (France) were used. The transformation temperature was identified from a bulk resistivity-temperature curves as a kink point of the activation energy. In a low temperature phase (calcite I), the activation energy  $E_a$  of  $\sigma \cdot T$  is  $c. 1.05 \pm 0.05$  eV, and in high temperature phase (calcite V)  $E_a$  is  $c. 0.75 \pm 0.05$  eV. The pressure dependence of  $T_c$  for the transformation in calcite V is positive for pressures up to 1 GPa  $dT_c/dP \sim +20^\circ/\text{GPa}$  and becomes negative for the pressures 1-2 GPa:  $-20^\circ/\text{GPa}$ . The transformation calcite I -IV is less evident from the present observations. The activation energy of electrical conductivity between I and V phases increases gradually to from 0.95 to 1.05-1.15 eV and then decreases to  $c. 0.75$  eV. The gradual increase of  $E_a$  may correspond to a kinetic phenomena of retaining R-3c symmetry at temperatures above  $c. 850^\circ\text{C}$ . However, the pressure dependence of the kink of the activation energy is also  $+20^\circ/\text{GPa}$ . The kinetics transformation of calcite in aragonite has been monitored by measuring a variation of the electrical resistance of calcite at  $10^3$  Hz with time in the stability field of aragonite. Products of the phase transformation have been analysed with a powder diffractometer. Variations of the electrical resistance with time correlate with the degree of phase transformation  $\xi(t)$ . The degree of transformation calcite to aragonite has been fitted to the expression:  $\xi(t) \sim [1 - \exp(-t/\tau)]$ , where  $\tau$  is a characteristic time of the phase transformation at a temperature  $T$ . For example,  $\tau$  of the transformation of calcite to aragonite at 2.5 GPa and 760°C is 7.5 h, at 1.5 GPa and 680°C is 8.8 h. The temperature of a-b-phase transition in quartz has been characterise at 0.5, 1, 1.5 and 2 GPa from the electrical impedance measurements of

polycrystalline samples. The difference in activation energies of  $\sigma \cdot T$  in  $\alpha$ - and  $\beta$ - quartz is rather small and increases with the pressure. For example at 0.5 GPa the activation energies  $E_a$  of  $\sigma \cdot T$  for a and b-phase are 1.04 and 1.26 eV, at 1 GPa 1.1 and 1.3 eV, at 1.5 GPa 1.18 and 1.41 eV, at 2 GPa 1.23 and 1.53 eV, respectively. The calculated activation volume  $\Delta V$  for  $\alpha$ - and  $\beta$ -phases is about the same 0.18 and 0.25  $\text{cm}^3/\text{mol}$ . The estimated phase transition temperature  $T_c$  from heating and cooling cycles are slightly different.  $dT_c/dP$  obtained in this study from heating and cooling cycles is smaller than has been reported from laser interferometry  $256^\circ/\text{GPa}$  [2] and close to the  $T_c$  and  $dT_c/dP$  data reported in [3].

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### GROWTH OF TOPAZ SINGLE CRYSTALS FROM SUPERCRITICAL AQUEOUS FLUIDS AND ITS CHARACTERIZATION

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Topaz often occurs in some kinds of pegmatites, greisens and hydrothermal veins. Until the last time large crystals of topaz haven't been received, but a spontaneously crystallization was realized many times [1, 2]. However, topaz synthesis becomes an important problem because solving can help to comprehend the genesis of topaz in nature, and help to solve problem of synthesis of gem-quality crystals. Our team accomplished synthesis of topaz single-crystals, based on recently got experimental data on studying of processes of joint transfer of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in supercritical fluids in terms of straight temperature gradient [3]. Crystals were grown in autoclaves (volume 50  $\text{cm}^3$ ) with temperatures from 600 up to 800°C, pressures from 20 up to 200 MPa and temperature difference between top and bottom parts of autoclave from 20 up to 100°C. Acid (pH 1-2 after experiments) aqueous-fluorine fluid was chose as a crystallizing medium. Nutrient was presented by quartz and topaz single-crystal bars with ZX-orientation, sizes 4x4x50 mm, and was placed in the top part (colder part) of autoclave, and sections of topaz with different orientations were hanged up in the bottom part (the hotter part) of autoclave. Intense dissolution of nutrient bars and growth of topaz crystals were observed with fluid density from 0,1 to 0,45  $\text{g}/\text{cm}^3$  (pressure about 40-200 MPa). However with density less than 0,33  $\text{g}/\text{cm}^3$  quartz began intense transferring to the bottom part of autoclave and crystallizing there jointly with topaz as a small spontaneous crystals. In general, as a result of made experiments, a method of reproducible synthesis of topaz single crystals on seed (cuts {001} and {112}) with growth rates 0,15-0,22 mm/day is found.

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### EXPERIMENTAL STUDY AND COMPUTER SIMULATION OF DEPENDENCE OF MORPHOLOGY OF QUARTZ CRYSTALS ON GROWTH CONDITIONS

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The experimental study and computer simulation were carried out to investigate morphological variations of polyhedral quartz crystals depending on their growth conditions. The quartz crystals were grown under temperature range (T) from 210 up to 900°C and pressure (P) from 2 up to 500 MPa in both isothermal (T>400°C) and temperature gradient conditions (T.210°C). As medium of crystallization, pure water (alone or with addition of some surface-active substances) and aqueous solutions of different electrolytes (NaCl, LiCl, LiF, NH<sub>4</sub>F, AlF<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, NaOH, KOH, etc) were used. In isothermal conditions, amorphous silica or cristobalite were used as nutrient [1,2], and quartz crystals smaller than 1 mm were formed. In temperature gradient experiments, synthetic quartz was used as nutrient, and plates and bars with different forms, sizes and crystallographic orientations prepared from synthetic quartz were used as seeds. The runs were performed in heat resisting autoclaves (T up to 800°C, P up to 200 MPa) as well as in installations of high gaseous (T up to 900°C, P up to 500 MPa) and hydrothermal (T up to 700°C, P up to 300 MPa) pressures. The computer simulation of time-depending morphological evolution of quartz crystals was performed using on earlier designed program, and morphodroms were drawn [3]. The experimental results have shown that the habit of crystals are controlled by many parameters: initially by given form, sizes and crystallographic orientation of seeds, as well as by T-P parameters, composition of solutions, and growth time. The computer simulation has allowed to visualize morphological evolution of habit of quartz crystals in time in dependence on relative growth rates of main faces. As whole the experimental results have confirmed that growth temperature influences on habit of quartz crystals similarly as observed earlier for natural quartz crystals. In addition to this, it was experimentally proved that other factors such as composition, pH, density, supersaturation of solutions, sizes and shapes of primary quartz grains or blocks, position of growing crystals in space as well as duration of their growth have considerable influence upon growth rates of major faces and thus habit. The work of Russian author has been supported by Russian Basis Research Foundation (Grant No 00-05-64525).

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### HIGH-PRESSURE DEFORMATION MECHANISM IN THE ZEOLITE SCOLECITE: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

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Scolecite (Na<sub>0.32</sub>Ca<sub>7.71</sub>Al<sub>15.60</sub>Si<sub>24.36</sub>O<sub>80</sub>·26.51H<sub>2</sub>O; s.g. F1d1) is a calcium fibrous zeolite with an ordered distribution of the Si and Al cations. Its crystal structure displays tetrahedral chains parallel to the *c* direction, forming channels which host one calcium atom and three water molecules. The pressure-induced structural modifications in scolecite were studied by means of *in-situ* synchrotron XRPD and by density functional computations. The unit cell parameters were refined up to 8.5 GPa and reductions of 5.0, 7.0, 2.0, 2.0 and 13% were found in *a*, *b*, *c*,  $\beta$  and *V*, respectively. A slight increase in the slope of the linear pressure-volume dependence was observed at about 6 GPa, suggesting an enhanced compressibility at higher pressures. The weakening and broadening of the diffraction peaks revealed the increasing of structural disorder with pressure, preventing the refinement of the lattice parameters above 8.5 GPa. Diffraction patterns collected in decompression showed that the disordering is irreversible. Since it was impossible to perform crystal-structure refinements, atomic coordinates were determined by means of Car-Parrinello simulations, within unit cells of dimensions suggested by the XRPD experiments. The discontinuous rise in compressibility at about 6 GPa was reproduced by the computation, that allowed us to attribute it to the re-organization of the hydrogen bonding network, with the formation of water dimers. Moreover, we found that, with increasing pressure, the tetrahedral chains, parallel to *c*, rotate along their elongation axis - with the progressive squashing of the channels - and display an increasing twisting along an axis perpendicular to *c*. We also observed modifications of the Ca polyhedra under pressure and the increase (from 4 to 5) of the coordination number of one of the two Al atoms, resulting from the approach of a water molecule. This last transformation should trigger the irreversible disordering of the system.

### VAPOUR-LIQUID EQUILIBRIUM STUDY OF SILICON TETRACHLORIDE-CO<sub>2</sub> SYSTEM

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Supercritical CO<sub>2</sub> (critical P and T are 73.8 bar and 31.1 °C respectively) occurs as fluid inclusions over a wide range of conditions in the Earth's crust from greenschist facies to granulite facies. Whether it can transport inorganic components at elevated P-T conditions has not been considered in the geological literature. Numerous studies have been conducted on

vapour-liquid equilibrium of various organic compounds and carbon dioxide; however, there is very little published work on the phase equilibria of binary systems involving inorganic compounds and CO<sub>2</sub>, particularly metal and non-metal chlorides like silicon tetrachloride (SiCl<sub>4</sub>). Initial studies on solubility of TiCl<sub>4</sub> in supercritical CO<sub>2</sub> by Tolley and Tester (1989) were followed by studies on TiCl<sub>4</sub>-CO<sub>2</sub> and SnCl<sub>4</sub>-CO<sub>2</sub> systems (Giles et al., 1992; Tolley et al., 1993; Wiegand and Seward, 1997). In this study we present experimental results for the binary system SiCl<sub>4</sub>-CO<sub>2</sub> at temperatures up to 150 °C and pressures up to 140 bar. Experimental approach involved separate sampling and analysis of both liquid and vapour phases (with minimal disturbance to the equilibrium) using thermal conductivity detector (TCD), as well as sealed-ampule experiments in order to determine homogenization temperature at the optically observed point of disappearance of the liquid-vapour phase boundary. The results demonstrate that the binary system exhibits a two-phase equilibrium region extending up to approximately 160 bar. Theoretical calculations using ab initio Monte Carlo approaches are underway for the modeling of the experimental data as well as reconstruction of the phase envelope at elevated P-T conditions.

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### LOCALIZATION OF DEFORMATION IN A TWO-PHASE ROCK: TORSION EXPERIMENTS ON CALCITE-ANHYDRITE AGGREGATES

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We deformed calcite-anhydrite aggregates in torsion to large amounts of shear strain in order to study the influence of the two phases on the deformation behaviour, and to test whether localization may occur in two-phase aggregates. We chose deformation conditions where calcite and anhydrite have approximately a similar strength. Torsion experiments were performed on fine-grained (5 - 8 µm) calcite/anhydrite samples with volume proportions of 0/100, 30/70, 50/50, 70/30 and 100/0. The experiments were performed at 600°C, 300 MPa confining pressure and a constant shear strain rate of 1.10<sup>-3</sup> s<sup>-1</sup>, up to a maximum shear strain of 12.5. Rheological data show that the pure anhydrite (peak stress = 125 MPa) is the strongest material and calcite the weakest (peak stress = 70 MPa). The calcite-anhydrite mixtures have strengths in between the end-members. However after a shear strain of 1, the anhydrite end-member weakens dramatically (50%), whereas the calcite end-member shows no or hardly any weakening. The 50/50 sample shows a significant weakening (40%), whereas weakening in the sample containing 70% calcite is much less pronounced, suggesting that at this composition, calcite still controls the deformation behaviour. At a shear strain of 3,

approximately similar steady-state stress values are observed for all the different compositions, indicating that composition does not have a large influence anymore on the strength once steady-state conditions are achieved. It is concluded that the evolution of the deformation behaviour with strain is strongly dependent on the distribution and the volume ratio of the two-phases. In addition, several experiments (calcite/anhydrite 50/50) were stopped at various amounts of shear strain. On the bulk sample scale, we observe a progressive localization of the deformation in the two-phase aggregates, while deformation of monophase rocks is always very homogeneous. This suggests that in nature localization may be triggered by the presence of a second phase.

### HIGH PRESSURE-TEMPERATURE AQUEOUS SYSTEMS IN THE HYDROTHERMAL DIAMOND ANVIL CELL (HDAC)

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The hydrothermal diamond anvil cell (HDAC) has been used to place aqueous samples under conditions up to 2.5 GPa and 1000°C (Bassett, et al., 1993). Optical microscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray absorption fine structure (XAFS), infrared absorption, luminescence, and Raman spectroscopy have been used to analyze these samples (Bassett et al., 1996). Critical behavior, melting, phase transitions, reactions, ionic structure and speciation, and compositional changes have been observed and measured. Shen et al. (1992) accurately determined equation-of-state (EOS) relationships of aqueous fluids by maintaining a constant sample volume in the HDAC. Visual observations are all that are needed to establish EOS relationships, which have been both an objective and a means for determining density and pressure in aqueous samples and in fluid inclusions. Darling and Bassett (2002) determined the P-T conditions of metamorphism in natural fluid inclusions from the Adirondack Mountains using the HDAC to prevent decrepitation resulting from high homogenization pressures due to the presence of carbon dioxide. Visual observation and X-ray diffraction are used for studying phase transitions. Wu et al. (1997) showed that dehydration-rehydration in montmorillonite is a reversible phase transition. XRF has been used for in-situ measurements of chemical changes in phases. Bassett et al. (2000) have used XAFS to determine species and their structures in aqueous solutions of Zn, Cu, and La using two modifications to the HDAC for XAFS analyses of elements with low-energy absorption edges, e.g., first-row transition elements (K-edge) and rare-earth elements (L(3)-edge). In the HDAC for XAFS by transmission, the amount of diamond in the beam has been reduced to 0.3 mm. In the HDAC for XRF and fluorescence XAFS, the amount of diamond traversed has been reduced to 0.16 mm.

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### SOLUBILITY OF H<sub>2</sub>O AND CO<sub>2</sub> IN SILICIC MELTS - IMPLICATIONS FOR MAGMA DEGASSING

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The solubilities of H<sub>2</sub>O and CO<sub>2</sub> in rhyolitic to dacitic melts coexisting with a H<sub>2</sub>O-CO<sub>2</sub> fluid were investigated at pressures 100-500 MPa and at temperatures 800-1250°C using internally heated argon pressure vessels at relatively oxidizing conditions (ca NNO + 2). The water content of the quenched glasses was determined by IR spectroscopy and/or by KFT. At 1250°C the water solubility is higher in dacitic and rhyodacitic melts than in rhyolitic melts at 200 MPa. At 500 MPa, the same trend is observed at low melt water content (<7 wt.% water), but at higher water contents (higher water fugacities) the trend inverts. In rhyolitic glasses carbon is only incorporated as molecular CO<sub>2</sub> which can be accurately measured using the IR absorption band at 2340 cm<sup>-1</sup> (Tamic et al. 2001). In contrast, in dacitic and rhyodacitic glasses, carbon is incorporated as both CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup>. The quantitative determination of the total dissolved C-species by IR-spectroscopy is complicated because the weak carbonate band is difficult to separate from the background in the spectra, especially in water-bearing glasses. Moreover, the CO<sub>2</sub>/CO<sub>3</sub><sup>2-</sup> ratio systematically decrease with water content. Thus, SIMS was used to quantify total CO<sub>2</sub> contents. At same pressure and fluid composition, the CO<sub>2</sub> solubility is systematically higher in dacitic than in rhyolitic melts, e.g., by 0.05 wt% at 200 MPa and equilibrium with pure CO<sub>2</sub> fluid (dacite: 0.15 wt% at 1250°C; rhyolite: 0.095 wt% at 800-1100°C, when using the newly determined molar absorption coefficient of 1266 l/mol cm). In both melts at constant pressure the CO<sub>2</sub> solubility increases non-linearly with CO<sub>2</sub> fugacity indicating an enhancement of CO<sub>2</sub> solubility by dissolved water. Using the volatile solubility data, the evolution of a dacitic magma fluid-saturated at 200 MPa and 850°C (equilibrated with pure H<sub>2</sub>O or H<sub>2</sub>O/CO<sub>2</sub>=1:1) during isothermal decompression was modeled.

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### DISTRIBUTION AND SPECTROSCOPIC PROPERTIES OF Cu(II) IN SYNTHETIC Cu(I)<sub>10</sub>Cu(II)<sub>2</sub>Sb<sub>4</sub>S<sub>13</sub> TETRAHEDRITE: EPR AND SQUID INVESTIGATION

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Tetrahedrite, (Cu, Ag)<sub>10</sub>(Fe, Zn, Hg, [])<sub>2</sub>(Sb, As)<sub>4</sub>S<sub>13</sub>, a very important mineral for its wide chemical variability, presents a peculiar structure and electronic features. Crystalline powders of pure Cu-bearing tetrahedrite, Cu(I)<sub>10</sub>Cu(II)<sub>2</sub>Sb<sub>4</sub>S<sub>13</sub>, have been synthesized in order to fully characterize the nature of the Me-substitution and the relative stabilization of natural Me-bearing tetrahedrites. The spectroscopic and magnetic techniques confirmed the presence of two Cu(II) atoms per formula unit. Cu(II) appeared randomly distributed together with Cu(I) over the tetrahedral site, with a ratio Cu(I)/Cu(II) 2:1. EPR spectra, collected at different temperatures ranging from 130K to 298K, point to the presence of S-bridged Cu(II) dimers, constituted by two adjacent corner-sharing tetrahedral sites. The temperature dependence of the spectra was attributed to changes of the interaction between paramagnetic centers, which could be related to small structural variations of the unit cell. Pulsed EPR experiments, performed at liquid helium temperature, revealed a small fraction of superficial paramagnetic Cu(II) atoms, which show an electrostatic interaction with protons belonging to the wax used for incorporating the sample for the magnetic investigations. As concerns the bulk magnetic properties of the pure synthetic compound studied, SQUID measurements have revealed a strong variation in the  $\chi T$  versus T data, which appear completely reversible. No evidence of magnetic hysteresis was detected. A model, consistent with all magnetic and spectroscopic features, is proposed, taking into account not only of the Cu(I)-Cu(II) interaction, as a function of their distribution, but also of the rotation of tetrahedra due to the changes of cell dimensions with temperature.

### PHASE RELATIONS IN MORB'S AT 200 MPa: THE EFFECT OF WATER AND OXYGEN FUGACITY

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Phase relations in a MOR-basaltic composition have been investigated experimentally in an internally heated pressure vessel at 200 MPa, 950 to 1150°C, as a function of the bulk water content present in the system and as function of fO<sub>2</sub>. The vessel was equipped with a rapid quench system and a H<sub>2</sub>-membrane to determine the fO<sub>2</sub> prevailing in the samples. The combination of these two techniques allows to quench large

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volume samples (several cm<sup>3</sup>) in highly depolymerised systems (a MORB melt with 9 wt% H<sub>2</sub>O can be quenched to a bubble- and crystal-free glass). The capsules were filled with a water-bearing glass (containing between 0.5 and 4.5 wt% H<sub>2</sub>O). Experiments were made at two fO<sub>2</sub> corresponding to that of the buffers MnO-Mn<sub>3</sub>O<sub>4</sub> (oxidizing) and QFM (reducing). At reducing conditions, capsules of AuPd were pre-saturated with iron and the glasses were also pre-equilibrated at the corresponding fO<sub>2</sub>. Following phases were observed: glass, olivine, clino- and orthopyroxene, plagioclase, magnetite, ilmenite and amphibole. Amphibole is only observed at water-saturated conditions and below 1000°C. The increase of X<sub>fo</sub> in olivine and of melt Mg# due to increasing aH<sub>2</sub>O is confirmed. In addition, it is shown that increasing the bulk water content (at constant fO<sub>2</sub>) has the same effect due to increasing melt fraction. The CaO content of olivine is dependent on the anhydrous melt composition, but also on aH<sub>2</sub>O. Thus, CaO content of olivine is a potential hygrometer. The comparison of the experiments at different fO<sub>2</sub> allows to quantify the effects of the crystallization of oxides (ilmenite and/or magnetite) on liquid lines of descent. Water has no stabilizing effects on Fe-Ti oxides, in contrast to observations of Sisson and Grove (1993). The different liquid lines of descent (calc-alkaline vs. tholeiitic) at reducing and oxidizing conditions result mainly from the absence or presence of magnetite.

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### SOLID STATE TRANSFORMATIONS OF CARBONACEOUS MATERIALS UNDER PRESSURE (UP TO 8 GPa) AND TEMPERATURE (UP TO 1473 K)

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High-pressure (up to 8 GPa), high-temperature (up to 1473 K) experiments have been carried out with two synthetic cokes, a lamellar graphitizing anthracene-based coke (AC) and a microporous non graphitizing saccharose-based coke (SC), and a coal. The structural and microtextural evolution of the products has been characterized by coupling high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. With all precursors, graphitization is strongly enhanced, or even initiated in the case of the non graphitizing SC, by hydrostatic pressure. Indeed, triperiodic graphite was detected by HRTEM in all samples synthesized at 1273 K and 2 GPa. Additionally, the increase of average degree of ordering is linearly correlated with the duration of the experiment. The evolution of the coal is intermediate between the two synthetic cokes. In these experiments, graphitization under pressure appears to be a progressive and continuous process which proceeds heterogeneously through the carbonaceous matrix. The products recovered from high-pressure experiments are therefore strongly structurally and microtexturally heterogeneous and this heterogeneity raises important problems for the characterization. We discuss the causes of this heterogeneity and the way to take it into account in the study of such materials. In order to complete these experiments, we have

performed kinetic experiments under pressure (2.5 GPa, 1273 K), with in situ energy dispersive X-ray diffraction using a multi-anvil apparatus at the HASYLAB-DESY synchrotron facility (Hamburg). A new diffraction band appears quasi immediately under temperature with a low d<sub>002</sub> and an increasing intensity with time. These preliminary results show that very fast transformations occur in comparison to the slow general process represented by the evolution of the products recovered from quenched experiments.

### CHLORIDE DISTRIBUTION BETWEEN HYDROUS FLUID AND BASALT AT 0.1 - 0.2 GPa ; EFFECT OF CHLORIDE ON Pt SOLUBILITY

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Experiments were performed on a synthetic haplobasaltic melt (Ab25-An55-Di20) as starting material. Experiments were performed at 1200°C, 0.1 and 0.2 GPa on a synthetic haplobasaltic melt (Ab25-An55-Di20) to determine the partitioning of chloride between fluid and silicate melt. Starting materials were diluted HCl solutions (5.0 to 25.0 wt% Cl) and dry glass sealed in Pt capsules. All experiments (total: 20) were conducted in internally heated pressure vessels equipped with a rapid quench set-up. The experimental products were always bubble free glasses (except one experiment with vesicles). Chlorine in glasses and free fluid was analyzed by microprobe and chloridometer, respectively. Water in glasses was analyzed by Karl Fischer Titration and microprobe (by difference method). The chloride content in the glasses varies between 0.4 to 2.9 wt% Cl, depending upon the amount of fluid and also on fluid concentration. The calculated distribution coefficient [D<sub>cl</sub>=(wt%Cl in fluid/wt% Cl in melt)] varies from 2.0 to 8.4, which is in agreement with previous results of Webster et al. (1999). No pressure effect on D<sub>cl</sub> is observed. However, D<sub>cl</sub> increases slightly with increasing chloride content of the charge. Experiments performed with pure H<sub>2</sub>O fluids show that water solubility is higher when Cl is present in the melt (4.9 and 6.1 ±0.15 wt% H<sub>2</sub>O in melts containing 0 and 2.9 wt% Cl, respectively). This suggests that the solubility of water in basaltic melts does not vary inversely with Cl content in melts containing up to 2 wt% Cl, in contrast to observations of Webster et al. (1999). Determination of Platinum concentration in glass is in progress and is made by isotope dilution. Preliminary results show that Pt solubility is higher in H<sub>2</sub>O bearing basaltic melts when compared with anhydrous melts.

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#### HYDROGEN MOBILITY IN PYROPE

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The quantification of hydrogen mobility in nominally anhydrous major mantle minerals is an important parameter for modeling the hydrogen cycle in the Earth's interior (Ingrin and Skogby, 2000). Recently, Wang et al. (1996) performed dehydrogenation experiments in air, on natural pyrope megacrysts ( $\text{Py}_{70}\text{Al}_{16}\text{Gr}_{14}$ ) leading to the diffusion law :

$$D_{\text{out}} \text{ (m}^2\text{/s)} = 1.77 \exp [-(254.3 \text{ kJ/mol}) / RT]$$

In order to identify the mechanism of hydrogen mobility and the different defects involved, this study compares the results obtained by FTIR spectrometry from two types of experiments : dehydrogenations and hydrogen-deuterium exchanges. The samples used are cut from a natural pyrope megacryst ( $\text{Py}_{80}\text{Al}_{15.5}\text{Gr}_{3.5}$ ) from Dora Maira.

H-extraction annealings performed at five temperatures between 800 and 1000°C show two distinct H-defects (at 3602 and 3650  $\text{cm}^{-1}$ ) with two different kinetics. The absorption band at 3650  $\text{cm}^{-1}$  becomes empty six times faster than the other. This suggests that hydrogarnet substitution ( $\text{SiO}_4 = \text{H}_4\text{O}_4$ ) is not the only mechanism for hydrogen incorporation in pyrope (Lager et al., 1989; Rossman et al., 1989). The activation energies for the two defects are equal (230 kJ/mol) and are very close to the previous data which suggests the same mechanism for the H-extraction control. However, both kinetics are more than one order of magnitude lower than Wang's data. The defects may be different since the OH absorption bands they observed are not located at the same wavenumbers (3575 and 3680  $\text{cm}^{-1}$ ).

The H-D exchange experiments executed at four temperatures between 700 and 950°C, show that exchange kinetics are identical for both defects and that the H-D exchange is faster than its extraction. Moreover, the measured activation energy is almost half that of Wang (138 versus 254 kJ/mol), but agrees with those of pyroxenes and olivine. Consequently, the H mobility mechanism is expected to be the same as for these other mantle minerals.

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#### HYDROGEN DIFFUSION IN POLYCRYSTALLINE DIOPSIDE: FIRST RESULTS

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The quantification of the hydrogen mobility in upper mantle rocks requires the knowledge of diffusion laws of hydrogen inside minerals including that at the grain-boundaries. However, up to now no diffusion data for hydrogen at grain-boundaries have been published. The frequent contamination at grain-boundaries of natural mantle rocks by hydrous phases as well as the too large grain size of these rocks precludes their use for experiments. A polycrystalline diopside sample has been synthesised in a piston cylinder from powder of a natural gem quality diopside (grains size 60 to 100 micron). The sample has been sintered at 800°C, 20 kbar for 24 hours in presence of deuterated water. A slice of the sample (85 micron thick) has been cut and kept as a reference. The remaining part ( $2.2 \times 3.4 \times 3.4 \text{ mm}^3$ ), has been annealed at 700°C during 1h in Ar/10% $\text{H}_2$  gas flowing through  $\text{H}_2\text{O}$ . A 54 micron thick section has been cut at the surface and another, 67 micron thick, in the centre, at 1.1 mm from edges. Analyses have been conducted by micro-FTIR at the synchrotron light source at LURE (MIRAGE beamline). The reference slice exhibits a homogeneous concentration of D defects equal to 300 ppm  $\text{D}_2\text{O}$ . In the surface slice, after annealing in hydrogen, analyses show that 75-80 percent of D were replaced by H. A loss of H and D (in the same proportions) is also visible, the average concentration of hydrous species decrease to 50 ppm  $\text{H}_2\text{O}$ . Analyses performed on the central slice show that the D-H exchange was also efficient at the sample core, with a mean H/D ratio of 60 percent, with ratios that can decrease up to 30 percent in the middle of some grains. Comparison of these results with the diffusion data on diopside single crystal (Hercule and Ingrin, 1999) shows that hydrogen diffusion in polycrystalline samples is at least one order of magnitude faster than in single crystal. *This study was financially supported by the EU through the Human Potential Program HPRN-CT-2000-00056.*

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#### SILICON - IRON EXCHANGE IN CALCIUM SILICATE PEROVSKITES AT TRANSITION ZONE CONDITIONS

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CaSiO<sub>3</sub> perovskite is likely an important constituent of the Earth's transition zone and lower mantle. From studies performed on MgSiO<sub>3</sub> perovskite it is known that the incorporation of trivalent cations introduces oxygen vacancies in the system, which in turn causes appreciable changes in physical properties such as elasticity and electrical conductivity. This has important implications for the interpretation of geophysical data. In this study we focus on the effects of iron incorporation into CaSiO<sub>3</sub> perovskite.

In multianvil experiments performed on the CaSiO<sub>3</sub> - CaFeO<sub>2.5</sub> join we have observed that, at the P - T conditions of the Earth's transition zone, iron can be incorporated into CaSiO<sub>3</sub> perovskite, although solubility in the endmember CaSiO<sub>3</sub> perovskite is limited. We have, however, synthesised an intermediate perovskite phase in this system with the composition Ca(Fe<sub>0.4</sub>Si<sub>0.6</sub>)O<sub>2.8</sub>, which we observe to be stable above 11 GPa over a large P - T range. Unlike CaSiO<sub>3</sub> perovskite, which becomes amorphous upon decompression, the incorporation of iron stabilises the crystal structure such that it is preserved during quenching and can be examined in detail by optical microscopy, X-ray diffraction, Mössbauer spectroscopy, electron microprobe, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). All observations indicate that the structure can be characterised by oxygen deficient tetrahedral double layers perpendicular to the pseudocubic [111]-direction, alternating with eight octahedral perovskite layers, which are one half each occupied by silicon and iron. This phase displays a new type of defect perovskite superstructure. The structure seems to be related to a distorted rhombohedral structure, which raises the possibility that a high temperature phase transition may occur. In more iron rich compositions no further phases with the perovskite structure were identified, and the endmember Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> composition with the brownmillerite structure breaks down into CaFe<sub>2</sub>O<sub>4</sub> and CaO at pressures below 7 GPa.

#### MELTING RELATIONS OF CARBONATE-SILICATE ROCKS FROM DIATREMES OF THE CHAGOTAI COMPLEX (WEST UZBEKISTAN): EVIDENCE FROM EXPERIMENTS AT 1200-1700°C AND 4-7 GPa

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The Chagotai Complex is located in the Southern Nuratau (West Uzbekistan). Carbonate-silicate rocks including essentially carbonate varieties (melanocratic carbonatite) prevail in this complex; they compose dykes and two diatremes. Carbonate-silicate rocks contain diamond crystals; their spatial distribution is extremely non-uniform and varies from single up to hundreds of grains per 15-20 kg of rock (Djuraev, Divaev, 1999). The grain size ranges from 0.05 to 0.2 mm and the forms are mainly octahedral with smooth, sharp edges.

Melting relations were experimentally studied for two natural samples of melanocratic carbonatite (Grt, Cpx, Cal, Bt, Chl, Ap, Mag). The study was aimed on (1) experimental reconstruction of high-pressure mineral associations in carbonate-silicate rocks and (2) investigation of carbonate-silicate magma crystallization under high PT-parameters. Experiments were carried out on an "anvil with hole" apparatus (Litvin, 1991).

Experiments at 1700°C provide skeletal Prp-Grs-Alm garnet (in the first sample) and Hd-Di clinopyroxene (in the second sample) crystals in the groundmass of close-grained carbonate-silicate intergrowths (Grt+L and Cpx+L parageneses). At 1600°C garnet appears in the second sample (Grt+Cpx+L). Carbonate is registered in both samples at 1500°C (Grt+Cpx+Cal+L). All other experiments conducted under 1400-1200°C demonstrate subsolidus association of garnet, clinopyroxene, and carbonate (Grt+Cpx+Cal). Cpx in experiments under 7.0 GPa contains potassium (>0.5 wt% K<sub>2</sub>O); at 4.0 GPa clinopyroxene is K-free, but K-phases (biotite, K feldspar) are observed.

Based on the experiments, the schematic diagram of melting relations in carbonate-silicate system under 7.0 GPa and 1200-1700°C was plotted. The silicate mineralization obtained is typical for high-Ca eclogite from kimberlite pipes (Sobolev et al., 1969).

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### HIGH-PRESSURE PHASE TRANSITIONS IN LAWSONITE

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The compression behavior of lawsonite  $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$  has been studied under hydrostatic conditions at room temperature up to 9.8 GPa. The P-V data of the orthorhombic phase have been analysed using a 3rd-order Birch-Murnaghan equation of state (EoS). The derived EoS parameters for the volume data are:  $V_0=676.10(3) \text{ \AA}^3$ ,  $K_0=122.1(4) \text{ GPa}$  and  $K''=5.6(1)$ . The isothermal bulk modulus is in good agreement with the value of  $K_{0T}=123(2) \text{ GPa}$  calculated from the elastic moduli measured by Brillouin spectroscopy (Sinogeikin et al., 2000). The values of the room pressure linear moduli do not show the same agreement with the Brillouin data, however. A careful analysis of the plot of the "normalised stress",  $F_E$ , versus the finite strain,  $f_E$ , (Angel, 2000) for the lattice parameters  $a$ ,  $b$  and  $c$ , reveals a change in slope at a pressure of  $\sim 4 \text{ GPa}$  for all three lattice parameters. In addition, reflections with  $h+k=\text{odd}$  forbidden by  $Cmcm$  symmetry are present at pressures above 4.1 GPa. We conclude that the phase transition is from the low-pressure  $Cmcm$  structure to a  $Pm\bar{c}n$  phase, similar to that found on cooling below 273 K at 1 bar. Considering only the lattice parameters up to 4 GPa for the 3rd-order Birch-Murnaghan EoS fitting, we obtain linear moduli in very good agreement with the results of previous Brillouin measurements of the elastic tensor at room conditions. The evolution of the spontaneous strain associated with the phase transformation has been calculated in order to characterise the transition behaviour. A further phase transition from the orthorhombic  $Pm\bar{c}n$  phase to a monoclinic phase has been observed on increasing pressure above 9.5 GPa.

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### PHASE EQUILIBRIA AND P-T-fH<sub>2</sub>O-fO<sub>2</sub> CRYSTALLIZATION CONDITIONS OF THE LYNGDAL GRANODIORITE (SOUTHERN NORWAY) AND THE ORIGIN OF A-TYPE GRANITES IN ANORTHOSITE COMPLEXES

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The Proterozoic Lyngdal granodiorite (300 km<sup>2</sup>, 60-65 wt% SiO<sub>2</sub>, 930 Ma) belongs to a series of A-type granitoids (the HBG suite: Vander Auwera et al., submitted). This suite is coeval and spatially associated with the post-collisional Rogaland Anorthosite-Mangerite-Charnockite (AMC) suite (930 Ma, Schärer et al., 1996) and shows a trend from ca. 59 wt% SiO<sub>2</sub> to ca. 76 wt% SiO<sub>2</sub>. It shares many geochemical

characteristics with anorogenic rapakivi granitoids, yet granodiorites dominate over granites, the latter being derived by fractional crystallization from the granodiorites (Bogaerts et al., submitted). In order to constrain both crystallization (P, T, fO<sub>2</sub>, H<sub>2</sub>O in melt) and source conditions, crystallization experiments on two samples of the Lyngdal granodiorite (60 and 65 wt% SiO<sub>2</sub>) were conducted in a IHPV at 4-2 kb (Al-in-hornblende, Johnson & Rutherford, 1989), at an fO<sub>2</sub> of NNO/NNO+1 (presence of titanite-magnetite-quartz, Wones, 1989), and under fluid-saturated conditions with various H<sub>2</sub>O/CO<sub>2</sub> ratios for each temperature. At 4 kbar and H<sub>2</sub>O-saturation, the liquidus for both compositions is near 1000°C with magnetite, ilmenite, apatite and clinopyroxene as near-liquidus minerals. The stability field of low-Ca pyroxene is restricted to H<sub>2</sub>O-melt < 6 wt% for all temperatures. Plagioclase is the sole feldspar between 775-950°C and amphibole appears at ca. 880°C for high aH<sub>2</sub>O at 4 kbar. It breaks down to pyroxene when H<sub>2</sub>O-melt < 5 wt%, and is absent in the experiments at 2 kb for the sample at 65 wt% SiO<sub>2</sub>. The comparison between experimental and natural phase equilibria indicates that the Lyngdal granodiorite crystallized between 4 and 2 kbar, the magma having 6 wt% H<sub>2</sub>O in melt at early stages and with an fO<sub>2</sub> of NNO/NNO+1. These oxidized and wet conditions sharply contrast with the dry and reduced characters inferred for the Rogaland anorthosite suite, on the basis on phase equilibria (Vander-Auwera and Longhi., 1994). This rules out the Lyngdal granodiorite being a fractionation product of the associated anorthosite complex. These results show that contrasted types of magmas can be generated during a single regional magmatic event within a restricted geographical area and that A-type granitic magmas need not necessarily to be dry and reduced.

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### EFFECT OF ALUMINIUM ON THE COMPRESSIBILITY OF STISHOVITE

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The recycling of oceanic crust into the deep Earth offers a way of enriching the mantle in silica (Wyssession, 1996). In such a subduction context, the high-pressure phase of silica, stishovite, present in the basaltic and the sedimentary portion of the slab, has been shown to contain small amounts of aluminium (Ono, 1998). The incorporation of this element and its possible coupling with oxygen vacancies influences the density and the compressibility of mantle phases, as has been evidenced for silicate perovskite (Andraut et al., 2001). Such parameters are important in the assessment of the structure and the chemistry of the deep mantle. In this study, the effect of aluminium on the compressibility of aluminous stishovite was investigated using a laser-heated diamond anvil cell and in situ X-ray diffraction at the ID30 beamline of ESRF (European

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Synchrotron Research Facility). The starting material was an aluminous silica glass. Cryogenically loaded argon served as the pressure-transmitting medium. After each compression step the stresses were relaxed by annealing the sample with CO<sub>2</sub>-laser radiation. The pressure was measured using the shift in the fluorescence doublet of a ruby chip located in the sample chamber. The X-ray diffraction patterns were treated using the Rietveld method. The spectra show the presence of argon, stishovite and corundum, the system being over-saturated in this last component. Comparing our data set with that of pure stishovite, also collected with ruby as a pressure standard, we observe a decrease of compressibility of aluminous stishovite respect to pure stishovite. This is consistent with a substitution mechanism of Al<sup>3+</sup> into the structure charge compensated by the creation of oxygen vacancies, such as Si<sup>4+</sup> = Al<sup>3+</sup> + O. It thus appears that the addition of aluminium into stishovite makes it softer, a result drastically different to that observed for silicate perovskite.

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### THE ACTIVITY OF SILICA IN TiO<sub>2</sub>-RICH MELTS, AN EXPERIMENTAL INVESTIGATION

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We have studied the effect of TiO<sub>2</sub> on the activity of silica in silicate melts using the Pd-equilibration method whereby silicate melts are equilibrated with pure Pd metal (Chamberlin et al., 1994). An anorthite-diopside eutectic composition (DA) was chosen as base for these experiments. TiO<sub>2</sub> was added to DA and mixtures with 5, 10, 17 and 32% wt. TiO<sub>2</sub> were produced. The composition with 32% TiO<sub>2</sub> is rutile saturated at temperature of 1300°C. By adding SiO<sub>2</sub> to DA composition up to silica saturation appropriate silica standard was produced. Experiments were conducted with a loop technique in a one atm vertical tube furnace with controlled oxygen fugacity. The Si and Ti contents in metal loops and oxide concentrations in glasses were determined using a JEOL Superprobe. We found, that TiO<sub>2</sub> contents at least up to 6-8 mol.% do not affect SiO<sub>2</sub> activity in silicate melts. It was found that Ti, like Si, a lithophile element, partitions readily into Pd-metal at reducing conditions. The activity coefficient of Ti in Pd-metal is estimated to 5.8·10<sup>-10</sup> at 1300°C, two orders of magnitude below activity coefficient of Ti in Pd-metal (Fechner, 2000), for the same temperature. Additional experiments demonstrated that the Ti-Pt solid solution is even more non-ideal than the Ti-Pd alloy and that of γTi in Pt doesn't obey Henry's law. It was also found that at fO<sub>2</sub> below some critical value the liquidus phase rutile is replaced by a new so far unknown phase with a composition corresponding to MgTi<sub>3</sub>O<sub>7</sub>.

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### ESTIMATION OF THE MANTLE SOURCE COMPOSITION FROM GABBROIC INTRUSION COMPOSITION

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The problem of estimation of the upper mantle composition might be decided by using the dynamic models of partial melting of the mantle source. The primary mantle magmas should be in equilibrium with the olivine composition Fo>89. The parental magma of gabbroic intrusions with Fe/Mg ratios capable of coexisting with mantle olivines, could be interpreted as primary mantle magmas. The calculation data of the mantle source compositions were used for examination of high-magnesia layered gabbroic intrusions - Centralnii (Western Mongolia) and Majalic (Tuva). Parental magma compositions of these intrusions were estimated by COMAGMAT program 3.0 (Ariskin et al., 1993). Our preliminary results show that the Centralnii intrusion parental magma was picritic magma with 100 Mg/(Mg+Fe)=83,6, and REE abundances 1-6 chondrites. The parental magma could have been in equilibrium with the olivine composition Fo-94,9. The Majalic intrusion parental magma is characterized by 100 Mg/(Mg+Fe)=86,9 and REE abundances 1-10 chondrites. The Majalic parental magma had Fe/Mg ratios capable of coexisting with olivine composition Fo-95,9. The behaviour of heavy rare earth elements of these intrusions parental magmas suggests that residual garnet remains in their mantle sources. The Al<sub>2</sub>O<sub>3</sub> content in Centralnii intrusion parental magma is consistent with its generation at 25 kbar, while Al<sub>2</sub>O<sub>3</sub> content in Majalic intrusion parental magma can be explained by melt segregation at upper mantle pressures that ranged from 35 to 40 kbar. Thermodynamic calculation of partial melting of peridotite using the MELTS algorithm (Ghiorso et al., 1994) indicates that parental magma of both Centralnii and Majalic gabbroic intrusions can be derived, in terms of major elements, from the same depleted lherzolite source (100 Mg/(Mg+Fe)=92,1). It appears to be similar to Vourinos ophiolitic complex (100 Mg/(Mg+Fe)=92,8) (Moore, 1970). The parental magma composition variations of these intrusions could be explained by different physical parameters of the melting process (pressure, temperature and degree of partial melting). The variations in composition of the gabbroic intrusions mantle sources situated in the same area seem to be controlled by local major element heterogeneity in the mantle.

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### EXPERIMENTAL STUDY OF SULFUR AND CHLORINE SOLUBILITY IN RHYODACITE AND ANDESITE MELTS OF UNZEN VOLCANO, JAPAN

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Solubilities of sulfur and chlorine (H-O-S; H-O-Cl; and H-O-S-Cl fluids) have been studied for the rhyodacite (groundmass) and andesite compositions of Unzen magmas at T=850 and 1050°C, P=50-300 MPa,  $f(\text{O}_2)=\text{NNO}$ , t=120 hours. All experiments were fluid saturated (fl/melt ratio<0.05). Experiments at T=850°C were conducted in cold seal pressure vessels, pressurized by water. High-temperature runs were made in an internally heated pressure vessel equipped with a rapid quench device and a Shaw-membrane to control hydrogen fugacity inside the vessel (Berndt et al., in press). The formation of sulfides buffers the solubility of sulfur in rhyodacite melt in equilibrium with (H-O-S)-fluid at the level of 30-50 ppm at T=850°C. Pressure has a negligible influence on the sulfur solubility in the melt of rhyodacite composition at this temperature. Experiments at higher temperature (1050°C) and P=200 MPa show no buffering effect of sulfides but a continuous increase in the concentration of dissolved sulfur with the amount of added S (and fluid  $f(\text{S}_2)$ ) both for rhyodacitic and andesitic compositions. Chlorine in (H-O-Cl)-fluid - melt system is preferentially partitioned into the fluid phase ( $D_{\text{Cl}} = C_{\text{Cl}}(\text{fl}) / C_{\text{Cl}}(\text{m}) = 3.9-5.9$  for rhyodacite and  $D_{\text{Cl}}=3.2-3.4$  for andesite at T=1050°C) and the distribution coefficient increases with increasing Cl content (up to 5 wt%) in the fluid. Increasing the Cl concentration in the melt at T=1050°C and P=200 MPa from 0 to ~1 wt% enhances the solubility of water from 5.5±0.2 to 6.0±0.1 wt% and from 5.7±0.2 to 6.0±0.1 wt% for andesitic and rhyodacitic melts, respectively. These results are in contrast with the conclusions of Webster et al. (1999) for andesitic and more silicic magmas. Increasing sulfur content in the (H-O-S-Cl)-fluid at T=850°C and P=200 MPa has no influence on Cl solubility in rhyodacite melt at low amount of added chlorine and decreases Cl solubility at high Cl concentrations.

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### METAL-SILICATE INTERACTIONS AT HIGH PRESSURE AND TEMPERATURE IN A DIAMOND ANVIL CELL

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The main feature of the Earth is its differentiation into a iron-metal rich core and a silicate mantle. There is a little doubt that the density of the Earth's outer core, inferred from seismology, requires that it is constituted of an alloy of liquid iron and light elements (Birch, 1952). However, the nature of the light alloying elements is still uncertain as it depends in a large measure on the conditions of accretion of the Earth and formation of the core. In the present study we use the laser-heated diamond-anvil cell (LHDAC) to study the high-pressure and temperature interactions between metal and silicate. Our first aim is to compare our partitioning behaviour of Ni and Co between metal and silicate liquids at low pressures (5-12 GPa) with results from multi-anvil devices in the Si-Al-Fe-Mg-Ca-Ni-Co-O system (Thibault and Walter, 1995). For high-pressure and high-temperature experiments, we used diamond anvils with 500 microns culets, and stainless-steel gaskets preindented to a thickness of 40 µm and drilled to a diameter of 100-150 µm (depending on a maximum pressure reached). We used both compacted powders with several silicate glass compositions (ranging from SiO<sub>2</sub> to basaltic composition simulating that of model C1 chondrite) and a 25 µm thick Fe-Ni-Co alloy foil. Thermal insulation from the diamonds was achieved by solid argon pressure medium. Pressures were measured at room temperature before and after laser heating, with the ruby-fluorescence method. The samples were heated by a multimode YAG laser for an average of 10-15 minutes. Temperatures were determined spectro-radiometrically with a fit to a grey-body Planck function. Samples recovered after the runs were analysed by electron microprobe (the electron beam is less than 1 µm and the resolution is about 1 µm). In addition, we have analysed our samples using secondary ion mass spectrometry (SIMS) analysis. A successful overlap of results of these different analysis techniques will substantially increase confidence in the extension of experiments to lower-mantle conditions. Our preliminary results in the system Si-Al-Fe-Mg-Ca-Ni-Co-O, show a good agreement with those of multi-anvil experiments at low pressures (5-12 GPa) (Thibault and Walter, 1995), and with increasing pressure until 50 GPa we observe the expected decrease of the partition coefficients of Ni and Co for the same redox conditions. We will present and discuss our results in all the systems studied as well as the solubility of Ar in silicate melts and iron-rich metal phases.

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### STABILITY OF SiO<sub>2</sub>-POOR ALKALISILICATES IN AIR

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SiO<sub>2</sub>-poor alkaalisilicate liquids are of great interest in Earth sciences and glass industry as part of model systems thanks to which the properties of more complex melts can be understood. In view of their high hygroscopicity and possible reaction with atmospheric CO<sub>2</sub>, however, these materials have led to a number of difficulties which has long restricted their use. Preliminary experiments on a CO<sub>2</sub>-bearing binary potassium silicate melt with 43 mol% K<sub>2</sub>O have shown that water intake is reversible on slow heating below the glass transition range, so that viscosity or thermal expansion measurements could be made safely in the supercooled liquid field (Bourgue & Richet, 2001). To gain more detailed insight on this process, we have investigated in this study the reactions with air of sodium and potassium silicates at or near room temperature. To investigate the effects of water absorption, we have made density, thermal expansion and heat capacity measurements. Information regarding the kinetics of absorption and exsolution, and the mechanisms of these reactions has been obtained by Raman spectroscopy with a heating-wire cell as described by Mysen & Neuville (1995). The results will be presented and discussed. The thermodynamics of dissolution of some of these glasses into water will be evaluated and the difficulties met to extract all the CO<sub>2</sub> dissolved in these glasses will be mentioned. Finally, special attention will be paid to the bias that can affect measurements made on partially altered samples.

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### FERROPERICLASE - A LOWER MANTLE PHASE IN THE UPPER MANTLE

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Ferropériclase is common in diamonds from Guinea (Stachel et al., 2000) and coexistence with enstatite proves lower mantle origin. In one diamond, the inclusion paragenesis is olivine and ferropériclase (touching and non-touching). Ferropériclase and ringwoodite may coexist at the lower mantle boundary and the olivines could be retrograde products from ringwoodite. This is not feasible because (i) touching and non-touching olivines and ferropériclases are chemically identical and retrograde adjustment of Fe and Mg of the touching pair could not be observed and (ii) an Fe/Mg distribution of 4 is consistent with Fe/Mg partitioning between ferropériclase-olivine rather than ferropériclase-ringwoodite (Fei, 1998). Thus, diamond, ferropériclase and olivine grew in the upper mantle in a low silica-activity environment.

An argument used against this was the high sodium content of 0.36 wt.-% supposed to be indicative of very high pressures. Sodium may, however, be incorporated in ferropériclase on crystal chemical grounds only together with Al and Cr. Our experiments from 3 to 5 GPa and 1300 to 1600°C along joins MgO-jadeite and MgO-ureyite yielded olivine + periclase + spinel + liquid. Sodium in periclase ranged from 0.6 to 2 wt.-% with aluminum in amounts necessary for charge balance. Up to 20 wt.-% Cr were found and Cr may also be incorporated as divalent or in a defect structure.

In conclusion, high sodium content in ferropériclase is not indicative of lower mantle origin. In the present case, Na-bearing periclase together with olivine reflects a region of low silica-activity in the upper mantle which may originate by interaction of carbonatitic melts with dunite precipitating magnesite later to be reduced by methane on diamond formation. Alternatively, ferropériclase, olivine and diamond may precipitate directly from carbonatite melt on interaction with a more reduced environment.

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### PHASE RELATIONSHIPS AND TOPOLOGICAL CONSTRAINTS IN THE SYSTEM $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$ AT 1 ATM

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High temperature experiments were performed in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$  (MASCr) at temperatures ranging from 1250°C to 1560°C at 1 atm. Bulk compositions were prepared as oxide mixture pellets, with  $\text{SiO}_2\text{:Al}_2\text{O}_3$  ranging from ~1:1 to 1:4.5 wt.%, and  $\text{Cr}_2\text{O}_3\text{:Al}_2\text{O}_3$  ranging from 1:9 mol toward Al-free compositions. Run products were characterized by X-Ray Powder Diffractometry, BSE images and EDS-WDS microprobe analysis.

Chromium is strongly incorporated into crystals, coexisting with very chromium-poor glasses. The whole range of chromian solid solution in spinel and corundum is covered. Sapphirine is widespread in aluminosilicatic compositions. It presents a very high chromia content (up to 29 wt%), and appears to be the only quaternary compound in the system.

The presence of liquid at temperatures as low as 1250°C suggests that the thermal minimum in the system MASCr is shifted to lower temperatures compared to MAS. At 1400°C a chromian sapphirine is found in a subsolidus four phase assemblage, coexisting with Cr-mullite, magnesiochromite and cristobalite. Phase relationships at 1560°C and 1250°C, by comparison with available data, suggest a complex topology in the silica-rich region of the system, involving the existence of a cotectic quaternary line raising from the ternary invariant point at 1590°C in the SACr system, and the presence of one or more quaternary invariant points. Composition of liquids coexisting with sapphirine and enstatite in the quaternary system are much silica richer than they are in the MAS system. This suggests that the cotectic quaternary surface of cordierite is constrained to lower chromium contents. Applications of experimentally defined phase relationships include refinement of currently available thermodynamic datasets on Cr-bearing systems, processing of Cr-refractories, and industrial waste treatment to permanently incorporate dangerous heavy metals in stable crystalline assemblages.

### AN EXPERIMENTAL INVESTIGATION OF HYDROGEN SOLUBILITY IN PYROXENES ALONG THE DIOPSIDE-JADEITE TIE-LINE

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Considerable focus has recently been placed on the study of structurally-bound hydrogen in nominally anhydrous minerals (NAMs) thought to be stable in the upper mantle. Previous studies of natural samples have demonstrated that the pyroxene omphacite contains the most water, and is possibly the most important mineral in terms of recycling water back into the

mantle during subduction. An experimental program is currently underway to investigate hydrogen solubility in pyroxenes along the diopside ( $\text{CaMgSi}_2\text{O}_6$ ) – jadeite ( $\text{NaAlSi}_2\text{O}_6$ ) solid-solution series. Hydrogen solubility in jadeite has been studied from 1.7 to 10 GPa using FTIR spectroscopy on synthetic samples. A technique has been developed to produce large mm-sized, relatively crack- and inclusion-free crystals. Starting materials with considerable excess water are used and experiments are run for up to 10 days. Run temperature is varied during each experiment to initially produce complete melting and then allow crystal growth from the quenched melt.

Unpolarised and polarised spectra for jadeite are characterized by sharp peaks at 3613 and 3372  $\text{cm}^{-1}$ , and a broader hump centered around 3552  $\text{cm}^{-1}$ . Spectra obtained from samples synthesised below 2.5 GPa also exhibit a large and very broad hump centered around 3430  $\text{cm}^{-1}$ . A similar broad feature is noted in spectra from diopside-rich omphacite crystals synthesised at 1.0 GPa. This feature may be associated with M2 vacancies. The sharp peak at 3613  $\text{cm}^{-1}$  noted in all the spectra is perhaps analogous to a similar sharp peak noted in natural and synthetic diopside samples which occurs at slightly lower wave numbers.

Hydrogen contents for the samples studied so far are high in comparison to other NAMs, up to 2000 ppm, which is in-line with data from natural samples. Full characterization of the effects of pressure on hydrogen content in jadeite and omphacite is in progress.

### COMBINED EXPERIMENTAL PHASE-EQUILIBRIA AND LOW-TEMPERATURE ADIABATIC CALORIMETRY TO DERIVE ACCURATE ENTHALPY AND ENTROPY VALUES FOR ACCESSORY MINERALS

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The derivation of thermochemical data for minerals to predict their stability in natural systems is one of the major issues of the experimental mineralogy. The phase relations between main rock-forming silicates can now be accurately modelled using internally-consistent thermodynamic databases. Accessory minerals, like REE-bearing minerals or phosphate minerals, are absent from these thermodynamic databases although they can be of primary petrological and geochemical importance. The success of internally-consistent databases in tackling phase relations shows that the thermodynamic characterisation of new phases should combine both experimental brackets which put tight constraints on  $\Delta_r G(T,P)$  (where “r” stands for reaction) and calorimetric measurements. We have already performed thermodynamic extractions out of experimental brackets for some phosphate minerals as bearthite, trolleite, lazulite or  $\text{MgAlPO}_4\text{O}$ . Every time, it appeared that additional low-T adiabatic calorimetry measurements could still better constrain the third-law entropy ( $S_{i,298}^\circ$ ) derived for

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these phases. The range of formation enthalpy ( $\Delta_f H_{i, 298}^\circ$ ) consistent with the brackets will also be significantly reduced when  $S_{i, 298}^\circ$  is tighter constrained since both parameters are correlated. In this contribution, our low-T adiabatic calorimeter will be presented along with first Cp data obtained for lazulite,  $MgAl_2(PO_4)_2(OH)_2$ , from ambient down to 25 K. In addition, preliminary HP and HT phase relations in the  $La_2O_3$ - $SiO_2$ - $P_2O_5$ - $CaO$ - $H_2O$ - $MgO/Al_2O_3$  systems will be shown, which aim at the derivation of thermochemical data for La-hydroxybritholite,  $La_6Ca_4(SiO_4)_6(OH)_2$ .

### BACTERIAL BIOFILM DEVELOPMENT WITHIN A SIMULATED NEAR SURFACE FRACTURE : BIOFILM STRUCTURE AND ITS IMPLICATIONS FOR MINERAL-FLUID INTERACTIONS

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Bacterial biofilms (complex bacterial communities supported by a hydrated exopolymeric matrix) form a reactive biological interface between minerals and solutions in many geological systems, including saturated near surface fracture-dominated aquifers. The mineral-fluid interface, once modified to a mineral-biological-fluid interface, has a greater surface area, surface roughness and an altered number of active sorption sites presented to solutions. Hence such modified interfaces will display a modified reactivity with dissolved trace metals. However, the initial colonisation, development and resulting architecture of these biofilms is poorly understood in terms of mineral surface coverage, initial bacterial adhesion mechanisms and biofilm structural development within water saturated fracture systems. In this work, a single species biofilm (*P. Aeruginosa* PA01) was developed within a simulated fracture and imaged using confocal scanning laser microscopy (CLSM). Subsequent image segmentation and isosurface generation of biofilms allowed improved visualisation of biofilm structure and its relationship to colonised surfaces. We also present evidence of flow-induced biofilm features, including the first evidence of the mechanics of flow induced biofilm "sloughing". Subsequent experimentation using the same equipment under temperate groundwater conditions (bacterial growth on a quartz substratum at 10°C using low nutrient concentrations) should reflect typical bacterial colonisation behaviour in natural systems of this type.

### EXPERIMENTAL DATA AT 6 GPa ON THE SYSTEM $CaCO_3$ - $MgCO_3$ AND A THERMODYNAMIC MODEL OF THE SOLID SOLUTION

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A series of multi-anvil experiments have been performed in the system  $CaCO_3$ - $MgCO_3$  at 6 GPa between 800 and 1500°C. The starting materials consist of various mixtures of the trigonal carbonates pure ordered dolomite (natural), magnesite (natural), and calcite (synthetic) that cover the compositional range. At the experimental conditions  $CaCO_3$  exists in its orthorhombic high-pressure form, aragonite. With increasing temperature Ca-Mg-disorder in dolomite increases and above 1200°C the Ca and Mg cations are randomly distributed.

The breakdown reaction of stoichiometric dolomite to aragonite and magnesite occurs at 6 GPa between 900 and 1000°C and is in agreement with Luth 2001. The solid solutions in the system are temperature dependent. Two miscibility gaps appear in the T-X $MgCO_3$  diagram: one between aragonite and dolomite, and one between dolomite and magnesite. The non-stoichiometry of the dolomite depends on its degree of disorder. On the Ca-rich side the difference in the crystal structures between aragonite and dolomite does not allow a complete solid solution. A small two-phase field for disordered dolomite plus aragonite remains until melting occurs. Dolomite melts incongruently to aragonite and liquid. On the Mg-rich side the miscibility gap is cut by the melting curve at around 1400°C where magnesite coexists with a dolomitic liquid.

Using Raman spectroscopy, X-ray powder diffraction, and electron microprobe analysis techniques phase and mineral compositions have been determined. Using the compositions of the coexisting phases two temperature dependent Margules parameters are derived for the dolomite - magnesite subsystem. Before melting occurs at 1350°C  $Mg_{0.606}Ca_{0.394}CO_3$ -dolomite coexists with  $Mg_{0.867}Ca_{0.133}CO_3$ - magnesite, the two calculated Margules parameters are  $W_{12} = -30.6$  kJ and  $W_{21} = -4.0$  kJ.

Luth RW, *Contributions to Mineralogy and Petrology*, **141**, 222-232, (2001).

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### RESIDUAL GASES IN LAVA FROM ACTIVE PU'U O'O, KILAUEA, HAWAII

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While the volatile content and composition of magmas characterizes the tectonic regime of their genesis, extensive degassing during ascent and emplacement of magmas leaves us with a residual gas content, only. Here, we consider the effect of emplacement on residual gases of basalt glass from Pu'u O'o, Hawaii, and specifically the effect of reheating and changes of their redox state. Residual gases, trapped during hammer-dipping and subsequent quenching of basalt melt from Pu'u O'o, Hawaii, were detected with mass spectrometry (DEGAS, [1]) during heating. Compared to the amount of gas liberated from other basalt glasses, e.g. MORB, this lava has a lower content by several orders of magnitude. Extensive degassing occurred probably during the approximately 12 km transport to the ocean. Gases escape, in principle, by two different mechanisms, sudden release resulting in one or more spikes, and gradual escape by diffusion. We observe no gas release at temperatures below the glass transition temperature  $T_g$  (680°C), and no direct relation with crystallization temperatures (850°C and > 920°C [2]). A sudden and intensive release of hydrogen at 820°C correlates with a reducing atmosphere (increasing EMF), and oxidation of the sample. The oxidation enthalpy derived for the entire EMF experiment that did not achieve equilibrium, is about -57.4 kJ/mol and agrees qualitatively with -67 and -105 kJ/mol, derived for powdered glass and chunks, respectively, that had been oxidized towards equilibrium conditions [2]. These results may indicate that the emplacement of lava that allows structural relaxation via cooling or reheating and concomitant crystallization effects the original oxidation state.

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### HIGH TEMPERATURE, LARGE STRAIN DEFORMATION TESTS ON QUARTZ AGGREGATES

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Cylindrical samples of natural water-rich quartz aggregates (Dover flint, England) were deformed in torsion in a Paterson gas-medium apparatus at constant strain-rate of  $10^{-4}$ s<sup>-1</sup>, temperatures of 1250, 1300 and 1400 K, and 350 MPa confining pressure. Here we present the results of tests at 1400 K. Samples were heat treated at 350 MPa at 1400 K, for different period of time (0.5 to 6h) under drained and undrained conditions. According to the phase stability diagram of the system SiO<sub>2</sub>-H<sub>2</sub>O, melt can be expected to be present. FTIR analysis of as-

is samples showed bulk water content of about 10<sup>5</sup>H/10<sup>6</sup>Si. Samples pre-heated for 0.5h or longer contained less than 10<sup>4</sup>H/10<sup>6</sup>Si. Fluid loss was even higher in deformed samples.

Samples heat treated 0.5h and deformed to low shear strain ( $\gamma < 0.2$ ) under undrained conditions yielded at half of the stress of those deformed under drained conditions, suggesting that the strength depends on the water content (or pore fluid pressure). Microstructures of undrained samples showed evidence of tensile fracturing, suggesting that the pore pressure was close to the confining pressure. On the other hand, drained samples showed no evidences of cracking.

Other samples heat-treated for 0.5h were deformed to high shear strains ( $\gamma > 1.5$ ). These showed steady-state stress up to a shear strain of  $\gamma = 2$ , then they hardened. Strain hardening was primarily correlated with the development of cracks. Microstructural observations suggest that the strain accommodating mechanism was granular flow, probably enhanced by melting along grain boundaries, since no SPO and only a very weak LPO was observed.

The sample heat-treated for 6h and deformed to  $\gamma = 2.4$  showed steeply inclined crystobalite grains (metastable at this conditions). We interpret the crystobalite as fibres growing parallel to the minimum shear stress.

### MELTING RELATIONS ON THE OMPHACITE – GARNET JOIN AT PRESSURE OF 7.0 GPa: EXPERIMENTAL MODELING OF ORIGIN OF DIAMOND-BEARING ECLOGITES

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The eclogite system on the omphacite – garnet join was chosen for experimental study as a model for the mantle source region and diamond – bearing rocks. The boundary multicomponent compositions are represented (in mol.%) by omphacite of the diopside-46,24; hedenbergite-8,85; acmite-13,68; jadeite-31,23; composition and garnet of the pyrope-15,21; almandine-53,35; grossular-31,44 composition. The compositions were calculated as the most representative for the Maksutov complex (Southern Urals) and reflect some key peculiarities of eclogite minerals from the mantle nodules in kimberlite diatremes.

The omphacite – garnet join studied is the inner section of the ternary omphacite – (pyrope + grossular-30%) – (almandine + grossular-30%) system. The ternary system is expected to give more complete information as to evolution of the major mineral composition in the mantle source region. For the pressure of 7.0 GPa, the melting diagram of the omphacite – garnet join is constructed. Both clinopyroxene and garnet are presented as liquidus phases. For subsolidus conditions, the clinopyroxene solid solution and clinopyroxene + garnet assembly fields are identified. Melting relations are controlled by the pseudoinvariant equilibrium at 1500°C (the equilibrium seems to be eutectic in agreement with the reaction clinopyroxene + garnet = liquid).

Melting relations on the multicomponent omphacite – garnet join are more under influence of the eutectic jadeite – pyrope system than the peritectic diopside – pyrope one if the relation revealed at 4 GPa (Bell & Davis, 1969; Litvin, 1991) are of value for 7 GPa. Phase equilibria on the pyrope – almandine join at 7 GPa (Butvina et al., 2001) are characterized by the complete series of solid and liquid solutions without extreme points (Roseboom's type I). Constitution of the ternary omphacite – (pyrope + grossular) – (almandine + grossular) phase diagram may be rather influenced with jadeite – pyrope system than diopside – pyrope one, and it is expected to characterize by divariant eutectic line and not include invariant equilibria at 7 GPa. The ternary melting equilibria are of key importance for the origin and evolution of diamond – bearing eclogites in the mantle conditions. Support: grant 01-05-64508 Of RFBR, 215-05 Integracia.

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### EXPERIMENTAL DEFORMATION OF CLINOPYROXENE AGGREGATES

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We have conducted an experimental deformation study on the rheological behavior of clinopyroxene aggregates under dry conditions at low strains in a uniaxial deformation apparatus and at high strains using a torsion set-up. Coarse-grained natural clinopyroxene samples from Sleaford Bay and fine-grained aggregates hot-pressed from Sleaford Bay powders were first dried in a 1-atm oven at 1000°C for 10 hours under controlled conditions. The samples were then deformed in a Paterson apparatus at confining pressures of 300 - 430 MPa and temperatures of 1150-1250°C with the oxygen fugacity buffered by either nickel-nickel oxide or iron-wüstite powders.

Our low-strain uniaxial study yielded a flow law for dislocation creep for natural clinopyroxenite with a stress exponent of  $n = 4.7 \pm 0.2$  and an activation energy for creep of  $Q = 760 \pm 40$  kJ/mol. In the hot-pressed samples, mixed-mode deformation behavior was observed, with diffusional creep ( $n = 1$ ) at lower differential stresses and dislocation creep (with  $n$  and  $Q$  similar to those of the natural samples) at higher differential stresses. Within the dislocation creep field, the predried hot-pressed samples generally yielded creep rates that were about an order of magnitude faster than the natural samples. Optical and electron microscope investigations of the deformation microstructures of the natural and hot-pressed samples show evidence for mechanical twinning and activation of dislocation slip systems.

High-strain deformation experiments were performed in torsion on natural and hot-pressed aggregates under similar conditions. Simple-shear microstructures and textures were analyzed using optical microscopy and EBSD. Hot-pressed samples were significantly weaker than natural samples. Stepping tests were performed to determine the evolution of the stress exponent with strain. We present a comparison of our

rheological data at low and high strains, and discuss the difference in rheological behavior between natural and synthetic aggregates.

### A HT-XRD STUDY OF SYNTHETIC MAGNESIAN-FERRISPODUMENE: TRANSITION TEMPERATURE VS. CATION COMPOSITION AND ORDERING

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We synthesised magnesian-ferrispodumene in the MgO-LiO<sub>2</sub>-FeO-SiO<sub>2</sub>-H<sub>2</sub>O system. Single-crystal structure refinement at room T and EMP analyses show that this pyroxene is monoclinic  $P2_1/c$  with composition  $M^2(Li_{0.85}Mg_{0.09}Fe^{2+}_{0.06})M^1(Fe^{3+}_{0.85}Mg_{0.15})Si_2O_6$  ( $a = 9.638(3)$  Å,  $b = 8.709(2)$  Å,  $c = 5.258(2)$  Å,  $\beta = 109.83(3)^\circ$ ,  $V = 415.2$  Å<sup>3</sup>). Li is ordered at M2, and Fe<sup>3+</sup> at M1, Mg and Fe<sup>2+</sup> distribute over both octahedral sites. Structure refinements done at different temperatures show that at 105°C magnesian-ferrispodumene undergoes a reversible displacive phase transition  $P2_1/c \Rightarrow C2/c$ . It is evidenced by the disappearance of the  $h+k = 2n+1$  reflections and by abrupt changes in the unit cell parameters. It is known from previous HT-XRD work that in Li-clinopyroxenes the transition temperature is inversely related to the size of the M1 cation [70°C in LiCrSi<sub>2</sub>O<sub>6</sub> (Behruzi et al., 1984); 10°C in LiGaSi<sub>2</sub>O<sub>6</sub> (Sato et al., 1995); -44° in LiFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub>, (Redhammer et al., 2001)]. The studied crystal has an aggregate ionic radius at M1 larger than LiFe<sup>3+</sup>Si<sub>2</sub>O<sub>6</sub>; therefore its transition temperature should be < -44°C. It is also known (Prewitt et al., 1971) that the transition temperature in ferromagnesian clinopyroxenes increases with decreasing aggregate cation radius at M1 and M2, and thus depends on the Fe<sup>2+</sup> ordering between M1 and M2 (Cámara et al., 2002). The transition temperature experimentally measured for magnesian-ferrispodumene can be thus explained by the presence of significant Mg at M2 which shortens the aggregate radius at that site. This study suggests the possibility of a complex thermodynamic behaviour accompanying variable cation substitutions at both the M1 and M2 sites in clinopyroxenes.

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#### REACTION SEQUENCE VS CHEMICAL COLLINEARITY IN THE $P_nW$ POLYSOMATIC SERIES. A HREM STUDY OF Mn-PYROXENIDS FROM CAMPIGLIA MARITTIMA (LIVORNO, CENTRAL ITALY)

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Late crystallisation stages of the Campiglia Marittima quartz-clinopyroxene-ilvaite skarn were characterised by Mn-activity increase at the metasomatic front. Mn-pyroxenoids became stable with respect to johannsenite. Textural observations at the petrographic thin section scale suggest two distinct crystallisation mechanisms: (a) pyroxenoids overgrowing johannsenite and directly precipitating from a fluid rich system; (b) pyroxenoids pseudomorphically replacing for pyroxenes. We focused the TEM investigation on these latter sites, finding microstructures distinctive of a solid-state transformation involving the movement of a reaction front through the original johannsenite (i.e. "bulk reaction mechanism"; Veblen, 1985). Comparatively few observations recall a unit-cell by unit-cell topotactic replacement of johannsenite by pyroxenoids (i.e. "lamellar reaction mechanism"; Veblen, 1985). Johannsenite-pyroxenoid solid-state transformation occurred at temperatures lower than 260° C. Either ordered pyroxmangite or disordered intergrowths of rhodonite and pyroxmangite occur at the reaction front with johannsenite, showing  $(001)_{Pxd} // (11\bar{1})_{Jh}$ . Based upon existent ternary phase diagrams for the system  $CaSiO_3$ - $MnSiO_3$ -(Mg,Fe)SiO<sub>3</sub> (Abrecht, 1985), minor changes in the iron plus magnesium concentration are supposed to play a relevant role in determining the mineral assemblage at the reaction front. Moreover, crystal chemical considerations indicate that the maximal calcium content of pyroxmangite is 2/7, rather than 1/7. In the light of these observations, pyroxmangite may behave as stable phase in the replacement of johannsenite rather than metastable as previously stated. As further remark, the  $P_nW$  polysomatic series can now be considered not only structurally but also compositionally collinear.

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#### DISSOLUTION OF MAFIC MICROGRANULAR ENCLAVES BY DECOMPRESSION MELTING IN A WATER-SATURATED GRANITIC MAGMA

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Several experimental runs on interaction between tonalitic microgranular enclaves and a granitic melt have been performed in "piston - cylinder" apparatus (experimental

details in Castro et al. 1999), using as starting materials small rock fragments of a tonalitic enclave and powdered hydrous granitic synthetic glass. Our experiments were carried out at pressures from 10 kbar to 4 kbar, at three different temperatures: 900°C, 850°C and 750°C, to check the consequences of decompression. Results at 10 kbar show no changes in the tonalitic enclaves and only partial crystallization of the granitic glass for low temperature, but for higher temperatures, partial dissolution of the tonalitic enclaves by the more acid hydrous melt can be observed by identifying dissolution textures in the tonalitic fragments, and by changes in the melt (glass) composition that becomes more monzogranitic compared with the starting composition of the enclosing glass. Experimental runs were held at 10 kbar for 4 days and then brought to a lower pressure of 4 kbar for 4 days for a given temperature, in this process the dissolution of the tonalitic enclave is enhanced due to reaching water saturation of the melt by dropping pressure. Changes of the analyzed melt to more CaO, FeO and MgO compositions as well as dissolution textures on the crystal surfaces which formed the tonalitic enclave were monitored. These results have implications in the generation of monzogranite magmas from pelitic or greywacke rock sources in which the CaO content is insufficient to produce monzogranite melts. The tonalitic enclaves that are partially dissolved may be early intrusions into the migmatitic area or intrusions of intermediate magmas coeval with granite magma generation. Many geochemical and isotopic features of monzogranites (e.g. the low Sr isotopic ratios) are accounted for by this mechanism of enclave dissolution during ascent and emplacement.

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#### PRELIMINARY RESULTS ON EXPERIMENTAL CRYSTALLISATION UNDER COAXIAL STRESS

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Magmatic fabrics are common in volcanic and plutonic rocks. In the latter, these textures are often used as markers of regional deformation patterns. However, the origin of such fabrics is still not well understood. The most commonly accepted hypothesis is that these textures originate by a magmatic flow mechanism. We are currently testing another hypothesis, namely: the possibility that deformation affects crystallisation and thus, fabric patterns.

The main difficulty in such experiments comes from an antagonism between the low viscosity of magmas (i.e. fast deformation) at relevant geological temperatures and the slow kinetic of crystallisation. To overcome this problem, we start our deformation experiments with an already partially crystallised magma (crystallinity = 30%), which increases the viscosity by about 1 order of magnitude

The experimental procedure is divided in two steps: synthesis in IHPV at 850°C, 300 MPa, during 10 days, of partially crystallised glass cylinders (starting material: a rhyodacitic glass,

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69% SiO<sub>2</sub>, with 3 wt% bulk H<sub>2</sub>O), followed by the deformation of the cylinder at the same pressure but at a temperature below that of synthesis (in the range 700-800°C), in order to induce a second crystallisation stage. The effect of deformation is characterised by comparing deformed and undeformed charges produced at the same temperature from the same starting materials.

To this end, we have designed a deformation apparatus (Champallier et al., 2001). This first prototype works at high strain rate and does not allow to accurately determine the onset of deformation at HP-HT. The resulting deformed cylinders all displayed complex crossed fabric patterns difficult to interpret.

A new deformation apparatus, overcoming the problems of both onset and strain rate, is currently being tested. It will be presented with the results on fabrics and nucleation obtained from deformation/crystallisation experiments.

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### EXPERIMENTAL INVESTIGATION OF Cl AND H<sub>2</sub>O SOLUBILITIES IN GRANODIORITE MELTS

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Experimental determinations of the chlorine solubility in the model water-saturated melts of granodioritic composition have been done in the wide range of the alteration of water-chloride fluid compositions from 0 to 98 wt.% chlorides at 1 kbar - 1000°C and 0,3 kbar - 1250°C. Water forms (H<sub>2</sub>O mol., OH) content have been determined in the experimentally derived glasses by precise IR-FTIR spectroscopy and considered together with Cl content. The same glasses are characterized with common IR-spectroscopy in respect to their medium-range structure. The influence of various contents of chlorine, water and alkali and earth-alkali metals on the medium-range structure of quench glasses have been characterized. The complex infrared absorption bands in the range of frequencies 300-600 cm<sup>-1</sup> have been approximated by two contours, those are related to oscillations of four- and six membered aluminosilicate and silicate rings (Simakin et al., 1998; Sykes et al., 1990; Zotov et al., 1998). Possible model of chlorine solubility is suggested based on the data obtained. The following main results can be enumerated. (1) At P=1 kbar and at total saline fluid more than 15 wt.% the chlorine and water solubilities in granodiorite melt are 0,5-0,7 wt.% and 3,5-3,65 wt.% accordingly. Abrupt increase of chlorine solubility (to 0,9-1 wt.%) occurs at total saline fluid 6-15 wt.%, then water content decreases to 3,0-3,3 wt.%. At saline fluid 0% the water content in the quench glasses is 3,0-3,3 wt.%. (2) Transition from feldspar-like (4-membered) aluminosilicate structural elements to tridimite-like (6-membered) ones at the action of dissolved water and chlorine has been fixed by IR-spectroscopy of quenched glasses. (3) TEM microscopy proves absence of the salt phase in the studied glasses. (4) Data obtained can be interpreted from the point of view of the structure of the polymerized granite-granodiorite melts. Chloride of metals seems to

form fill in solutions in the aluminosilicate network. Incorporation of chlorides is assumed to be accomplished by the formation of cavities made of 6-membered (tridimite-like) aluminosilicate structural elements. [The work has been supported by the RFBR (projects 99-05-65439, 99-05-64106, 00-15-98504 and 01-05-64837).]

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### PHASE DIAGRAM OF MgSiO<sub>3</sub>: NEW DAC DATA

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New data on the equilibrium phase relations in the MgSiO<sub>3</sub>-system are presented. Experiments were performed in the diamond cell by heating pure glass samples in rhenium or iridium micro-heaters embedded in an argon pressure medium with two YLF lasers. The transformations of lower pressure polymorphs to perovskite and reversals were measured by Raman spectroscopy on the temperature-quenched samples. Pressures were measured from unheated ruby chips in the argon pressure medium. The slope of the MgSiO<sub>3</sub> ilmenite - perovskite phase boundary, measured in the range of 21-24 GPa and 1800-2250 K, is strongly negative (-0.005 ± 0.001 GPa/K). This phase boundary yields the same temperature of 1800-1900K at the pressure of the 660 km seismic discontinuity (23.8 GPa) as the γ-spinel to perovskite + MgO transition in the Mg<sub>2</sub>SiO<sub>4</sub> system (Chudinovskikh & Boehler, 2001; Shim et al., 2001). At higher temperatures the P-T conditions of the stability fields of MgSiO<sub>3</sub> garnet and (β-phase + stishovite) differ from most of the multi-anvil results but show good agreement with thermodynamic data (Fei et al., 1990).

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### AB INITIO CRYSTAL STRUCTURE REFINEMENT AND PROTON DYNAMICS OF THE HYDROUS FORSTERITE ( $[\text{MgH}_2\text{SiO}_4] \cdot 3[\text{Mg}_2\text{SiO}_4]$ )

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Recently Hy-2a hydrous olivine ( $[\text{MgH}_2\text{SiO}_4] \cdot 3[\text{Mg}_2\text{SiO}_4]$ ), a new DHMS phase was found as nanometer-sized inclusions in  $\text{Fo}_{82}$  natural forsterite from the mantle peridotite nodule 9206, Udachnaja kimberlite pipe (Khisina et al 2001). In this presentation we are going to report the results of *ab initio* structure optimization of the hydrous olivine, based on the crystal chemical model suggested earlier by Khisina and Wirth (in press). The purpose of this study was to obtain the most stable configuration of protons in the Hy-2a structure possessing the lowest lattice energy, by assuming formation of  $\text{Me}^{2+}$  vacancies in either M1 or M2 octahedral sites (Churakov et al., submitted).

The calculations predict a preferential stability of structures with hydrogen atoms located in M1 vacancies relative to configurations formed by M2 vacancies or ones with protons in interstitial sites. The structures with the M2 vacancies are comparable in energy with configurations characterized by interstitial location of protons. In the lowest energy structures found for the Hy-2a all of the hydrogen atoms are located in the vacant M1 polyhedrons. Optimal arrangement of protons in the vacancy is distinguished by two bifurcated hydrogen bonds, O1-H1...(O2/O3) and O2-H2...(O1/O3). Two further structures with slightly higher energies are characterized by short hydrogen bonds O2-H2...O1 and O3-H3...O1 or bifurcated hydrogen bonds O2-H2...(O3/O1) and O1-H1...(O3/O2). Having little higher energy over optimal configuration these structures may also present in natural samples in minor amount. Analyses of *ab initio* molecular dynamics trajectories carried out on the Hy-2a structure at 1000°C indicate that the H atoms in M1 vacancies remain preferentially bonded to the O1 and O2 sites.

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### HP STRUCTURAL EFFECTS AND COMPRESSIBILITY OF BIKITAITE

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Bikitaite is a rare zeolite, belonging to the mordenite group. It is the only natural zeolite with mono-dimensional water chains as extra-framework content, which may make it a good candidate for the storage of nanophases in complex matrices. Its baric behaviour was investigated in the range 0-4 GPa by X-ray single-crystal diffraction with a Merrill-Bassett diamond anvil cell using glycerol, as a non penetrating pressure-transmitting medium; ruby chips and a small crystal of quartz as pressure calibrants. A strong anisotropic compression was observed by linear regression of lattice parameters-*P* data, bikitaite being softer along the *c* axis ( $\beta_c = 9.3(1) \cdot 10^{-3} \text{ GPa}^{-1}$ ), than along *b* ( $\beta_b = 6.6(1) \cdot 10^{-3} \text{ GPa}^{-1}$ ) and *a* ( $\beta_a = 2.4(1) \cdot 10^{-3} \text{ GPa}^{-1}$ ) ( $\beta_a:\beta_b:\beta_c = 1: 2.75 : 3.9$ ). Fitting the cell-volume - pressure data set to a second order Birch-Murnaghan equation of state, as indicated by the finite strain-stress plot, yielded  $K_0 = 44.2(4) \text{ GPa}$ , with  $K_1 = 4$  and  $V_0 = 295.58(2) \text{ \AA}^3$ . The evolution of the bikitaite structure with *P* was studied by comparing of the results of refinements with data collected at 0.0001, 3.2 GPa and after decompression. The structure can be described as sheets of six-membered rings parallel to (001), connected by pyroxene-like chains. 8-ring and 5-ring channels run along [010] and inside the 8-ring channel there is a unidimensional chain of water molecules, which is linked to the framework through the extra-framework Li atoms. Under pressure, the kinking of the pyroxene-like chain decreased the free diameters of the 5-ring channels, strongly reducing the distance between the *ab* planes. On the contrary the "hexagonal planes" were more rigid. The positions of the extra-framework cations and water were maintained at HP even through the configuration of the water chains changed slightly: the distances between the water molecules decreased whereas the kinking angle of the chain increased.

### PHASE EQUILIBRIA AND PRE-ERUPTIVE P-T-fO<sub>2</sub>-fH<sub>2</sub>O-fS<sub>2</sub> CONDITIONS OF DACITE FROM VOLCÁN SAN PEDRO (CHILEAN ANDES)

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The pressure, temperature, oxygen fugacity, volatile content and compositions of subduction related silicic magmas is a highly investigated topic because of known climatic and societal potential hazardous effects, and the implications for the differentiation of the continental crust. Melt inclusions combined with thermobarometers provide a means of estimating such parameters, but a complementary approach is to perform phase equilibrium experiments at various P-T-fvolatile conditions. With the assumption that the bulk-rock composition is representative of a liquid, we have performed a phase equilibrium study of a dacite (66 wt% SiO<sub>2</sub>, 2.7 wt% K<sub>2</sub>O) from Volcán San Pedro, the Holocene edifice of the Quaternary Tatara-San Pedro complex (Chilean Andes). The dacite contains phenocrysts of plagioclase (Pl), hornblende (Hbl),

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biotite (Bt), clinopyroxene (Cpx), orthopyroxene (Opx), Fe-Ti oxides (Mt), pyrrhotite, and apatite. Coexisting Fe-Ti oxides gave a pre-eruptive temperature of  $\sim 850^\circ\text{C}$  and an  $f\text{O}_2 \sim \text{NiNiO}+1$ , whereas pyrrhotite composition indicates an  $f\text{S}_2 \sim 0.02$ . We have performed experiments in IHPV at  $800\text{-}950^\circ\text{C}$ ,  $100\text{-}400$  MPa, and with redox conditions from the Ni-NiO buffer to  $\sim 2.5$  log units above. Water contents ranged from undersaturated ( $\text{XH}_2\text{O} = 0.6$ ) to saturation, and S from 0 to 1 wt% bulk. The full mineral assemblage (Pl+Cpx+Opx+Hbl+Bt+Mt) present in the lava is not stable at any of the investigated experimental conditions, notably by the lack of Cpx+Bt coexistence. Moreover, in S-free experiments Bt is only stable at  $< 825^\circ\text{C}$ , which is lower than the Fe-Ti oxides temperature. In contrast, in experiments with 0.5-1 wt% added S, Bt is stable up to  $875^\circ\text{C}$  (+Hbl+Opx+Pl+anhydrite+pyrrhotite). This suggests that the San Pedro dacite magma was stored at  $\sim 6$  km, at  $850^\circ\text{C}$ , close to water-saturated conditions, with a log  $f\text{O}_2$  of NNO+1 to NNO+2, and importantly, contained significant amounts of sulfur ( $0.1 < S < 1$  wt% bulk).

### HIGH-TEMPERATURE DENSITY OF LANTHANIDE-BEARING MELTS: PRELIMINARY RESULTS

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Igneous rocks commonly contain several hundred ppm of lanthanides, or under exceptional circumstances even more, distributed in various concentrations amongst major and accessory minerals. In general, lanthanides are partitioned more extremely than major elements making them more sensitive indicators of the petrological and mineralogical processes that occur. Therefore, they are a powerful tool in the thermodynamical modelling to accurately predict the crystal-melt phase equilibria in a magma, in order to trace petrogenetic processes and define compositional heterogeneities within the upper mantle. The development of such mathematical models requires a reliable thermodynamic database which includes volumetric data available for both major and trace element oxide liquids. Efforts have been made to extend the volumetric database of silicate melts on a variety of multi-component systems for the most naturally abundant oxides during the last decades. However, there is no reliable volumetric dataset for other significant oxides, such as lanthanides. Therefore, in order to fill this gap and to provide a new volumetric dataset, which will allow the available models in the literature to be extended to lanthanide-bearing liquids, we are conducting density measurements on various lanthanide-bearing silicate melts using the Pt-based double-bob Archimedean method. In this paper, we present preliminary density measurements obtained in air from 1350 to 1550 K for various lanthanide-bearing sodium disilicate melts (from cerium to lutetium including lanthanum). The densities range from 2.25 to  $2.83 \text{ g/cm}^3$  and indicate that adding lanthanide oxides leads to an increase in melt density that varies as the atomic number of the lanthanides increases. Further investigations on different compositions containing various amounts of lanthanide are still in progress in order to determine the partial molar volume of the lanthanide oxide liquids.

### CARBONATES VS. GRAPHITE STABILITY IN HYDROUS MAFIC SYSTEMS AT HIGH-PRESSURE

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The analysis of modern oceanic crust show not only major addition of  $\text{H}_2\text{O}$ , but also of  $\text{CO}_2$ , as main volatile components. Carbon-bearing phases and C-O-H fluids are therefore expected to play a fundamental role in the evolution of subduction zone systems (Yaxley & Green, 1994; Molina & Poli, 2000; Kerrick & Connolly, 2001).

In order to determine the mutual stability of carbonates and graphite in metamorphosed altered oceanic crust, we performed high pressure experiments in the model system  $\text{Na}_2\text{O-CaO-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ , in the presence of a C-O-H fluid, where  $f\text{H}_2$  is controlled by Ni-NiO (NNO) and hematite-magnetite (HM) buffers. Experiments were carried out on seeded gels using both end-loaded and single-stage piston-cylinder apparatus, at pressures up to 3 GPa and temperatures to  $730^\circ\text{C}$ . C-O-H fluid phase was generated from oxalic acid dihydrate and from silver oxalate. Two basaltic compositions at variable XMg were investigated. In agreement with previous experiments by Molina & Poli (2000), a large amphibole-carbonate phase field is present at  $P \leq 2$  GPa, with a single carbonate (calcite or dolomite) at  $P < 1.6\text{-}1.8$  GPa and coexisting magnesite and dolomite at higher pressure. The abundance of carbonates is closely related to the amount and composition of fluid added. However, in experiments at 2.2 and 2.4 GPa buffered by NNO, two carbonate assemblages are replaced by graphite  $\pm \text{NaCaAl}$  silicate (scapolite), whereas graphite disappears in HM runs, being scapolite the main carbon bearing phase.

Preliminary experimental results suggest that the stability of magnesite and dolomite in deeply subducted oceanic crust is restricted to highly oxidizing conditions and  $\text{H}_2\text{O}$ -poor bulk compositions.

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### CHARACTERIZATION OF A UHP PHENGITE 3T (SULU, CHINA) AND OF ITS EXSOLVED MILLIMETRIC LAMELLAE OF PHLOGOPITE

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Single-crystal X-ray diffraction study was performed on a phengite 3T from a quartz-phengite vein, crystallized in UHP metamorphic conditions (Dabie-Shan complex, Sulu region,  $P \sim 30$  kbar,  $T \sim 750^\circ\text{C}$ ) in presence of hydrothermal fluids. The flakes show deep green colour, are not deformed, large (decimetres) and thick (centimetres). Anisotropic refinement

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(s.g. P<sub>3</sub>12, a=5.2248(6)Å, c=29.737(5)Å) converged to R=3.5. According to the values of the refined electron content no ordering occurs in the octahedral sites (14.3(2) el in M2 and 14.7(2) el in M3); a significant electron density residual (about 0.7 el in the ΔF; 0.3(1) el refined value) occurs in the 'empty' M1 site. These results are in agreement with the WDS electron-probe chemical analysis (K<sub>0.95</sub>Na<sub>0.01</sub>Ba<sub>0.01</sub>)(Al<sub>1.37</sub>Fe<sub>0.26</sub>Mg<sub>0.41</sub>Ti<sub>0.02</sub>)Σ=2.06(Si<sub>3.48</sub>Al<sub>0.52</sub>)O<sub>10</sub>(OH)<sub>2</sub> which shows slightly more than two M cations corresponding to 29.93/2.06=14.53 el for M2 and M3, 0.87 el for M1.

By optical microscopy a minor lamellar mica phase is observed within the matrix of phengite. These lamellae are of brown colour, uniaxial and in the same optical orientation of the matrix. The following crystal-chemical formula (K<sub>0.63</sub>Ca<sub>0.01</sub>)(Al<sub>0.51</sub>Fe<sub>0.76</sub>Mg<sub>1.38</sub>Ti<sub>0.09</sub>)Σ=2.65(Si<sub>3.18</sub>Al<sub>0.82</sub>)O<sub>10</sub>(OH)<sub>2</sub> is obtained from the data of an EDS electron-probe chemical analysis. Also taking into account the poor quality of the data, due to the very small dimensions of the lamellae, the brown sample shows phlogopitic composition.

An X-ray powder diffraction pattern on the natural sample confirms the presence of two trigonal phases with clearly different unit cells: a minor one (green phengite, a=5.214(4)Å, c=29.77(1)Å) and a major one (brown mica, a=5.28(1)Å, c=30.04(5)Å). All the brown lamellae examined by single-crystal X-ray diffraction showed trigonal symmetry, except for one resulting in a 1 M monoclinic polytype.

One can assume the following subsequent events took place: crystallization of 3T phengite at high P/T conditions; exsolution of iso-oriented 3T phlogopite within the phengite matrix; minor phase transition of the phlogopite from 3T to 1 M symmetry.

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### SYNDEFORMLATIONAL REACTION OF PLAGIOCLASE AND OLIVINE IN EXPERIMENTALLY DEFORMED PLAGIOCLASE-OLIVINE AGGREGATES

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We investigated the effect of chemical disequilibrium on the deformation of plagioclase peridotite by performing simple shear deformation experiments on plagioclase-olivine mixtures at 900°C and confining pressures of 1.0 and 1.5 GPa.

In An<sub>92</sub>-Fo<sub>92</sub> mixtures the applied confining pressures represent different degrees of overstepping on the mineral reactions Plg + Ol = Sp + Px and Plg + Ol = Gt + Px and produce chemical

reactions. An<sub>60</sub>-Fo<sub>92</sub> mixtures, also used in experiments, are in chemical equilibrium at these confining pressures, and allow the study of crystal plastic deformation of non-reacting samples.

Mixtures of olivine(2):plagioclase(1) were prepared from 2-6 μm powders of Fo<sub>92</sub>, An<sub>92</sub> and An<sub>60</sub>. The mixtures were placed between dunite pistons, cut at 45 degrees to the compression direction. Prior to deformation, the samples were heated at 1000°C for 6 hours in a CO-CO<sub>2</sub> gas mixture and subsequently hot pressed for 24 hours at 0.7 GPa and 900°C. Our experiments were carried out in a Griggs apparatus under a constant strain rate of 5x10<sup>-5</sup>sec<sup>-1</sup>.

In absence of reaction, An<sub>60</sub>-Fo<sub>92</sub> and pure olivine samples show strain hardening with no yield up to stresses equal to the confining pressure.

Significant reaction induced weakening is observed in the An<sub>92</sub>-Fo<sub>92</sub> samples deforming at lower stresses than pure olivine and unreacted samples.

The syndeformational reaction between An<sub>92</sub> and Fo<sub>92</sub> results in fine-grained (<1 μm) Ol-Sp-Gt-Px reaction products. These products form along An<sub>92</sub>-Fo<sub>92</sub> grain contacts. They coalesce and accommodate most of the deformation by granular flow.

The mineral reaction is not observed in an undeformed An<sub>92</sub>-Fo<sub>92</sub> sample, held hydrostatically at 900°C-1.5 GPa for the same duration as the deformation experiments.

Hence, the Fo<sub>92</sub>-An<sub>92</sub> syndeformational reaction is enhanced by the deformation. The reaction itself is associated with a switch in deformation mechanism from crystal to granular flow of reaction products.

### WATER DIFFUSION IN NATURAL OLIVINE AND SYNTHETIC FORSTERITE

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The interaction on upper mantle minerals with water is known to have a major influence of a range of physical and chemical properties. Thus, characterization of solubility and kinetics of incorporation for water in nominally anhydrous minerals is important in order to understand the behavior of Earth's deep interior. Experimental studies on the olivine-water system indicate that significant amounts of OH can dissolve within olivine as point defects (Bell and Rossman, 1992; Kohlstedt *et al.*, 1996; Kohlstedt and Mackwell, 1998).

Our study is based on hydrogenation of single-crystal samples by piston-cylinder and TZM cold-seal vessel experiments. We use FTIR analyses in order to constrain the speciation of the mobile water-derived defects in iron-bearing and iron-free olivine, and the rates of diffusion of such species under uppermost mantle conditions (0.2 to 1.5 GPa, 900 to 1100°C, 1 to 20 hours). Hydrogen defect transport in single crystals of olivine and forsterite is investigated for diffusion parallel to each crystallographic axis. Defect diffusivities are obtained by fitting a diffusion law to the OH content as a function of position in the sample.

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Our current results indicate that incorporation of hydrogen species into iron-bearing olivine is a 2-stage process with an initial stage of proton-polaron exchange ( $D_H = D/2 = 10^{-11}$  m<sup>2</sup>/s at 1000°C parallel to [100]). The different concentration profiles show a clear anisotropy of diffusion, with fastest diffusion parallel to [100]. On a longer time scale, diffusion of hydrogen species occurs through incorporation of proton-metal vacancy pairs ( $D_V = D/3 = 10^{-12}$  m<sup>2</sup>/s at 1000°C parallel to [001]), with fastest diffusion along [001]. Although there is no proton-polaron exchange in iron-free forsterite, we have quantified the second process of incorporation in samples of synthetic forsterite, which display similar behavior to the iron-bearing samples.

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### OXYGEN IONIC CONDUCTIVITY IN MgSiO<sub>3</sub> PEROVSKITE: POSSIBLE PRE-MELTING SIGNAL?

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MgSiO<sub>3</sub> perovskite is thought to be the major constituent of the Earth's lower mantle. Consequently, knowledge of its chemical and physical properties is fundamental to our understanding of the processes occurring within the deep Earth.

We have measured the electrical conductivity of MgSiO<sub>3</sub> perovskite with a NaSiO<sub>2.5</sub> content of 0.3 mole%. This results in an extrinsic oxygen vacancy content of 0.0015 PFU and should ensure that these are the dominant charge carriers in the experimental temperature range (1273-2133 K). At 24-26 GPa the electrical conductivity of this perovskite increases Arrheniusly between 1273 and 1900 K with an activation energy of 1.4 eV, consistent with predicted oxygen mobility. Using the Nernst-Einstein equation to calculate the O-diffusivity from these data suggests that O<sup>2-</sup> will be 10 to 100 times more mobile than Si<sup>4+</sup> in MgSiO<sub>3</sub> perovskite.

There is a discontinuous change in conductivity at 1900 K, with the high temperature region having an activation energy closer to 4 eV. This change is reversible and reproducible. The high temperature region is most likely to be due to either a change from extrinsic to intrinsic conduction, or pre-melting of the oxygen sub-lattice. The discontinuous nature of the transition leads us currently to favour pre-melting, however we require further experiments to confirm this.

Pre-melting of the anion sub-lattice is observed in many perovskite structured materials and often accompanies the transition to cubic symmetry. The change in electrical conduction mechanism observed here occurs at a rather low homologous temperature ( $T/T_m \sim 0.75$ ) for pre-melting phenomena. We note, however, that it is close to recently observed transition temper-

atures, and the temperature at which laser heating power-temperature relationships undergo a discontinuous change in MgSiO<sub>3</sub> perovskite.

If pre-melting does occur in MgSiO<sub>3</sub> perovskite under P-T conditions pertinent to the Earth, this will significantly affect the physical properties of the lower mantle.

### DATA BANK FOR PETROLOGY AND GEOCHEMISTRY OF VOLCANICS FROM ERCIYES MOUNTAIN, CENTRAL ANATOLIA, TURKEY

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We have collected about 300 data for major oxides including SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> or FeO, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>O or LOI; and trace elements including Ba, Rb, Sr, Y, Zr, Nb, Th, Pb, Ga, Zn, Cu, Ni, V, Cr, Hf, Cs, Ta, Co, Li, Be; and rare earth elements including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. We evaluated the data using Harkers diagrams for accuracy and consistency; and applied discriminant diagrams using MinPet and NewPet programs. We observed inconsistencies on classifications, magmatic and tectonic environments. We also applied some 30 of our data to the Erciyes volcanics. We hope that this will help to evaluate the Central Anatolian volcanics quantitatively.

### DATA BANK FOR PETROLOGY AND GEOCHEMISTRY OF VOLCANICS FROM HASANDAG-MELENDIZ MOUNTAINS, CENTRAL ANATOLIA, TURKEY

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We have collected about 350 data for major oxides including SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> or FeO, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>O or LOI; and trace elements including Ba, Rb,

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Sr, Y, Zr, Nb, Th, Pb, Ga, Zn, Cu, Ni, V, Cr, Hf, Cs, Ta, Co, Li, Be; and rare earth elements including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. We evaluated the data using Harkers diagrams for accuracy and consistency; and applied discriminant diagrams using MinPet and NewPet programs. We observed inconsistencies on classifications, magmatic and tectonic environments. We also applied some 30 of our data to the Hasandag-Melendiz volcanics. We hope that this will help to evaluate the Central Anatolian volcanics quantitatively.

### Si AND O DIFFUSION RATES IN OLIVINE AND DIOPSIDE AS A FUNCTION OF $fO_2$ AND ACTIVITY OF ENSTATITE: THE CONNECTION BETWEEN DISLOCATION FLOW AND DIFFUSION VIA POINT DEFECTS

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Oriented single crystals coated with thin films enriched in <sup>29</sup>Si and <sup>18</sup>O have been used to study the simultaneous diffusion of Si and O in minerals such as olivine and diopside. The thin films were produced by pulsed laser deposition, a versatile method which provides well controlled chemistry and geometry, as characterized by Rutherford-Backscattering analysis, Interference Microscopy and Transmission Electron Microscopy (Dohmen et al., *subm. to EJM*). As produced, the thin films are amorphous (typical thickness 200-300 nm), but after pre-annealing the films crystallize as uniform polycrystalline layers with ideal contact to the single crystal substrate.

Diffusion experiments were performed at 1100-1500°C under controlled oxygen fugacity (CO-CO<sub>2</sub> gas mixture) and in case of olivine (Fo<sub>90</sub>) the silica activity was controlled additionally using solid state buffers (magnesiowuestite or orthopyroxene). The isotopic depth profiles along the c-axis (~0.58 nm) of unannealed, pre-annealed, and annealed samples were measured using SIMS (University of Edinburgh).

Our results show that O-diffusion in olivine is much faster than Si-diffusion as expected from earlier studies [Gerard & Jaoul, 1989; Ryerson et al., 1989]. Activation energies for diffusion are found to be 344 ±13 kJ/mol for oxygen and 511 ±25 kJ/mol for Si in olivine. Both diffusion rates increase with increasing silica activity, whereas only oxygen diffusion in olivine is affected by oxygen fugacity. Our diffusion coefficients are smaller than those measured in earlier studies, by up to two orders of magnitude for Si in olivine [Houlier et al., 1990]. The activation energy for Si diffusion as well as its dependence on silica activity is identical to that measured for dislocation flow in single crystal olivines. This result provides a simple connection between atomistic diffusion jumps and macroscopic deformation behavior, and removes the necessity for complex models relating the two. Work is in progress to determine the activation energy for diffusion in diopside, to test if this relationship can be extended to silicates in general.

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### SELF-CONSISTENT EQUATION OF STATE OF MINERALS UP TO 3000 K AND COMPRESSION UP TO X=0.6

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The self-consistent calculation of thermodynamic functions of minerals requires strong thermodynamic relationships between all thermodynamic functions. However, data treatment on heat capacity, thermal expansion coefficient, volume and adiabatic bulk modulus, as a rule, is performed without considering the volume as a function both of temperature and pressure. In a similar manner, data treatment on volume that can be measured by current methods up to 3000 K and 200 GPa is carried out without taking into account heat capacity and other energy properties at zero pressure. Hence, the energy and volume properties of solids from different sources, even the most authoritative ones, cannot be considered as self-consistent.

The main purpose of this study is to extend the Zharkov and Kalinin (1971) formalism to range 0-3000 K and up to compression  $x=V/V_0=0.6$ . The Helmholtz free energy written as:  $F(V,T)=U_0+E(V)+F(V,T)+F_a$ , where  $E(V)$  is a part of energy depending only on volume,  $F(V,T)$  is a thermal part of the free energy (quasiharmonic part),  $F_a$  is the anharmonic part.

Energy vs. volume at 0 K isotherm may be expressed in a number of convenient forms. The thermal part of the free energy is expressed by the Bose-Einstein and Einstein functions (Kut'in and Pyadushkin 1998). Entropy, internal energy, heat capacity at constant volume, thermal pressure, bulk modulus and  $dP/dT$  can be easily obtained from the free energy. The volume dependence of the Grüneisen parameters and characteristic temperatures are written in the form proposed by Molodets (1995). The intrinsic anharmonicity, which is important at high temperatures, has to be taken into account; the classical anharmonic free energy expression ( $F_a = aT^2$ ) and other model expressions were found to work quite well.

In this report we will discuss equations of state of NaCl (Dorogokupets, 2001), corundum and periclase.

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# EMPG IX

## Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

### STRUCTURAL INVESTIGATION OF ADELITE AND COBALTAUSTINITE, TWO MEMBERS OF THE ADELITE-DESCLOIZITE GROUP

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Compounds crystallizing in the adelite-descloizite structure type have the formula  $M1^{1+,2+}M2^{2+,3+}(OH)(X^{4+,5+,6+}O_4)$ , M1 = Na, Ca, Pb; M2 = Mg, Al, Mn, Fe, Co, Ni, Cu, Zn; X = Si, P, V, As, Mo. More than a dozen of minerals belong to this group, however, investigations on synthetic compounds are rare. Compounds with accurate structure refinements exhibit space-group symmetries Pnam or  $P2_12_12_1$ . The deviation from the centrosymmetric parental structure is moderate. Single-crystal X-ray structure investigations were performed for adelite,  $CaMg(OH)(AsO_4)$  (Palache et al., 1951) and cobaltaustinite,  $CaCo(OH)(AsO_4)$  (Nickel & Birch, 1988). The acentric space group  $P2_12_12_1$  was proved for both minerals:  $a = 7.468(1) / 7.475(1)$ ,  $b = 8.953(2) / 8.976(2)$ ,  $c = 5.941(1) / 5.916(1)$  Å; NONIUS four-circle diffractometer, CCD detector, capillary-optics collimator, Mo tube, graphite monochromator; program SHELXL (Sheldrick, 1996),  $R1 = 0.018 / 0.020$ ,  $wR2 = 0.038 / 0.048$ ; 1378 / 1364 reflections [1355 / 1342 with  $F_o > 4\sigma(F_o)$ ] up to  $2\theta = 65^\circ$ ; for non-hydrogen atoms anisotropic displacement parameters were refined; the H atom was found from a difference Fourier map and was refined isotropically. The type structure exhibits  $M2O_6$  octahedra (elongated tetragonal dipyramids in case of divalent Cu atoms due to Jahn-Teller distortion) edge linked to chains parallel to [001]. Each of the  $XO_4$  tetrahedra link two such chains to a three-dimensional network. Cavities house the M1 atoms. Their coordination varies from [7] to [8] depending on the space-group symmetry. In adelite / cobaltaustinite the average M2-O and As-O bond distances are 2.0754 / 2.0867 and 1.6924 / 1.6911 Å. The average M1-O bond distance is 2.5238 / 2.5187 Å; the coordination polyhedron is a slightly distorted tetragonal antiprism. O-H is 0.85 / 0.84 Å, O-H...O is 2.766 / 2.714 Å.

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### ISOMORPHISM PECULIARITIES OF THE SYSTEM CHATKALITE - MAWSONITE, $Cu_6FeSn_2S_8$ - $Cu_6Fe_2SnS_8$

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Mawsonite,  $Cu_6Fe_2SnS_8$  is the mineral related to stannite group with the structure derivative of sphalerite type (Szymanski, 1976). Based on the formula and x-ray data similarity the rare mineral chatkalite,  $Cu_6FeSn_2S_8$ , found in 1981, has been assigned to the same structure type (Kovalenker et al., 1981). The chatkalite structure is not carried out till now because of its rarity and of the absence of available crystals. The element composition and the "Metals:S" ratio of these two minerals are identical, and lead to the conclusion about the isomorphous replacement Fe-Sn. For prove this idea the experimental study of the series  $Cu_6FeSn_2S_8$  -  $Cu_6Fe_2SnS_8$  has been carried out for the first time. Compounds  $Cu_6Fe_{2-x}Sn_{1+x}S_8$ , synthesized by melting the elements in necessary proportions under condensed system, have been studied using ore microscopy, x-ray, microprobe, and moessbauer spectroscopy. Although the whole isomorphous series chatkalite-mawsonite was not obtained, but end members as well as some intermediate ones have been studied. In connection with the recent results on the complex type of isomorphism in stannite type compounds, i.e. kesterite (Rusakov et al., 2001), and kuramite-stannite series (Evstigneeva et al., 2001) the valence state and the co-ordination of  $^{57}Fe$  and  $^{119}Sn$  in these compounds are have been studied. Moessbauer spectra of  $^{57}Fe$  under the room temperature have the ultrafine structure of paramagnetic type. Iron in chatkalite corresponds to  $Fe^{2+}$ . Mawsonite contains  $Fe^{3+}$ . Spectra of other members of the series present the superposition of two well-resolved partial spectra ( $Fe^{2+}$  and  $Fe^{3+}$ ). The number of  $Fe^{3+}$  increases but of  $Fe^{2+}$  decreased as the total Fe contents increases. Moessbauer spectra of  $^{119}Sn$  are of paramagnetic type, and present two type of  $Sn^{4+}$ : a) with strong ionic bond  $Sn^{4+}-S$ , and strong covalent bond  $Sn^{4+}-S$ . The covalence of bond  $Sn^{4+}-S$  increases, but of  $Fe^{2+}-S$  decreases as the Fe content increases. Authors thank the Russian Foundation of Basic Researches for financial support (Project\_00-05-64609).

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# EMPG IX

## Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

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

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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 (SnO<sub>2</sub>, from Bolivia and Malaysia), eakerite, various perovskite-based polymorphs (SnSrO<sub>3</sub>, CaSnO<sub>3</sub> and CdSnO<sub>2</sub>) as well as SnO, SnCl<sub>2</sub> 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% SnO<sub>2</sub>, 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 SnO<sub>2</sub>, 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 SnO<sub>2</sub> contents of the 0.6, 1.0 and 1.2 glasses are: 1.0%, 0.6% and 0.6% SnO<sub>2</sub>, 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)O<sub>6</sub><sup>8-</sup> octahedra share corners (<Sn-O-Si> 150°) with SiO<sub>4</sub><sup>4-</sup> tetrahedra. However, the most reduced glasses show significant contributions arising from weakly bounded Sn(II)O<sub>n</sub> 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

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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-Al<sub>2</sub>O<sub>3</sub>) and water. In an average karstbauxite, such as occurring on the island of Naxos (Greece), 6-8 wt% H<sub>2</sub>O 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

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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

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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 SiO<sub>2</sub>-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

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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 CO<sub>2</sub> 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 H<sub>2</sub>O-CO<sub>2</sub> mixtures ( $X_{H_2O} = 0.96$ ) and to a total H<sub>2</sub>O-CO<sub>2</sub> fluid density of about 0.98 g/cm<sup>3</sup>. 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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## EMPG IX

### Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

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

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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  $\beta$  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

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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-K<sub>2</sub>O-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. 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 H<sub>2</sub>O saturation and fluid speciation, three different charges were loaded for each bulk composition, two at fluid saturated conditions and fO<sub>2</sub> buffered either by graphite or by NNO and one with H<sub>2</sub>O added as Al(OH)<sub>3</sub> 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

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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

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The solubility of natural wollastonite (Ca<sub>3</sub>[Si<sub>3</sub>O<sub>9</sub>] (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<sub>woll</sub> 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 Si<sub>3</sub>O<sub>9</sub>-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

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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 SiO<sub>2</sub>-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

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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  $4\pm 2$   $\mu\text{m}$  (TEM). We checked that deformation did not induce dynamic recrystallization. Experimental deformation rates on  $2\times 2\times 5$  mm<sup>3</sup> blocks were  $10^{10}$  to  $10^{-6}$  s<sup>-1</sup>, 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°C : a deformation mechanism with low activation energy E =  $300 \pm 100$  kJ.mol<sup>-1</sup>. 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<sup>-1</sup> and the stress exponent close to 1. Diffusion creep along grain boundary made of destabilized omphacite could be invoked. 2) At T  $\geq$  900°C, we find E = 750 kJ.mol<sup>-1</sup> 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

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The important role played by volatile diffusion in bubble growth dynamics makes knowledge of H<sub>2</sub>O and CO<sub>2</sub> 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 H<sub>2</sub>O 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<sup>-1</sup> mol<sup>-1</sup>) 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).

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

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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  $1150^\circ\text{C}$  to  $950^\circ\text{C}$  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)

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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 =  $9.5 \pm 2.3$  wt.%, CaO =  $6.0 \pm 1.1$  wt.%; (II)MgO =  $6.7 \pm 1.4$  wt.%, CaO =  $8.2 \pm 2.6$  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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#### HIGH-PRESSURE STUDY OF CHONDRODITE, $Mg_5(SiO_4)_2(OH/OD,F)_2$ : STRUCTURE, O-D...F/O GEOMETRY AND COMPRESSIBILITY

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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

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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  $\leq 0.8$ , 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

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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

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to limit the extents of the Fe<sup>2+</sup> oxidation, solutions of Na-dithionite in water were prepared at first (Harder, 1978). In addition small amounts of ferrous crystals were seeded into the solution, so that silica microtubular structures were obtained. These structures are formed via continuous polymerization of the amorphous silica as result of abrupt pH reduction induced by the Fe-salt dissolution.

The growth of crystal phases takes place in a second step by the selective nucleation at the sites provided by the porous silica matrix in the internal walls of the "silica garden" microtubules. No direct precipitation from the solution by three-dimensional nucleation was observed. This fact clearly indicates that the crystallization products are connected with a heterogeneous nucleation process, related to the inner surface of the silica garden.

From the morphological point of view, the SEM micrographs of the resulting crystals, Figure 1(a) closely resemble the natural occurrence of glauconitic minerals from siliceous substrates. In addition, elemental analysis performed at the level of a single crystal, by EDX, approach the stoichiometry of glauconitic minerals with low potassium content.

Further structural characterization carried-out by HREM has revealed the existence of a gradient variation in the structural characteristics of the microtubules across the radius fig1(b). Lattice fringes analysis shown the existence of single-crystal domains with average sizes in the order of 15 nm and d-spacing corresponding to (001) and (003) reflections of 2:1 layer silicates, in sharp contact with the amorphous silica host in the internal surfaces. Single domains, with kaolinite and smectite-like layers, were also observed fig 1(c).

The XRD spectra of the whole sample shown the presence of a crystalline fraction over-imposed to the background from the amorphous silica. Rietveld analysis of the crystalline part was performed by using the Celadonite ( s.g. C2/m) as starting structural model. XPS analysis was employed to determine the Al-coordination and the relative Si/Al ratios .

The previous study suggests that a complex structural transformation take place just at the internal wall of the microtubules, leading the formation of layered Al-Fe-Mg-silicates. The obtained crystals have several ordering degrees as result of non-stoichiometric interface reactions, in a similar way to the "smectite" to "illite" transformation in natural systems.

Furthermore, the polymerization process heavily determines thermodynamical conditions inside the tubes. In particular a nearly neutral pH and the availability of silica monomers are expected to occur at the interface. These factors and the presence of reducing conditions seem to be determining conditions for layer silicate formation.

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### CHEMICAL MIGRATION ASSOCIATED WITH IRON OXIDATION-REDUCTION IN SILICATE MELTS

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Since pioneering works of Bowen and later Osborn, the impact of iron redox state on structure, viscosity and phase equilibria in silicate melts has received great attention. In contrast, kinetics and mechanisms of iron oxidation-reduction in geologically relevant silicate melts remain poorly understood. We have developed several experimental approaches to determine the rate-laws and mechanisms of iron oxidation-reduction in aluminosilicate melts/glasses. The general strategy consists of monitoring the chemical changes that occur after a given duration of exposure of a ferric iron-bearing glass to a reduced environment. The reducing media used are pure H<sub>2</sub>, Ar/H<sub>2</sub>, H<sub>2</sub>/CO<sub>2</sub> and CO<sub>2</sub>/CO mixtures in one-atmosphere furnaces or cold seal pressure vessels. Run products are analyzed through (1) the color changes in the glass due to ferric-ferrous transformations, (2) Mössbauer spectroscopy and (3) EMPA or FTIR for chemical analyses of run products. In nominally anhydrous glasses (Alb+iron and Andesites) under reducing conditions the growth rate of the reduced layer is reaction-limited. The rate of the limiting reaction is controlled by the amount of iron in the melt and the CO content of the gas. Opposed migrations of K and Na are also observed with the reduced layer being Na-richer. No increase of the OH-content in the quenched glasses is observed and the mechanisms are identical in H<sub>2</sub>/CO<sub>2</sub> and CO/CO<sub>2</sub> gases. In the Ar-H<sub>2</sub> mixture, no alkali migration is observed. In an H<sub>2</sub>-bearing atmosphere, ferric iron in natural rhyolitic obsidians is reduced by the incorporation of H-bearing species without migration of other major elements. In a CO/CO<sub>2</sub> mixture, no reaction is observed after an exposure of 4 days. The growth rate of the reduced layer is a diffusion-limited process. In addition, the reduction-rate is positively correlated with fH<sub>2</sub>. Inward migration of either H<sub>2</sub> or proton-electron pairs could explain the macroscopic observations.

### THE BREAKDOWN OF SYNTHETIC POTASSIC CORDIERITE AT LOW P-T CONDITIONS - AN EXPERIMENTAL STUDY

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An experimental study on the breakdown of K-cordierite into phlogopite and Mg-cordierite has been studied at 1 Kbar and 700-900°C, under hydrothermal condition. Potassic cordierite was obtained by sintering the co-precipitated gel of composition K<sub>0.2</sub>Mg<sub>2</sub>Al<sub>4.2</sub>Si<sub>4.8</sub>O<sub>18</sub> at 1200°C. The synthetic K-cordierite was taken in Pt-capsule with 3 wt% of distilled water and sealed by arc-welding. Isobaric runs between 700 and 900°C

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were carried out using Tuttle reactors (LECO Corp., USA). Water was the pressurising medium and the measured P-T have an accuracy of  $\pm 50$  bars and  $\pm 5^\circ\text{C}$ . respectively.

The formation of phlogopite along with Mg-cordierite started at  $700^\circ\text{C}$ . This phlogopite with Mg-cordierite were persisted upto  $800^\circ\text{C}$ . Above this temperature, the formation of phlogopite reduced and Mg-cordierite increased, but at  $850^\circ\text{C}$ , little formation of phlogopite was noticed. At  $900^\circ\text{C}$ , only single phase of Mg-cordierite without phlogopite formation was observed. The presence or absence of phlogopite and Mg-cordierite formation in every experiment was confirmed by XRD. The chemical analysis of the phases was done using EPMA and the water in the channels of Mg-cordierite was confirmed by IR studies. It is confirmed that K-cordierite (containing 1.6 wt% of  $\text{K}_2\text{O}$ ) would breakdowns to ideal phlogopite + Mg-cordierite at low temperature and as the temperature increases only ideal Mg-cordierite was the stable phase without the formation of phlogopite. Also, it would be possible that the formation of melt occurs only above  $900^\circ\text{C}$  along with Mg-cordierite

### INDUCED PHASE TRANSFORMATION BY ELECTROCHEMICAL TREATMENT IN ARCHAEOLOGICAL MARINE OBJECT. XRD-RIETVELD ANALYSIS OF THE PRODUCTS

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The conservation of marine archaeological iron objects must start with a stabilisation treatment to remove the chlorides from the iron corrosion products and the residual metal in order to prevent the development of cyclic corrosion. In this work we have studied the electrolytic method applying low current densities, inserting a resistor in the electric circuit between the artefact and the power supply. To study the changes that this treatment produces, we made an electrolysis on a cast iron cannon ball fraction recovered from a marine water environment. To control the induced variation in the mineral phase by the chlorides extraction, we have analysed the XRD spectra by the Rietveld method, the mineralogical variation of the surface and the interior of the artefact before and after the treatment. Before the treatment, the main compound found on the corroded surface was Akaganeite, that has been structurally transformed by the electrolysis to goethite and magnetite. The inner composition of the object remains unaltered before and after the treatment and the main compounds are  $\alpha$ -iron and cementite.

### PREDICTION OF NON-ARRHENIAN VISCOSITY OF MULTICOMPONENT SILICATE MELTS

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Magma dynamics can control volcanic eruptions. Thus a description of the rheology of magma is an essential input variable for forward simulations of magmatic eruptions and for the interpretation of volcano monitoring data related to magma movements. Accurate quantification of magma rheology must be based on a robust model for the viscosity of the liquid. The first parameterizations of the viscosity of multicomponent silicate melts for geological purposes employed an Arrhenian dependence of the viscosity on temperature. Although a useful approximation over restricted ranges of temperature, the Arrhenian approximation leads to serious errors over larger temperature ranges. When such models are compared with the more complete viscosity data sets for multicomponent silicate liquids which have been coming on line in the past decade the discrepancy is apparent. As a response to this growing inadequacy of Arrhenian models, Hess and Dingwell (1996) developed the first empirical non-Arrhenian viscosity model for the binary system calcalkaline rhyolite –  $\text{H}_2\text{O}$ . Here, on the basis of ca. 350 viscosity data obtained on anhydrous melts, we present the first multicomponent non-Arrhenian model. Based on 350 new determinations of Newtonian viscosities of multicomponent liquids, ranging from basanite through phonolite and trachyte, to dacite in the range of (100 to 1012 Pa·s) and regressions using the 3-parameter Tammann-Vogel-Fulcher equation, a relationship between the chemical composition of the multicomponent defined in terms of the mole fraction of network modifiers, yields a good predictive tool for the calculation of the viscosity of multicomponent silicate melts. This parameterisation is proposed as the first reliable non-Arrhenian description of the Newtonian viscosity of multicomponent silicate melts.

Hess, K-U & Dingwell, DB, *Am. Mineral*, **81**, 1297-1300, (1996).

### SOLUBILITY OF SULFUR IN WATER-SATURATED AN-DI MELTS UNDER VARIOUS CONDITIONS

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The effect of red/ox conditions on the solubility of sulfur under the pressure of gases of the H-O-S system in melts of the An-Di composition close to eutectics ( $\text{An}_{35}\text{Ab}_{10}\text{Di}_{55}$  mol%) was experimentally studied on a high-gas-pressure equipment at a temperature of  $1200^\circ\text{C}$  and different pressure, from 2250 to 4760 bar. The powdered sample (150 mg) was molded in a platinum ampoule with a diameter of 5 mm and a height of 25 mm. Then sulfur (15-30 mg) and water (50 ml) were added. The fugacity of S was monitored by the Pt-PtS buffer reaction and amounted  $\log f_{\text{S}_2} = -0.394$ . The fugacity of hydrogen was specified outside by argon-hydrogen mixtures in which the molar fraction of hydrogen varied from 0.05 to 0.3. The capsule was sealed and placed in another capsule (diameter 8 mm) that also contained water. This second ampoule is needed to restrict diffusion of hydrogen from the reaction ampoule, which is observed at high temperatures. The pressure and composition of the fluid were selected in such a way that the fugacity of

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water in the H-O system at 1200°C, 2Kbar and specified molar fraction of hydrogen. The duration of the experiments was 3 days. The products of experiments were studied by optical methods and on the microprobe. The solubility of S varies in range 0.018-0.126 wt%, increase with increasing of the fugacity of oxydation components of fluid (O<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O) and decrease with increasing of the fugacity of the reduction species (H<sub>2</sub>, H<sub>2</sub>S).

Table 1: Physicochemical conditions in experiments on studying the solubility of sulfur (T=1200°C).

Entry no	P, bar	X <sub>H2</sub>	f <sub>H2</sub>	f <sub>H2O</sub>	f <sub>H2S</sub>	f <sub>SO2</sub>	lgf <sub>O2</sub>	C <sub>S</sub> %
1	2250	0.05	142.50	1943	394.79	0.2200	-9.483	0.126
2	2530	0.10	331.12	1836	915.98	0.0330	-10.275	0.064
3	3370	0.20	971.90	1631	2699.2	0.0030	-11.310	0.034
4	4760	0.30	2376.8	1427	6573.0	0.0005	-12.302	0.018

### THERMAL EXPANSIVITIES OF SUPERCOOLED HAPLOBASALTIC LIQUIDS

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Knowledge of the expansivity of silicate melts is a vital component in the construction of accurate pressure-volume-temperature (PVT) equations of state. The present study is a contribution in directly determining supercooled liquid expansivities by container-based dilatometry. The thermal expansion of supercooled liquids in the haplobasaltic (anorthite-diopside) system have been determined. The expansivity data obtained in this study agree well with estimates provided by previous dilatometric determinations in the system that have relied on alternative experimental strategies. The data have been combined with high temperature, superliquidus determinations of melt density to obtain expressions for the volume-temperature relationships of liquids in the anorthite-diopside system. The volume-temperature data clearly indicate a non-linear temperature dependence of volume for all melts investigated. The variation is most striking for diopside where the coefficient of volume thermal expansion decreases about 56% from temperatures near the glass transition to superliquidus temperatures. With increasing anorthite content the degree of variation appears to decrease. An<sub>42</sub>Di<sub>58</sub> exhibits a decrease of 39% of its coefficient of thermal expansion and An<sub>98</sub>Di<sub>02</sub> of 33%, respectively. The expansivities obtained in this study cannot be reproduced using published models based on linear volume-temperature relationships. They require instead a reanalysis of existing P-V-T-equations of state for silicate melts.

### EXPERIMENTAL DATA ON GEOCHEMISTRY OF REE AND Y IN THE FLUORINE-BEARING GRANITE AND NEPHELINE-SYENITE MAGMAS

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Distribution of REE (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu) and Y between coexisting alumina-silicate and aluminium-fluoride melts has been investigated in the model system Si-Al-(Na, K, Li)-O-F with H<sub>2</sub>O excess at 8000°C and 1 kbar. As it was shown in previous publications (1993, 2001) compositions of the silicate melts correspond granites, syenites and nepheline syenites widely widespread in the nature. Atomic ratios of (K, Na, Li)/Al/F in fluoride melt are close to that in cryolite: 3/1/6. Partition coefficients K<sub>p</sub> (silicate melt / fluoride one) are not depended on element concentration (Henry's law). For all parts of the system without lithium K<sub>p</sub> value typically lies between 2 and 50. Their spectra are similar: the value of K<sub>p</sub> increases from La up to Sm, has a maximum between Eu and Ho, and further decreases towards Lu. In common coefficients for light REE are higher then for heavy ones. Yttrium has the highest coefficients. Distinctions between Na-, Na-K- and K- quartz normative parts of the system are not significant for elements of the cerium group. In the range between Tb and Lu K<sub>p</sub> decrease from 40-12 in the Na- to 5-2 in the K- part of the system. Partition coefficients in nepheline normative parts of the system, especially in myaskitic one are lower then quartz normative one. In the case of Na and K are partly replaced by Li, partition coefficients decrease dramatically down to values of the order of 10<sup>-3</sup>. They increase little by little from La towards Lu. They are the most negligible for Y. Coefficient distinctions between the potassium and sodium lithium compositions are not significant. Experimental results make more understandable some geochemical regularities. The work is supported by Russian Fund of Fundamental Researches, grant 01-05-64512.

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### EFFECTS OF H<sub>2</sub>O ON THE RHEOLOGY OF ECLOGITE AND ITS CONSTITUENT MINERALS

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We previously studied the rheology of "dry" eclogite reconstituted from a sample from the Dabie-Sulu, UHPM belt, China (Jin et al., 2001); garnet was very much stronger and omphacite significantly weaker than a ~50:50 mixture. Deformation conditions were T = 1300-1600K, P = 3 GPa, and strain rate = 10<sup>-4</sup>/s-10<sup>-6</sup>/s. Infrared spectroscopy showed <10 ppm H<sub>2</sub>O in garnet and 150-200 ppm in omphacite. We are now investigating a "wet" eclogite of similar composition from this terrane with 300-400 ppm H<sub>2</sub>O in garnet and 1000-1200 ppm in omphacite. Preliminary results show that garnet of the "wet" sample is much weaker, omphacite strength is similar, and the rock strength is ~30% reduced. Thus, increase in H<sub>2</sub>O content of garnet by a factor of >30 produced a profound weakening

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whereas 7-8 fold increase for omphacite had little effect. In both cases, the microstructure after laboratory deformation was closely similar to that of the natural sample - little evidence of deformation in garnet and extensive deformation of omphacite in the "dry" sample and significant flattening of garnet in the "wet" sample. Whether or not garnet flowed by dislocation creep is not yet known.

Deformation of "wet" eclogite at temperature just above the wet solidus resulted reproducibly in exsolution of H<sub>2</sub>O, fluxing of ~0.1 vol.% melt, and triggering of a shearing instability. The fault gouge appears indistinguishable from gouge produced in normal brittle failure except for small amounts of glass. In contrast, the gouge is distinctly different from that of transformation-induced faulting associated with the olivine-spinel transformation or during dehydration of antigorite under conditions of negative net volume change. In the former cases, the "gouge" consists of sharply angular particles with a fractal size distribution whereas in the latter cases an extremely fine-grained matrix of the stable phase(s) occurs, in many cases containing irregularly-shaped clasts of the original material.

Jin Z-M, Zhang, J, Green HW & Jin, S, *Geology*, **29**, 667-670, (2001).

#### EXPERIMENTALLY-DETERMINED TRACE ELEMENT CHARACTERISTICS OF AQUEOUS FLUID FROM DEHYDRATED MAFIC OCEANIC CRUST AT 3.0 GPa, 650-700°C

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Altered oceanic crust undergoes dehydration as it is subducted. The released aqueous vapour has the potential to remove important amounts of trace elements and to modify trace element ratios in the overlying mantle wedge and in the residual eclogitic crust. To experimentally assess this process an oceanic tholeiite (MORB) has been enriched (10-100 ppm) in 25 trace elements and crystallized at 3.0 GPa, 650 and 700°C for 2 weeks, with 30-50wt.% added water. At 650°C the fluid coexists with omphacite, lawsonite, staurolite, coesite and accessory phengite, rutile, Ti-magnetite and talc. Changes at 700°C are that garnet is conspicuous, but lawsonite and staurolite are rare and talc is absent. LAM ICP-MS analyses establish patterns of trace element partitioning between minerals (data for omphacite, lawsonite, phengite, staurolite and garnet) and fluid, but not absolute values. Similarly ratios of trace element partitioning can be well constrained. The fluid shows strong enrichment of LIL relative to HFSE, but also shows decrease in Rb/Sr, Cs/Sr and Ba/Sr from 650 to 700°C, apparently controlled by residual lawsonite, and increase in La/Lu, clearly controlled by garnet. In addition, omphacite fractionates both Zr/Nb and La/Lu, contributing to a decrease in Zr/Nb and an increase in La/Lu in the fluid. Rutile (analyzed with an electron microprobe) with Nb/Ta ≈ bulk starting composition strongly takes up Nb and Ta, but cannot cause the almost 4-fold increase in the Nb/Ta ratio observed in the fluid relative to the bulk. If these results are applied to the trace element characteristics of convergent zone magmatism, relative to MORB, then involvement of a fluid derived by dehydration processes may increase

LIL/HFSE and decrease Zr/Nb. Absence of major change to La/Lu restricts the role of garnet. Residual rutile may explain Nb and Ta depletion without affecting Nb/Ta ratios.

#### THE ENTHALPY OF FORMATION AND INTERNALLY CONSISTENT THERMODYNAMIC DATA OF Mg-STAUROLITE

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The enthalpies of drop-solution in lead borate (2 PbO B<sub>2</sub>O<sub>3</sub>) of four Mg-staurolite samples, synthesized at 720°C and pressures between 2 and 5 GPa, were measured by high-temperature oxide-melt calorimetry at 702°C. Staurolite compositions, determined by electron microprobe analysis, Karl-Fischer titration, and thermogravimetry, are: Mg<sub>3.71</sub>Al<sub>18.17</sub>Si<sub>7.60</sub>O<sub>44.31</sub>(OH)<sub>3.69</sub>, Mg<sub>3.87</sub>Al<sub>17.65</sub>Si<sub>7.75</sub>O<sub>43.68</sub>(OH)<sub>4.32</sub>, Mg<sub>3.66</sub>Al<sub>17.76</sub>Si<sub>7.68</sub>O<sub>43.31</sub>(OH)<sub>4.69</sub>, and Mg<sub>3.58</sub>Al<sub>18.05</sub>Si<sub>7.43</sub>O<sub>43.01</sub>(OH)<sub>4.99</sub>. The enthalpy of drop solution of the bulk samples (as well as the calculated values for the enthalpy of formation from the elements of Mg-staurolite) are strongly correlated to the hydrogen content of the samples. The enthalpy of formation from the elements is best described by the linear relation  $\Delta_f H_{298}^0$  (Mg-staurolite) = (-25357.58 + 87.35 N) kJ mol<sup>-1</sup>, where N = number of hydrogen atoms per formula unit in Mg-staurolite. The enthalpy of drop solution of two partly dehydrated Mg-staurolite samples is in a good agreement with the linear relation. Phase-equilibrium data for Mg-staurolite (Fockenberg 1998) were recalculated using the stoichiometric formula Mg<sub>3.5</sub>Al<sub>18</sub>Si<sub>7.75</sub>O<sub>44</sub>(OH)<sub>4</sub>. Based on these mineral equilibria and the internally consistent data set of Berman (1988), a mathematical programming analysis of the thermodynamic data of Mg-staurolite gave  $\Delta_f H_{298}^0$  (Mg<sub>3.5</sub>Al<sub>18</sub>Si<sub>7.75</sub>O<sub>44</sub>(OH)<sub>4</sub>) = -25005.14 kJ mol<sup>-1</sup>, and  $S_{298}^0$  (Mg<sub>3.5</sub>Al<sub>18</sub>Si<sub>7.75</sub>O<sub>44</sub>(OH)<sub>4</sub>) = 937.94 J K<sup>-1</sup>mol<sup>-1</sup>. Thus, for the first time, reliable thermodynamic data for Mg-staurolite, based on experimental constraints, are provided.

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#### THE ROLE OF H<sub>2</sub>O IN MELTING AND DIFFERENTIATION OF THE EARTH'S MANTLE

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Water has a profound effect on the melting and differentiation of the earth's mantle. I will discuss the recent advances in experimental petrology, mineralogy and geochemistry that have provided a quantitative understanding of the role of water in petrogenetic processes. New experimental evidence and petrologic observation on the 3.5 Ga Archean komatiites and basaltic - komatiites from the Barberton Mountainland have

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established an important role for water in early Earth history. The most important role for water in modern melt generation environments has been in subduction zones. Experimental studies have illuminated the influence of water on the composition of silicate melts in equilibrium with the rock forming minerals (Olivine - Plagioclase - Clinopyroxene). The surprising result is that subduction zone magmas often contain large amounts of magmatic water (from 6 to 10 wt. percent). Studies of the influence of water on mantle melting have shown that water dramatically decreases the melt production rate by spreading the melting interval over a broad temperature range. This fact must be reconciled with the observation that mantle-derived subduction - zone melts represent some of the highest extents of melting found in the mantle. The resolution of this problem lies in the inverted thermal gradient present in subduction zones. Melting is initiated at the base of the mantle wedge under water-saturated conditions, and the melt ascends into shallower, progressively hotter mantle, where it reacts. As the melt ascends and flux melts the shallower mantle its water content continually decreases. The temperature - depth structure of the mantle wedge controls the melting process. Water also has an important influence on melt physical properties, and melt ascent occurs rapidly by porous flow. Trace element partitioning must be considered in terms of fluid transport from the slab as well as element partitioning in the mantle wedge.

### EFFECTS OF ALUMINIUM AND MINOR ELEMENTS ON THE LOWER MANTLE MINERALOGY

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Even if we only consider the presence of major elements (O, Si, Mg, Fe, Al, Ca), the lower mantle models are complicated by partitioning of these elements between the different phases, and the complex substitution mechanisms in the perovskite lattice. The lower mantle perovskite composition is close to (Al,Fe)-MgSiO<sub>3</sub>, with Al and Fe contents closely correlated with each other (see Wood and Rubie, 1996). The mechanisms of Al substitution and the amount of Fe (and of the FeIII/ΣFe) in the perovskite depend on pressure, temperature, Al-content and oxygen fugacity: an unique and definitive vision of the perovskite crystal chemistry is difficult for the whole mantle. Furthermore, the perovskite modulus K<sub>0</sub> is affected by the composition, particularly by the Al-content, and the amplitude of these effects remains controversial (Andraut et al., 2001 ; Daniel et al., 2001).

If we now integrate minor and trace elements to our model, things become more complex : perovskite can possibly accommodate a little amount of these elements, but in the case of Na that is the most abundant minor element in the lower mantle, previous experiments evidenced the formation of two phases : NaAlSiO<sub>4</sub> with the Ca-ferrite structure (Liu, 1977) and (Na,K,Ca)<sub>1</sub>(Mg,Fe)<sub>2</sub>(Al,Si)<sub>5.5-6.0</sub>O<sub>12</sub> NAL-phase (Miyajima, 1999). We present here the equations of state of both phases, and discuss their role in Na hosting in the lower mantle.

We emphasize that these phases are not only Na host phases, but also Al-rich phases. The presence of aluminous phases in the lower mantle was thought to be unlikely because Al-amounts well above the mantle content can be integrated into

the perovskite structure (Irifune, 1994). But in this study, we clearly evidence that the presence of minor elements, particularly alkaline elements, imposes the existence of at least one aluminous phase in the lower mantle.

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### H<sub>2</sub>O ACTIVITY IN H<sub>2</sub>O-N<sub>2</sub> FLUIDS AT HIGH PRESSURE AND TEMPERATURE MEASURED BY THE DISPLACEMENT OF THE BRUCITE-PERICLASE EQUILIBRIUM

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The activity of water in binary H<sub>2</sub>O-N<sub>2</sub> fluids has been determined experimentally at pressures of 5-13 kbar and temperatures of 680°-840°C. Temperature displacement of the simple brucite dehydration reaction was used to monitor H<sub>2</sub>O activity. The experiments were performed in a conventional 22 mm piston-cylinder apparatus with NaCl pressure medium and silver azide, AgN<sub>3</sub>, as a source of nitrogen. Reversals of the dehydration reaction were used to bracket the equilibrium fluid compositions. Final fluid compositions were obtained by a weight loss method. Reaction progress was additionally confirmed by optical and X-ray inspection of the solid run products.

Water activities were computed relative to the equilibrium brucite dehydration conditions in pure H<sub>2</sub>O as determined by Aranovich and Newton (1996) using thermodynamic data of Holland and Powell (1998). The mixing properties of the binary H<sub>2</sub>O-N<sub>2</sub> fluid were modelled with a van Laar-type equation:

$$RT \ln \gamma_1 = (X_2)^2 W \{ V_1^\circ (V_2^\circ)^2 / [(V_1^\circ + V_2^\circ)(X_1 V_1^\circ + X_2 V_2^\circ)^2] \}$$

where  $\gamma_1$  is the activity coefficient of H<sub>2</sub>O,  $X_i$  is the mole fraction of endmember  $i$  ( $1=H_2O$  and  $2=N_2$ ),  $V_i^\circ$  is the molar volume of the pure endmember  $i$  at the pressure (P) and temperature (T) of interest, and W is a regular solution parameter. The parameter W was fit as a function of pressure and temperature with the expression  $W = (A - BT)[1 - \exp(-20P)] + CP^{0.3}T$ , with  $A = 40005$  J,  $B = 51.735$  J/K,  $C = 14.848$  J/(K-kbar<sup>0.3</sup>), P in kbar and T in K. With these expressions, the activity-composition relations in H<sub>2</sub>O-N<sub>2</sub> fluids can be reconstructed over a broad P-T-X range using any equation of state (EOS) for pure H<sub>2</sub>O and N<sub>2</sub>. The activity-composition relations are similar to those predicted by the semi-empirical EOS of Duan et al. (2000) and the theoretical EOS of Churakov and Gottschalk (2001), although the former somewhat underestimates activities within the experimental pressure range while the latter overestimates activities of the components at pressures above 20 kbar.

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#### CARBONATE STABILITY AT HIGH PRESSURE IN SUBDUCTION ZONES

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In order to constrain the fate of subducted carbonates carried by altered oceanic floor, high pressure experiments have been conducted in a multi-anvil apparatus in the pressure range 5 - 10 GPa. Starting material consisted in a mixture of glass having the composition of an altered basalt, plus 10 wt% calcium carbonate (calcite). After recovery, polished samples were analysed by electron microprobe. At 5 GPa, the solidus was located between 1100 and 1150°C. A silicate melt was found to coexist with a vapour phase (presumably CO<sub>2</sub>) and an eclogitic residue (garnet + omphacite + coesite). At 7 GPa calcium-rich carbonatitic melts are produced and the upper limit for the solidus is at 1000°C. At 10 GPa a carbonatitic melt was also found, and the solidus appears to be located between 1000 and 1100°C. The presently available results show that the topology for the eclogite + carbonate system in the P - T space is qualitatively similar to that of peridotite + CO<sub>2</sub>. With increasing pressure, the solidus displays a temperature drop (cusp) corresponding to the transition from silicate to carbonatitic melts. However, in the eclogitic system the P - T location of this transition is shifted toward lower temperatures (by approximately 300°C) and higher pressures (by approximately 3 GPa) compared to the peridotitic system. This difference is attributed to the presence of iron whose effect is to depress the solidus (as in any silicate system) while increasing the pressure stability of calcite at the expense of dolomite/ankerite. One consequence of the presently determined phase relationships in the eclogite + carbonate system is that carbonates are likely to be removed from a subducting slab, either by decarbonation or by melting reactions.

#### EXPERIMENTALLY INDUCED NUCLEATION OF MONAZITE FROM FLUORAPATITE: THE IMPORTANCE OF FLUID COMPOSITION

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The (Y+REE) chemistry of either a metamorphic or an igneous rock is partly a function of the phosphate minerals it contains, e.g. fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F), monazite ((Ce,LREE)PO<sub>4</sub>), and/or xenotime ((Y,HREE)PO<sub>4</sub>). Studies of natural fluorapatite (Harlov and Förster, 2002) as well as experimental studies of chlorapatite (Harlov et al., 2002) indicate that these inclusions have originated in the apatite itself from the (Y + REE) budget available (> 0.5 oxide wt%) as the product of coupled

substitution and mass transfer during fluid-triggered metasomatic alteration. There is no evidence to suggest that they are the result of exsolution in the apatite during cooling or that they could represent independent grains later overgrown by the apatite. A natural inclusion free fluorapatite (Durango) has been experimentally metasomatised using a series of fluids (pure H<sub>2</sub>O; concentrated KCl, NaCl and CaCl<sub>2</sub> brines; CO<sub>2</sub>-H<sub>2</sub>O). This consisted of placing 20 mg fluorapatite + 5 mg fluid in a 3 mm/1 cm Pt capsule using either the piston cylinder apparatus (600-900°C; 1000 MPa; 1-4 weeks) or the hydrothermal apparatus (300-600°C; 500 MPa; 2-24 weeks). Nucleation of monazite from the fluorapatite occurred when the fluid was H<sub>2</sub>O; 50/50 KCl/H<sub>2</sub>O or 50/50 CO<sub>2</sub>/H<sub>2</sub>O. At 900°C, monazite nucleated in the interior of the fluorapatite grains and, at lower temperatures, only on the fluorapatite grain surface. These fluids (specifically H<sub>2</sub>O) allow for the leaching of Si<sup>4+</sup> and/or Na<sup>+</sup> from the apatite. The resulting charge imbalance, due to the coupled substitution reactions Si<sup>4+</sup> + (Y + REE)<sup>3+</sup> = P<sup>5+</sup> + Ca<sup>2+</sup> and Na<sup>+</sup> + (Y + REE)<sup>3+</sup> = 2 Ca<sup>2+</sup>, induces the nucleation and growth of monazite in or on the fluorapatite via dissolution-precipitation. In contrast, Ca<sup>2+</sup> and Na<sup>+</sup> in NaCl or CaCl<sub>2</sub> brines can enter the fluorapatite structure and replace Si<sup>4+</sup>, Na<sup>+</sup> and/or (Y+REE)<sup>3+</sup> thus maintaining charge balance and discouraging formation of monazite.

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#### FLUID INDUCED DEHYDRATION OF THE MAFIC LOWER CRUST FROM AMPHIBOLITE TO GRANULITE FACIES: NATURE AND EXPERIMENT

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Natural evidence for the role of low H<sub>2</sub>O activity fluids (CO<sub>2</sub> or concentrated brines) in the dehydration of H<sub>2</sub>O-rich, mafic amphibolite facies rocks to H<sub>2</sub>O-poor, orthopyroxene-bearing granulite facies rocks (700-900°C and 500-1000 MPa) for both highly localised dehydration zones (CO<sub>2</sub>; cm's) as well as regional terranes (brines; km's) (Harlov et al. 1998; Perchuck et al., 2000; Harlov and Förster, 2002) include the presence of K-feldspar micro-veins along quartz-plagioclase grain boundaries; plagioclase grains metasomatised in a K-rich fluid; monazite and/or xenotime inclusions in the apatite grains; biotite enriched in Ti, F, and Cl; and apatite enriched in Cl and F. These features are not seen in the "source" amphibolite facies terrane along the same traverse. When  $f_{HF}/f_{H_2O}$  for either biotite or apatite is plotted as a function of the distance from the fluid/heat source, a uniform decrease in  $f_{HF}/f_{H_2O}$  is observed across the granulite to amphibolite facies traverse suggesting the presence of a uniform low H<sub>2</sub>O activity uniform fluid front. Dehydration experiments (900°C; 1000 MPa; 3 weeks; Au cylinder) involving a cylinder of natural tonalitic biotite gneiss (plagioclase, quartz, biotite) (220 mg) and a concentrated KCl brine (20-30% H<sub>2</sub>O; 80-70% KCl) (8 mg) placed at the base of the cylinder have been conducted in the piston cylinder apparatus (CaF<sub>2</sub> setup). Micro-veins, primarily of K-feldspar, volunteered along quartz/plagioclase grain boundaries though only where biotite and quartz were in contact and caused the biotite to breakdown along its grain boundaries to numerous small orthopyroxene and clinopy-

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roxene grains + minor ilmenite. The same experiment involving a concentrated NaCl brine (20-30% H<sub>2</sub>O; 80-70% NaCl) resulted in veins approximating a granitic composition along quartz/plagioclase grain boundaries with numerous small orthopyroxene grains + minor ilmenite volunteering along biotite grain boundaries, again only when the biotite and quartz were in contact.

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#### HYDROTHERMAL SYNTHESIS OF ALLUAUDITE IN THE Na-Mn-Fe<sup>2+</sup>-Fe<sup>3+</sup>-P-O SYSTEM

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Alluaudite, a Na-Mn-Fe-bearing phosphate mineral, is known to occur in Li-rich granitic pegmatites. During the past decade, several compounds with the alluaudite structure were synthesized, but their stability was scarcely envisaged. This is the reason why we decided to investigate the Na-Mn-Fe<sup>2+</sup>-Fe<sup>3+</sup>-P-O system.

Starting from compositions ranging from Na<sub>2</sub>Mn<sub>2</sub>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub> to Na<sub>2</sub>Fe<sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub>, the hydrothermal syntheses were carried out between 300 to 800°C and 0.1 to 0.5 GPa, using horizontally arranged Tuttle-type cold-seal bombs. Pure alluaudite is obtained between 300 and 400°C, whereas alluaudite is associated with maricite, Na(Fe<sup>2+</sup>,Mn)PO<sub>4</sub>, between 600 and 800°C. Maricite exhibits a crystal structure different from that of natrophilite, NaMnPO<sub>4</sub>, which is isotypic with olivine (Le Page & Donnay, 1977; Moore, 1972). Surprisingly, as far as we know, maricite has never been observed in granitic pegmatites.

Between 700 and 800°C, alluaudite and maricite are associated with fillowite and/or with an undetermined phase. This phase could correspond to an orthorhombic polymorph of the arrojadite structure (Moore et al., 1981), with  $a = 25.892(4)$ ,  $b = 14.792(5)$ , and  $c = 10.364(2)$  Å, space group *Pnma*. A single crystal with a chemical composition close to NaMn<sub>4</sub>(PO<sub>4</sub>)<sub>3</sub>, recently investigated by Keller et al. (2001), has shown a crystal structure corresponding to that of fillowite (Araki & Moore, 1981).

From the electron microprobe analytical results on the alluaudite crystals, the presence of both Fe<sup>2+</sup> and Fe<sup>3+</sup> in the structure can be deduced, in agreement with the chemical data on natural samples. Compared with the starting compositions, the alluaudite solid solutions are also enriched in bivalent cations and depleted in Na and Fe<sup>3+</sup>, according to the substitution mechanism Na<sup>+</sup> + Fe<sup>3+</sup> = (Fe<sup>2+</sup>,Mn<sup>2+</sup>) + Fe<sup>2+</sup>. Additionally, the morphology of the alluaudite crystals shows significant variations with the experimental conditions.

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#### INTERACTION OF HYDROUS GRANITIC MELTS WITH CARBONATES: IMPLICATIONS FOR DEVOLATILISATION IN SUBDUCTION ZONES

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Interlayered pelites and carbonates are common in subducted oceanic sediments. The interaction of hydrous granitic melts produced in deeply subducted metapelites with carbonates has been investigated by piston cylinder sandwich experiments. At 1000°C, 4.5 GPa the paragenesis in a synthetic simplified pelite composition (KCMASH) containing 2.5 wt.% H<sub>2</sub>O consists of phengite + garnet + clinopyroxene + kyanite + coesite + hydrous granitic melt. Dolomite embedded in the pelite reacts with the hydrous granitic melt and produces the paragenesis garnet + clinopyroxene + dolomite + liquid. Qualitative mass-balance constrains this liquid composition to 60 wt.% CO<sub>2</sub>, about 10 wt.% of each of H<sub>2</sub>O, K<sub>2</sub>O and CaO and very small amounts of SiO<sub>2</sub>, MgO and Al<sub>2</sub>O<sub>3</sub>. This liquid therefore reflects rather a carbonatite melt than a water-rich CO<sub>2</sub>-H<sub>2</sub>O fluid. In the pelite adjacent to the dolomite layer, an increasing abundance of garnet, kyanite and melt and a decreasing amount of clinopyroxene, phengite and coesite has been observed. This suggests that the presence of carbonate enhances melt production in the pelite. No clear separation between the hydrous granitic melt and the "carbonatite-like" liquid has been observed indicating complete miscibility. Carbonate solubility in hydrous granitic melts has been further investigated in the range 3.5-4.5 GPa and 900-1000°C by mixing a pelite with different amounts of dolomite and calcite. The runs contain hydrous granitic melts coexisting with garnet, coesite, omphacite, carbonate and occasionally phengite and kyanite. Mass balance reveals that about 1.5-2 times more CO<sub>2</sub> than H<sub>2</sub>O is dissolved in the melt. We therefore propose that hydrous granitic melts are capable of transferring not only H<sub>2</sub>O but also significant amounts of CO<sub>2</sub> from subducted sediments to the mantle wedge. The physical properties, the ability to transport trace elements and the interaction with the mantle wedge of such melts are yet to be determined.

#### STATIC COMPRESSION OF IRON SILICIDES TO MEGABAR PRESSURE

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Seismic data indicates those both inner and outer cores are less dense than pure iron at core pressures and temperatures. This suggests that light elements as iron compounds are contained in the inner and outer core. The preferred candidates for the light element are sulfur, oxygen, carbon, silicon, and hydrogen. Because silicon is one of the most abundant elements in the Earth, silicon could contribute to the density deficit. However, there are little experimental data at the core pressures on the properties of iron-silicon alloys. We have investigated the in-situ high-pressure behavior of iron silicides, Fe with 17 wt.% Si

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and Fe with 9 wt.%Si, at room temperature using diamond-anvil cell. X-ray diffraction patterns of iron silicides were collected from ambient pressure up to 125 GPa using monochromatic synchrotron x-ray radiation and the imaging plate at the BL-13A beamline at the Photon Factory, National Laboratory for High Energy Physics (KEK). Pressure was determined by the ruby fluorescence method. In the pressure range, no pressure induced phase transitions are observed Fe-17 wt.%Si alloy, while Fe-9 wt.%Si alloy transforms from bcc phase into hcp phase between 16 and 35 GPa and the hcp phase is stable at least to 100 GPa. A third-order Birch-Murnaghan equation of state fitted to the pressure-volume data yields the bulk modulus of two iron silicides. The iron silicides are less compressible than the other iron compounds, such as FeS, FeC and FeH, and pure iron. This could provide constraints on the physical and chemical properties of the iron compounds under core conditions.

### ORDER-DISORDER IN FELDSPARS AND ITS INFLUENCE ON HEAT TRANSPORT PROPERTIES

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Thermal transport properties are important parameters to constrain dynamical processes within the Earth's crust. Alkali feldspars are among the most abundant rock-forming minerals and are responsible for ca. 12 vol.% of the crust. Albite  $\text{Na}[\text{AlSi}_3\text{O}_8]$  and orthoclase  $\text{K}[\text{AlSi}_3\text{O}_8]$  show a temperature depending miscibility and ordering behavior. We have chosen a variety of 5 single-crystal alkali-feldspars from different origin to study thermal diffusivity as a function of chemical composition and ordering of the crystals. Thermal diffusivity  $a$  is related to the mean velocity of phonons  $v$  and their mean free path length  $l$  according to  $a = 1/3 v l$ . The ordering of the distribution of Si and Al in tetrahedrons is refined by the Rietveld method from XRD-data. A transient technique was used to determine the anisotropic thermal diffusivity behaviour of feldspar between 22°C - 800°C. At temperatures lower than 350°C the thermal diffusivity behavior is dominated by a phonon-mechanism. At higher temperatures some samples show a pronounced temperature variation, which is described by a radiative heat transport mechanism characterized by a  $T^3$  dependency. For the phononic heat transfer the optical quality of the sample has a minor effect. The chemical variation of the crystals leads to different average phonon-velocities depending on chemical composition. However, these variations can only explain some small oscillations in the observed diffusivity behavior. The thermal diffusivity behavior of alkali-feldspars seems to be dominated by the ordering of the crystals. From a structural point of view, the distribution of Si-Al in the tetrahedrons is important for the scattering probability for phonons and therefore determines the mean free path length of phonons. With increasing disorder the scattering probability increases and the disordered structural units can be viewed as point defects for phononic heat-transfer.

### EXPERIMENTAL STUDY OF Fe-Mg INTERDIFFUSION IN LOWER MANTLE PHASES

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The lower mantle of the Earth, between 670 km and 2900 km depth, forms the largest part by volume of our planet. The two dominating phases of the lower mantle are  $(\text{Mg,Fe})\text{SiO}_3$  perovskite and  $(\text{Mg,Fe})\text{O}$ , magnesiowustite. Knowledge of diffusional properties of these phases is essential in understanding different fundamental processes such as rheology, chemical exchange during plume ascent and residence times of subducting slabs. In this study diffusion couple experiments of single crystals of magnesiowustite in Ni capsules and polycrystalline samples of  $(\text{Mg,Fe})\text{SiO}_3$  perovskite in MgO single crystal capsules have been performed or are currently in progress. To achieve pressures up to 26 GPa the multianvil apparatus has been used. Run durations of the experiments ranged from 40 minutes to 1 day at temperatures up to 2373 K. Diffusional behavior of the two investigated phases are very different and requires different analytical procedures for profile analysis. For  $(\text{Mg,Fe})\text{SiO}_3$  perovskite a transmission electron microscope, equipped with an energy dispersive spectrometer, has been used, whereas for magnesiowustite, profiles are long enough to be measured by conventional electron microprobe analysis. TEM investigations of microstructures also shows that subgrain boundaries can have pronounced effects on very short diffusion profiles in perovskite.

Preliminary results show that Fe-Mg interdiffusion coefficients for  $(\text{Mg,Fe})\text{SiO}_3$  perovskite are  $3.66 \cdot 10^{-20} \text{ m}^2/\text{sec}$  at 2023 K and relatively reducing conditions, and for magnesiowustite  $1.9 \cdot 10^{-13} \text{ m}^2/\text{sec}$  at 2023 K,  $f\text{O}_2$  close to the Ni-NiO buffer and containing 21 mole% FeO. Therefore, any process dominated by Fe-Mg interdiffusion in  $(\text{Mg,Fe})\text{SiO}_3$  perovskite takes place at considerably longer timescales than estimated by diffusional properties of magnesiowustite or upper mantle phases as long as no unusually strong oxygen fugacity effect exists.

### EFFECT OF QUARTZ-COESITE TRANSITION ON P-WAVE VELOCITY IN $\text{SiO}_2$ AND QUARTZ-BEARING ROCKS AT 4.1 GPa AND 4.5 GPa

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Compressional wave velocities ( $V_p$ ) in quartz and quartz-plagioclase pyroxenite have been measured in multi-anvil apparatus at 4.1 GPa and 4.5 GPa, and up to 1570 K, using the reflecting-transition combined method (Liu et al. 1999). Pressure is raised at a rate of  $4 \cdot 10^5 \text{ Pa/s}$  and temperature at a rate of 20 K/s. After keeping the temperature steady for 35 minutes,  $V_p$  is measured. At 4.1 GPa and temperature less than 900 K,  $V_p$  in quartz decrease with increasing temperature at slow rate. The temperature coefficient is  $0.00005 \text{ km}\cdot\text{s}\cdot\text{K}$ . At temperature higher than 900 K,  $V_p$  increase with temperature quickly.

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Observing the recovered samples indicate that at 4.1 GPa and 920 K, about 5 vol.% quartz has been transitioned to coesite, which suggests that the new-formed coesite is the main cause for the increase of  $V_p$ . The content of coesite increases with temperature. At 1050 K, the content of coesite is about 75 vol.%. The variation of  $V_p$  with temperature in quartz-plagioclase pyroxenite at 4.5 GPa is similar to that in quartz. At temperature higher than 1173 K,  $V_p$  in quartz-plagioclase-pyroxenite increase with increasing temperature. At 1243 K, about 3vol.% coesite have been in the sample and the other minerals (plagioclase and clinopyroxene) show no significant variation. This phenomenon again indicates that the quartz-coesite transformation may increase  $V_p$  in quartz-bearing rock.  $V_p$  in quartz-coesite system have been calculated using the Voigt-Reuse-Hill model. The results are in consistent well with our experimental results.

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### AN IN-SITU X-RAY DIFFRACTION STUDY ON KINETICS OF HIGH-PRESSURE TRANSFORMATION OF ENSTATITE

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Enstatite is one of the most abundant minerals in the Earth's upper mantle. It transforms to (modified) spinel plus stishovite, and to ilmenite at the depth of 500-600 km. Under subduction zone conditions, there is a possibility that these transformations are kinetically inhibited due to low temperatures (Hogrefe et al., 1994). In order to clarify kinetics of high-pressure transformation of enstatite, we performed *in-situ* X-ray diffraction experiments using "SPEED-1500" multi-anvil high-pressure apparatus installed at SPring-8, Japan.

Starting material is a powder of natural enstatite, ( $\text{Mg}_{0.99}\text{Fe}_{0.01}\text{SiO}_3$ ). It was annealed at 12-16 GPa and 1200°C for 100 minutes in the stability field of high-pressure clinoenstatite or spinel plus stishovite, and then compressed to the desired pressure at 500°C. Finally we heated the sample to the desired temperature at constant oil pressure with taking X-ray diffraction patterns every 10 seconds. In this way, we observed transformation kinetics from high-pressure clinoenstatite to ilmenite, and from spinel plus stishovite to ilmenite at 19.8-20.7 GPa and 950-1500°C. At 20.1 GPa and 1090°C, the enstatite-ilmenite transformation completed immediately in 10 seconds. At 20.0 GPa and 1000°C, the transformation started in 40 seconds and completed in 180 seconds. At 19.8 GPa and 950°C, the transformation started in 110 seconds and did not complete even in 40 minutes. On the other hand, the reaction rate from spinel plus stishovite to ilmenite was much slower even at higher temperature. The transformation started in 120 seconds and did not complete in 145 minutes at 20.7 GPa and 1500°C. These results imply that once enstatite decomposes into spinel plus stishovite, it becomes difficult to transform to ilmenite under subduction zone conditions.

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### ENTHALPIES OF MIXING FOR SYNTHETIC GERMANIUM-BEARING ALKALI FELDSPARS AND DIRECT HF SOLUTION CALORIMETRIC MEASUREMENT OF ENTHALPIES OF ELASTIC STRAIN ASSOCIATED WITH EXSOLUTION

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Hydrofluoric acid solution calorimetric measurements have been made at 50°C on a nine-member series of synthetic germanium-bearing alkali feldspars. Because of the rapid dissolution of these samples, the measured heats of solution are of particularly high precision, with an average standard deviation per sample of just  $\pm 0.37$  kJ/mol. A plot of enthalpy of solution against composition for the Ge-bearing samples parallels that for normal disordered Ge-free (sanidine-analbite) alkali feldspars (Hovis, 1988). Enthalpies of K-Na mixing for the Ge-bearing series are maximized at sodic compositions, consistent with asymmetry of the Ge-feldspar solvus (Kusatz et al., 1987), at a value of 5.4 kJ/mol, similar in magnitude to that of normal disordered alkali feldspars (Hovis, 1988).

Several exsolved Ge-bearing alkali feldspar samples were synthesized via subsolvus annealing of homogeneous specimens at temperatures ranging from 500 to 640°C and periods from 48 to 480 days. All such samples were examined by TEM and confirmed to have coherent and regularly spaced exsolution lamellae, with wavelengths in the various specimens ranging from 300 to 800 Å.

Enthalpies of elastic strain were determined for four of the exsolved Ge-bearing feldspars by comparing their heats of solution to those of unstrained versions of the same coexisting phases. The resulting enthalpies of elastic strain were found to be small, and in fact near the detection limits of the calorimetric system despite the high precision of the data. Collectively the results indicate elastic strain enthalpies that are less than 2.0 kJ/mol. These are consistent with values estimated independently by Tullis & Yund (1979) and Brown & Parsons (1993). The enthalpy of elastic strain determined for an exsolved Ge-free sanidine-analbite feldspar was less than the standard deviation of the calorimetric data.

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### THE NUCLEATION AND GROWTH OF POLYCRYSTALLINE QUARTZ: PRESSURE EFFECT FROM 0.05 TO 3 GPa

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Polycrystalline quartz was formed from amorphous silica with sea- and distilled-water at temperatures and pressures ranging from 50 to 450°C and 50 MPa to 3 GPa. The data, which show a sigmoidal curve on a  $\zeta$ -t plot, can be reasonably modeled using Avrami's nucleation and growth equation. The results reveal a dramatic pressure effect on the transformation rate, which increases by five orders of magnitude as pressure increases from 50 MPa to 3 GPa at 400 deg.C. For instance, it takes only 1 day at 3 GPa, instead of 300 years at 50 MPa, to transform 50% of silica to quartz at 100 deg. C. The pressure effect is more prominent at low-pressure than at high-pressure regimes; the transition pressure between the high- and low-pressure regimes depends on temperature; it is around 300 MPa at 400 deg.C. The nucleation rates were calculated using the measured growth rates and the extent of the transformation by fitting to the Cahn's kinetic model. The results show that pressure can significantly enhance both the nucleation and growth rates although the effect is stronger on nucleation than growth. This has been confirmed by the SEM observations, which show that grain sizes significantly decrease with increasing pressures, and has led to a new method to synthesize nano-size (< 100 nm) polycrystalline quartz in neutral solutions. The results also reveal that metastable quartz was nucleated and grown in the coesite stability field at low temperatures (< 400 deg.C). Polycrystalline quartz has been formed at temperatures as low as 50 deg.C at 3 GPa in a few days. This allows us to predict that polycrystalline quartz or coesite may be synthesized at ambient temperature within laboratory time if the pressure is high enough (e.g. > 4 GPa).

### CRYSTAL CHEMISTRY AND THERMODYNAMIC MIXING PROPERTIES OF HEDENBERGITE-PETEDUNNITE-JOHANNSENITE-DIOPSIDE SOLID SOLUTIONS

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Clinopyroxenes are common minerals in skarns and occur in phase assemblages with iron-, zinc- and manganese-ores. We directed our attention to the properties of diopside(di)-hedenbergite(hd)-johannsenite(jo)-petedunnite(pd)-solid solutions:  $\text{Ca}(\text{Mg,Fe,Mn,Zn})\text{Si}_2\text{O}_6$ . The zinc-content in pyroxenes is an indicator for the metallogenesis of a skarn (Nakano et al., 1994).

The binary solid solutions di-hd, di-jo and hd-jo show complete miscibility (Capitani & Mellini, 2000 and Nakano, 1998). For the solid solution hedenbergite-petedunnite a complete miscibility can be confirmed at pressures > 1.0 GPa. While hedenbergite is stable at low pressures, petedunnite is stable at pressures > 1.0 GPa. At lower pressures, petedunnite reacts with quartz to zinc feldspar, corresponding to the reaction jadeite + quartz = albite (Fehr & Huber, 2001).

The thermodynamic behaviour of multi-component solid solutions is controlled by the binary solid solutions of their end-members. The solid solution hedenbergite-diopside shows asymmetric mixing properties and two Margules parameters are necessary to describe the thermodynamic mixing behaviour (Meyre et al., 1997). The alteration of the molar volumina implies a non-ideality of the solid solution hedenbergite-petedunnite (Huber et al., 2000). At higher  $f_{\text{O}_2}$  hedenbergite decomposes to andradite, magnetite and quartz:  $9 \text{CaFeSi}_2\text{O}_6 + 2 \text{O}_2 = 3 \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + \text{Fe}_3\text{O}_4 + 9 \text{SiO}_2$ . The equilibrium constant of this reaction is determined by oxygen fugacity, which can be measured by means of emf methods. If hedenbergite-petedunnite solid solutions, take part in this reaction, the equilibrium constants reflect chemical potentials of hedenbergite in hedenbergite-petedunnite solid solutions. The activities of this solid solution were determined by emf-methods, directly. The measured activities lead to two Margules parameters to describe the hd-pd solid solution, showing asymmetric mixing properties. Thermodynamic parameters describing these ternary resp. quaternary solid solutions are still unknown.

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### STRUCTURAL AND CHEMICAL RESPONSE TO VARYING $^{14}\text{B}$ CONTENT IN OLENITE FROM KORALPE, AUSTRIA

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Long thought to be stoichiometric and contain only trigonal B, tourmaline has recently been shown to incorporate B on tetrahedral sites: a colorless olenite from the Koralpe, Austria contains approximately one  $^{14}\text{B}$  for every six tetrahedral (T) sites (Ertl et al. 1997; Hughes et al. 2000). Even greater amounts of  $^{14}\text{B}$  can substitute for Si in synthetic olenitic tourmaline (Wodara and Schreyer 1998, 2001). These discoveries have important implications for the crystal chemistry of the more widespread elbaite-schorl-rossmanite tourmalines typical of rare-element pegmatites.

To characterize the response of the tourmaline atomic arrangement to differing amounts of substitution of B for Si, five samples were separated from a rim-to-core section of the Koralpe tourmaline (nearly colorless rim to dark green core), over a distance of approximately 0.5 cm. After grinding to spheres, the crystal structures of the samples were undertaken using three-dimensional X-ray methods and yielded  $R$  values < 0.018.

From rim to core, the amount of tetrahedral boron decreases monotonically from 0.65 to 0.35 *apfu*  $^{14}\text{B}$  as refined from X-ray structure data. Over that range of  $^{14}\text{B}$  content, the mean T-O distance increases from 1.6103 to 1.6215 Å. Preliminary EMPA analyses undertaken before the structure crystals were separated show that the extensive substitution of  $^{14}\text{B}$  for Si that decreases from rim to core yields an increase in Si and a decrease in B from rim to core. In addition, FeO content increases from <1.0 wt.% at the rim to >7.5 wt.% in the core, reinforcing the assertion that  $^{14}\text{B}$  increases with increasing Al in tourmalines.

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### Fe-Mg EXCHANGE EXPERIMENTS ON CHLORITE IN THE SYSTEM $\text{MgO-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

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Fe-Mg chlorite is widespread in metamorphic and hydrothermally altered rocks. Stable assemblages in a wide range of temperatures and pressures indicate a positive correlation between  $\text{Al}^{3+}$ - and  $\text{Fe}^{2+}$ -contents in Fe-Mg chlorite. Data from (ultra)mafic and pelitic rocks constrain the Fe/Mg partitioning ( $K_D$ ) with several coexisting silicates and oxides.

Experimental studies on chlorite so far have been performed mainly in the Fe-free system. For intermediate and pure Fe-chlorite experimental data are more sparse and partially discrepant. To date, few experimental studies on chlorite have analyzed the chemical composition of reaction products.

In the present study Fe-Mg exchange experiments between natural chlorite and synthetic olivine and spinel have been performed to calibrate the relationship between  $\text{R}^{2+}\text{SiAl}_{-2}$ - and  $\text{FeMg}_{-1}$  exchange in chlorite as a function of temperature and bulk  $\text{XFe}^{2+}$ . Experiments are conducted at 25 kbar using piston-cylinder equipment technique because low pressure experiments turned out to yield overly sluggish reaction progress.

Phase equilibrium data so obtained are combined with data from the literature to derive a consistent set of thermodynamic data including mixing properties of Fe-Mg chlorite. Available site-mixing activity models for chlorite do not expand to a Gibbs Free Energy function required to compute chemical equilibria by G-minimization. The present study uses a concise speciation formulation to model the non-ideal Fe-Mg chlorite solution. The Gibbs Free Energy function is based on the four configurations amesite, Fe-amesite, penninite and Fe-penninite. These cover the whole compositional range accessible to chlorite in the system  $\text{MgO-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  (FMASH).

The derived solution model adequately reproduces available data on phase relations in the system MASH, including the composition of pure Mg-chlorite at its upper thermal stability. In the system FMASH, the positive correlation between  $\text{Al}^{3+}$ - and  $\text{Fe}^{2+}$ -contents in Fe-Mg chlorite as documented from natural assemblages is adequately predicted by the model.

### ARGON DIFFUSION CHARACTERISTICS OF SINGLE GRAIN PYROXENES USING LASER STEP HEATING

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Pyroxenes are seldom used in K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  dating. This is due to its low potassium content as an impurity, little knowledge of their diffusion characteristics and difficulty in mineral separation. Pyroxenes neither dehydrate during heating, nor make a structural transition and/or breakdown up to the melting point. These characteristics make them ideal candidates for argon diffusion studies in vacuum in spite of their low potassium content. Single grain analysis also requires little separation work.

We have developed a temperature controlled laser step heating system, and applied it to pyroxene dating. Sample temperature during laser heating is monitored by an infrared thermometer, which has a probe area of 330 micrometers diameter. Temperature of a grain is sent to a personal computer, and is converted to a voltage increment of the laser power supply to achieve a preset temperature within 30-60 seconds. In contrast to a heater-current temperature control, the system does not allow overshoot of the preset temperature, adopting a relatively long relaxation time for thermal diffusion.

The diffusion characteristics of pyroxenes vary among analyses. This may be a reflection of compositional dependence, but the estimated closure temperatures of the pyroxenes are relatively uniform. They are above muscovites and below hornblendes.

# EMPG IX

## Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

### SYNTHESIS, STABILITY AND CHARACTERISATION OF A SYNTHETIC AMPHIBOLE WITH COMPOSITION $\text{NaNaMgMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ : SOME PRELIMINARY DATA

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Several experiments on amphibole synthesis in the  $\text{Na}_2\text{O-MgO-SiO}_2\text{-H}_2\text{O}$  system yielded compositions close to the  $^{\text{B}}\text{Mg}$  analogue of richterite,  $\text{NaNaMgMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  (e.g. Witte et al. 1969). Maresch et al. (1991) described an amphibole composition with three protons per formula unit,  $\text{NaNa}_2\text{Mg}_5\text{Si}_8\text{O}_{21}(\text{OH})_3$ , related to the former by the  $\text{NaHMg}_{-1}$  exchange. Four syntheses were carried out in the T range 750-900°C at 50°C intervals at 4 and 5 kbar. Run powders were studied by X-ray diffraction, SEM-EDAX and IR spectroscopy. They are dominant amphibole with very small amounts (< 5%) of quartz. XRPD patterns were indexed in the C2/m space group, and cell dimensions were refined by the Rietveld method. A strong decrease in the *a* and  $\beta$  parameters (and in the cell volume) is observed at increasing *T*, whereas *b* and *c* are virtually constant. This evidence suggests a change either in chemistry or in structural conformation. Infrared spectra for the 750 and 800°C products shows a well-defined doublet with a sharper band centred at 3715  $\text{cm}^{-1}$ , and a second broader band centred at 3745  $\text{cm}^{-1}$ , which is due to several (possibly three) overlapping components. This band is compatible with the data of Maresch and Langer (1976) and Raudsepp et al. (1991), and can be ascribed to an OH group interacting with Na strongly delocalised at the A-site. Beyond 800°C, an additional band appears at 3674  $\text{cm}^{-1}$ , which is assigned to an OH group pointing toward an empty A-site (partial solid-solution toward cummingtonite), indicating that the amphibole formed at higher *T* departs from the nominal stoichiometry. The intensity of this band linearly increases with the temperature of synthesis. Using the curves of Hawthorne et al. (1997) we calculate that the 850°C sample has 5% and the 900°C sample 14% empty A-site.

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### THE Na-Li SUBSTITUTION AT THE M4 SITE IN CLINOAMPHIBOLES:

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The B-site occupancy is a key feature in amphibole crystal-chemistry, and is the base of amphibole classification and nomenclature (Leake et al., 1997). The solid solution between  $^{\text{B}}(\text{Fe}, \text{Mg}, \text{Mn})$  and  $^{\text{B}}\text{Na}$  amphiboles is restricted in natural samples (Deer et al., 1999), whereas recent work on metasomatic episyenites of the Pedriza Massif (Spain) showed nearly complete solid solution between  $^{\text{B}}\text{Li}$  and  $^{\text{B}}\text{Na}$  amphiboles both with A-filled and A-empty sites (Oberti et al., 2000; Caballero et al., 2002). To verify the limits and stability of solid-solution terms, syntheses were done along the ferri-clinoferroholmquistite  $\text{Li}_2\text{Fe}^{2+}\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$  - riebeckite  $\text{Na}_2\text{Fe}^{2+}_2\text{Fe}^{3+}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$  join. Experiments were done at 500°C and 4 kbar in an Internally Heated Pressure Vessel (IHPV), with a Ar-H<sub>2</sub> mixture as pressure medium, a Shaw membrane controlling buffering conditions, but a gold capsule limiting the hydrogen diffusion (Chou, 1987; Iezzi et al., 2001). The run products are amphibole and quartz < 5%. Amphiboles occur as acicular crystals 1 x 1-2  $\mu\text{m}$  in size, thus precluding EMP analysis and single-crystal-refinement. They were analysed by XRPD, SEM-EDAX, FTIR and Mossbauer methods. XRPD patterns were fully indexed in the C2/m space group, and cell dimensions refined by the Rietveld method. Both *a* and  $\beta$  increase as a function of the  $^{\text{B}}\text{Na}$  content, whereas *b* and *c* are constant over the entire join. The cell volume increases linearly. IR spectra in the OH-stretching region show a single sharp band relative to the  $^{\text{M1}}\text{Fe}^{\text{M1}}\text{Fe}^{\text{M3}}\text{Fe-OH-}[\ ]$  configuration; it is centred at 3614  $\text{cm}^{-1}$  for the  $^{\text{B}}\text{Li}_2$ , and linearly shifts to 3618  $\text{cm}^{-1}$  for the  $^{\text{B}}\text{Na}_2$  composition. Mossbauer spectra collected for the  $^{\text{B}}\text{Li}_2$ ,  $^{\text{B}}\text{Na}_2$ , and  $^{\text{B}}\text{LiNa}$  compositions, show  $\text{Fe}^{2+}$  distributed between M1 and M3, and  $\text{Fe}^{3+}$  ordered at M2; with a constant  $\text{Fe}^{2+}:\text{Fe}^{3+}$  ratio of 3:2. These evidences confirm that the products are close to the nominal compositions, and that the  $^{\text{B}}\text{Na} \rightleftharpoons ^{\text{B}}\text{Li}$  exchange was complete.

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**CRYSTAL-CHEMICAL APPROACH TO DESIGN OF NOVEL ACTINIDE WASTE FORMS**

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Searching for host phases for long-lived actinides immobilization is a very actual problem. Promising host for actinide wastes are garnet-structure phases of general formula (AVIII)<sub>3</sub>(BVI)<sub>2</sub>[XO<sub>4</sub>]<sub>3</sub>. It was found that incorporation of Ce<sup>4+</sup>, U<sup>4+</sup>, and Pu<sup>4+</sup> into REE - Al - Ga garnets was restricted by 4 - 6 wt.% only (1). In order to select the garnet-type compounds with higher solubility in respect of tetravalent actinides a structural-chemical research has been carried out. These elements can be inserted into the [A]VIII-sites of the structure if low charge and large cations occupy the [X]IV and [B]VI sites. The largest ion, which can occupy both IV- and VI-coordinated sites of the garnet structure, is Fe<sup>3+</sup> (rIV = 0.049 nm, rVI = 0.065 nm). Its radii are larger than those of Al<sup>3+</sup> (rIV = 0.039 nm, rVI = 0.054 nm) or Ga<sup>3+</sup> (0.047 nm, 0.062 nm). Hence, from crystal-chemical point of view, it can be expected that ferrite garnets have the highest loading capacity relatively to actinides. For confirmation of this conclusion about thirty ceramics were fabricated. The runs were performed by cold pressing mixtures composed of CaO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, Gd<sub>2</sub>O<sub>3</sub>, UO<sub>2</sub>, ThO<sub>2</sub> or PuO<sub>2</sub> and their sintering in air at 1400 - 1500°C for 1 - 2 hours. Initial batch compositions were prepared taking into account ideal garnet stoichiometry A<sub>3</sub>B<sub>2</sub>[XO<sub>4</sub>]<sub>3</sub> with various possible schemes of the three structural sites occupation. The samples were studied using XRD, SEM/EDS, and TEM. Maximal solubility of actinides reached up to 30 wt.% Th, 20% U, and at least 15% Pu was observed in the ferrite garnets (Ca,An,Gd)<sub>3</sub>(Zr,An,Fe)<sub>2</sub>Fe<sub>3</sub>O<sub>12</sub>, An = U, Th, or Pu.

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**FINE STRUCTURE OF INFRARED OH-STRETCHING BANDS IN NATURAL AND HEAT-TREATED AMPHIBOLES OF THE TREMOLITE-FERRO-ACTINOLITE SERIES**

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Fine structure in the principal OH-stretching bands of amphiboles of the tremolite-ferroactinolite series have been examined. In samples with partly filled A-sites, a broad (composite) band is observed at 3725~3680 cm<sup>-1</sup> and is assigned to mainly two types of configurations: (M1 M1 M3)-OH<sup>-A</sup>(Na,K):<sup>T1</sup>Si<sup>T1</sup>Al in which Al occurs at the T1 site, and (M1 M1 M3)-OH<sup>-A</sup>(Na,K)-<sup>O3</sup>(O<sup>2-</sup>,F<sup>-</sup>,Cl<sup>-</sup>); the component of (M1 M1 M3)-OH<sup>-A</sup>(Na,K):<sup>T1</sup>Si<sup>T1</sup>Si configuration is small, because Na and K at the A site are locally associated with Al at an adjacent T1 site. In tremolite, manganoan tremolite and Fe<sup>2+</sup>-poor actinolite, a weak shoulder on the principal A band at

~3669 cm<sup>-1</sup> is assigned to the configuration M<sup>4</sup>C a<sup>M4</sup>(Mg, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Na): (Mg Mg Mg) - OH<sup>-AV</sup>:<sup>T1</sup>Si<sup>T1</sup>Si(V=vacancy). Fine structure in the principal bands B (B' and B'') and C (C' and C'') are also observed: the higher frequency band B'' is assigned to <sup>M1</sup>Fe<sup>2+</sup> <sup>M1</sup>Mg <sup>M3</sup>Mg-OH<sup>-AV</sup>, and the lower frequency band B' to <sup>M1</sup>Mg<sup>M1</sup>Mg<sup>M3</sup>Fe<sup>2+</sup>-OH<sup>-AV</sup>; the higher frequency band C' is assigned to <sup>M1</sup>Fe<sup>2+</sup><sup>M1</sup>Fe<sup>2+</sup><sup>M3</sup>Mg-OH<sup>-AV</sup> and the lower frequency band C'' to <sup>M1</sup>Mg<sup>M1</sup>Fe<sup>2+</sup><sup>M3</sup>Fe<sup>2+</sup>-OH<sup>-AV</sup>. Supposing a random distribution of Mg and Fe<sup>2+</sup> at the M1 and M3 sites, the band intensity for B'' is twice that of B' and that for C'' is twice that C', respectively. Some broad OH-stretching bands attributed to (M1 M1 M3)-OH<sup>-AV</sup>:<sup>T1</sup>Si <sup>T1</sup>Al are observed at 3640 ~ 3580 cm<sup>-1</sup>. In amphiboles of the tremolite-ferroactinolite series which show substantial B=(MgMgFe<sup>2+</sup>)-OH stretching band, a new OH-stretching band at around 3641 cm<sup>-1</sup>, E, appear near the principal C band at around 3643 cm<sup>-1</sup> on heat treatment. The shape of this band E is similar to that of the original band B, and is assigned to (MgMgFe<sup>3+</sup>)-OH stretching and its local configuration is O<sup>2-</sup>-(MgMgFe<sup>3+</sup>)-OH. A weak and broad band A\*\* appear at ~3690 cm<sup>-1</sup> in some Na-bearing actinolites, and is ascribed to the (MgMgMg)-OH<sup>-A</sup>Na-O<sup>2-</sup> configuration.

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**FINE-STRUCTURE IN THE INFRARED OH-STRETCHING BANDS IN ANTHOPHYLLITE**

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The principal infrared OH-stretching bands in anthophyllites show fine structure due to the occurrence of two symmetrically distinct OH groups in the crystal structure. There are two distinct tetrahedral double-chains in the orthorhombic amphibole structure, the A-chain and the B-chain. The B-chain is much more rotated than the A-chain, and the stereochemistry around each of the OH sites suggests that the hydrogen bond to the bridging anion(s) of the B-chain is stronger than the hydrogen bond to the bridging anion(s) of the A-chain. This difference is sufficient to shift the frequency of the principal OH<sub>2</sub> stretching band(s) ~ 5 cm<sup>-1</sup> downward and allow resolution of the two bands in the infrared spectrum. This distinction could allow detection of possible OH-F ordering between the two distinct monovalent-anion sites in the orthorhombic amphibole structure.

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### STATE OF A MATURING METHODOLOGY: GIGAHERTZ ULTRASONIC INTERFEROMETRY

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Experimental determination of the anisotropic elastic properties of minerals plays an important role in interpreting Earth's seismic structure in terms of composition and mineralogy. Gigahertz ultrasonic interferometry (GUI) is a relatively new, rapidly evolving acoustical method that, when fully developed, will be used to measure P and S travel times in single crystals at non-ambient pressures and temperatures in a modified ultrasonic/X-ray diamond anvil cell. GUI has successfully reduced the sample-size requirements for single-crystal ultrasonics to about 50 microns, but has been essentially without the use of shear waves due to limitations in high-frequency piezoelectric shear transducers. A new method of generating shear waves with near-optical wavelength has been developed that features a P-to-S conversion inside a single-crystal MgO prism. Last year we demonstrated the exciting potential of this new method by measuring the ambient *P-T* elastic constants of single-crystal magnesiowüstite-(Mg,Fe)O with a variety of compositions. In the diamond cell, P-wave measurements have been made on (Mg,Fe)O of mid-range composition to 3.6 GPa at room temperature. A major challenge facing future single-crystal ultrasonic measurements at high temperature will be keeping the sample in contact with the acoustic transmitting anvil. In a pilot study, we measured P-wave travel times in San Carlos olivine to 250 °C at ~2.5 GPa without a bonding agent. We are also exploring the use of aerogel to act as a gentle transparent "spring". Recently, we produced a silica aerogel in 4:1 methanol:ethanol solution (alcohol), and loaded it along with a quartz (010) plate and several rubies in our ultrasonic cell. The samples in the new supportive pressure medium exhibited hydrostatic compression to the maximum pressure of ~5 GPa based on the axial ratio *c/a* of the quartz and peak widths of the ruby spectra, although we have yet to measure travel times in this configuration.

### PRESSURE DEPENDENCE OF OH RAMAN FREQUENCIES OF HYDROUS SILICATE PHASES

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The range of minerals in the Earth capable of hosting water in the form of H<sub>2</sub>O and/or OH ranges from ice to nominally anhydrous silicate phases. Proton site locations and hydrogen bonding in minerals can be investigated with different experimental methods: Vibrational and NMR spectroscopy, as well as x-ray and neutron diffraction techniques. Raman spectroscopic observations of OH stretching frequencies in conjunction with distance-frequency correlations are particularly important in

cases where bulk crystallographic methods cannot be used, such as disorder of protons or the small sample volume of high-pressure phases. We report pressure dependencies of OH stretching frequencies in highly hydrous phases: Phase E (synthesized by N. Ross) and clinocllore, measured in a diamond-cell to 19 GPa and 25 GPa respectively with Micro-Raman spectroscopy. OH stretching frequencies showing the common negative, but also unusual positive pressure dependencies, have been observed between 3400 cm<sup>-1</sup> and 3700 cm<sup>-1</sup>. A decrease in OH stretching frequency with increasing pressure can be attributed to a weakening of the intramolecular OH force constant, as for example caused by increased hydrogen bond interaction. H-H repulsion under compression might also be an important factor in the positive pressure dependencies of OH stretching frequencies. In the high-pressure Raman experiment on clinocllore we used moissanite anvils, which, unlike diamond-anvils, do not obscure the Raman signal in the OH stretching region.

### A MODIFIED DOUBLE CAPSULE TECHNIQUE FOR H<sub>2</sub>O UNDERSATURATED PISTON CYLINDER EXPERIMENTS IN CALC-ALKALINE SYSTEMS

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The experimental study of H<sub>2</sub>O-undersaturated Fe-bearing systems in piston cylinder apparatus is faced with iron loss to and H<sub>2</sub> diffusion through noble metal capsules. During the alloying of the iron with the noble metal container, the FeO from the experimental charge is reduced to form an FeX alloy (X = Au, Pt, AuPd, AgPd), liberating excess O<sub>2</sub> [1]. Hence, the loss of iron to noble metal capsules is ultimately related to the oxygen fugacity (*f*O<sub>2</sub>). Here we present a modification of the double capsule technique that permits us to perform experiments on H<sub>2</sub>O-undersaturated, iron-bearing systems under conditions naturally prevailing in calc-alkaline magmas. Au<sub>50</sub>Pd<sub>50</sub> or Au<sub>90</sub>Pd<sub>10</sub> capsules were preconditioned for 48 to 72h in a gas mixing furnace at QFM to QFM-1 using a synthetic basalt that was mixed from oxides and hydroxides. The recovered capsules were cut in half and mounted in epoxy, the other half was put into HF for ~48 hours to remove the silicate glass and then mounted in epoxy. The iron content of the capsules before and after treating with HF was determined along profiles of the bottom and the side wall of the capsules. Experiments at 1 GPa used a modified double capsule technique, where a preconditioned AuPd capsule is put into an outer Pt capsule which contains the same starting material. Two different NaCl-pyrex assemblies were used in order to impose different oxygen fugacities (*f*O<sub>2</sub>) on the experimental charges: (i) MgO inner sleeves and (ii) Pyrex-BN inner sleeves. Au<sub>90</sub>Pd<sub>10</sub> capsules contain ~0.3 wt% Fe after presaturation but before leaching. Microprobe traverses revealed no significant zoning indicating that equilibrium was achieved at the given temperature and *f*O<sub>2</sub>. However, after leaching with HF, the Fe content of the capsules was significantly higher (~0.45 wt% Fe), indicating that leaching the silicate glass with HF signifi-

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cantly changes the iron content of Au<sub>90</sub>Pd<sub>10</sub> alloys. High pressure runs at 1.0 GPa contained olivine+liquid. The fO<sub>2</sub> of these experiments was calculated using Fe-Mg Kd's (olivine-liquid) and the thermodynamic formulation of Kress and Carmichael [2]. Results indicate that preconditioned Au<sub>90</sub>Pd<sub>10</sub> capsules with a BN assembly are best suited for H<sub>2</sub>O undersaturated experiments at ~QFM+1.

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#### VERIFICATION OF THE FAXEN CORRECTION FACTOR USED FOR VISCOSITY DETERMINATIONS

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In viscosity measurements of silicate melts with the falling sphere technique a correction factor (the "Faxen correction factor") is often employed to account for the finite diameter of the sample (Faxen, 1925). Due to very large samples, dynamic neutron radiography allows to determine the effect of the sample size and hence to verify the magnitude of the necessary correction. Dynamic neutron radiography is the time- and position-dependent measurement of the attenuation of a neutron beam due to the absorption of the neutrons. In such experiments, silicate melts are generally transparent for neutrons, while the spheres can be made of highly absorbing material. In our experimental set-up, the ratio of the diameters of the sphere and the sample can be varied between 0.06 to 0.25. Furthermore, the long distance (90 mm) over which the fall of a sphere can be observed, allows to discontinuously change this ratio by manufacturing crucibles whose upper half has an inner diameter of 39 mm, while the lower half has an inner diameter of 20 mm. In nearly all of our experiments the velocity change of the falling sphere due to the change in the diameter of the crucible was significantly smaller than suggested by the commonly used expression for the Faxen correction factor. We can exclude thermal gradients or inhomogeneities within the sample as the cause of this behaviour, and hence conclude, that most probably the often used correction overcompensates the influence of the finite sample diameter by 10-15%. A more detailed evaluation will be presented at the conference.

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#### PARTIAL MELTING OF MUDSTONES AT 1 BAR; A CONSTRAINT ON THE PHASE DIAGRAMS FOR HAPLOGRANITE SYSTEM

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Partial melting of mudstones at P~1 atm during prolonged pyrometamorphic events was examined on the example of fused sedimentary rocks - clinkers from the Uralian burned dumps (Russia). During spontaneous coal combustion temperature obtained are high enough (700 - 1300°C) to cause partial or total melting of mudstones. Parent rocks contain SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and H<sub>2</sub>O more than 90 wt.% taken together and less than 0.5 wt% of CaO, that allows to use haplogranite system as suitable for consideration of their melting. The melt compositions were determined by microprobe analysis of 100 glasses from the clinkers. The glasses being the quenching partial melts, vary in silica and alkalis contents. In the Qz-Ab-Or-diagram the figurative points of normative glass compositions trace the Qz-Fsp cotectic (P<sub>H<sub>2</sub>O</sub>=0.5 kb) and form two clusters according to tie-lines in the field of quartz stability. These individual sequences reflect the increasing of partial melting degree. The first cluster originates at the cotectic for P<sub>H<sub>2</sub>O</sub>=0.5 kbar (Tuttle, Bowen, 1958), and the second one at the dry cotectic of Schairer (1950). It is surprising, inasmuch as in both cases melting was realised under the same dry conditions at P~1 bar. There are several reasons of ambiguous reconstruction of melting conditions. The first reason is the inconsistency of the experimental data for low-pressure conditions. As P<sub>H<sub>2</sub>O</sub> decrease cotectics shift toward Qz corner. It allows to expect that dry cotectic should be widely spaced from the Fsp joint. In this case the first glass compositions cluster conforms to assumed dry cotectic that is contradictory to experimental data of (Schairer, 1950). The existence of two distinguished glass compositions clusters is attributable to either the singularity of melted substrate compositions, or Na- and Si-evaporation from melt during the prolonged heat treatment. Financial support of RFBR (grant 01-05-65060).

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#### MODELING OF THERMODYNAMIC CONDITIONS OF METAMORPHIC-METASOMATIC FORMATIONS NEAR ORE-BEARING COMPLEXES

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In order to study the evolution of metamorphic processes and evaluate their thermodynamic parameters, late magmatic and superimposed metasomatic mineral assemblages were investigated near the contacts of ore-bearing metamorphic garnet-biotite-amphibole rocks of the Fedorovo-Panskiy massif. The massif is located in the central part of the Kola peninsula and contains two stratified platinum-bearing layers horizon. On the basis of a detailed research of structures of coexisting minerals parageneses, three consequent stages of crystallization and

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mineral formation have been distinguished. The observed natural process of transformation of rocks in time from the initial crystallization of magmatic substance up to the formation of mineral assemblages is justified by the carried out theoretical research, and the thermodynamic conditions are described by appropriate chemical reactions. On the basis of comparisons of phase interrelations and the obtained calculated material, some features of the evolution of parameters are established for the regressive metamorphism.

The conditions for the evaluation of the thermodynamic parameters obtained by using mineralogical geothermobarometers and by the date from the calculations serve as a basis for revealing of mineral facies of metamorphic and metasomatic processes of rocks of the investigated massif. The established orientation of metasomatism in near ore-bearing garnet-biotite rocks, reflected in P-T-t trends, a mineralogical of data modeling, testifies to local warming under corresponding rise of pressure in the natural system and a consequent drop of these parameters.

### WATER CONTENT IN DEEP SUBDUCTED CRUST: EVIDENCE FROM HYDRATED CLINOPYROXENE AND GARNET IN UHP METAMORPHIC ROCKS

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Input of water into the earth's interior is restricted to subduction zones. However, the subducted oceanic crusts are dehydrated in shallow depth, and then transformed to dry eclogite containing no hydrous minerals at temperatures over 700°C and pressures over 30 kbar. It is therefore believed that subducted crusts cannot carry significant water into deeper mantle. Recent studies reported that trace amounts of hydroxyl can be contained in nominally anhydrous minerals (e.g., Bell and Rossman, 1992). Trace water in these minerals is capable of recycling into the earth's interior at subduction zones. In order to evaluate how much water is transported into the upper mantle at deep subduction zones, we investigated the hydroxyl contents of clinopyroxenes and garnets in ultrahigh-pressure (UHP) metamorphic rocks in Kokchetav massif, which has been subducted to more than 150 km depth. As a result of infrared spectroscopic study, clinopyroxene and garnet in the eclogites contain hydroxyl up to 3020 ppm and 290 ppm, respectively. The hydroxyl absorbances increase with recrystallized pressure in both clinopyroxene and garnet. In clinopyroxene, the hydroxyl content correlates with increase of the CaEscola component, which contain vacancy on the M2 site. Same relation was reported from mantle xenoliths in Roverts Victor kimberlite pipe (Smyth et al., 1991). Because clinopyroxene and garnet represent about 40-50 volume% and 35-50 volume%, respectively, of eclogites, the bulk eclogites can contain approximately 1400 ppm hydroxyl, whereas these rocks do not contain any nominally hydrous minerals. Thus, subducted oceanic crust can carry H<sub>2</sub>O into the upper mantle, even in the absence of nominally hydrous minerals, and has an important bearing on physico-chemical properties of mantle dynamics.

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### CARBON SOLUBILITY IN OLIVINE

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The mass of carbon stored in the Earth's mantle probably far exceeds the combined total amount of carbon in the atmosphere, hydrosphere and sediments. However, quantifying the carbon storage capacity of the mantle is nearly impossible because data on carbon solubility in major mantle minerals are lacking. Previous attempts to measure carbon solubility in olivine proved unsuccessful because of serious experimental and analytical problems (e.g. Tingle et al., 1988).

We have carried out a series of experiments in which olivine was crystallized from a stoichiometric starting mixture of oxides in the presence of a sodium carbonate melt. Experiments were carried out at 1200°C and 10 to 35 kbar. The experiments yielded inclusion-free, clear and euhedral olivine crystals up to several 100 micrometers in size. To facilitate the unambiguous detection of dissolved carbon in these crystals, the sodium carbonate melt was enriched to contain 99 percent of the isotope 13-C.

Measurements of blank standards using a Cameca ims 6f ion probe always yielded significant amounts of 13-C due to the presence of vacuum contaminants. However, measurements of the carbon-saturated olivine samples yielded a clearly detectable signal of excess 13-C corresponding to carbon dissolved in the olivine. Some preliminary calibrations using carbon-containing glasses suggest a carbon solubility in olivine in the order of 5 to 10 ppm by weight under the conditions studied. Ongoing work will rely on reference single crystals which have been ion implanted by known doses of 13-C.

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### GRAIN SIZE DISTRIBUTION AND MICROSTRUCTURES OF GRANITOID CATACLASITES

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Deformation processes at the frictional-viscous transition are important for the understanding of earthquakes and fault mechanisms. Despite numerous field and experimental studies these processes are still poorly understood. Fracturing usually is the dominant deformation processes, but for small grain sizes diffusion creep might be of importance. The aim of this study is to compare the grain size distribution and microstructures of experimentally and naturally deformed granitoid in order to establish the deformation mechanisms.

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Digital images of cut hand specimens and thin sections obtained by optical and electron microscopy were analysed for their grain size distribution. The obtained 2D-radius of grains is recalculated to a 3D-radius. It was tested whether the grain size distribution is log-normal or power law distributed. The microstructures were also studied with light and electron microscopes. Bulk rock and phase composition of the undeformed and cataclastic granitoids were determined with XRF, XRD and EDX.

The grain size distribution for the naturally deformed cataclastic granitoids is similar on all scales of investigation. The range of grain sizes is very large (from centimetre to 0.1 micrometer). The grain size distribution qualitatively shows the same trend as found for experimentally deformed rocks (Marone & Scholz, 1989) and for naturally deformed rocks whose grain size distribution were determined by sieving (Anderson et al., 1983). Microstructural studies of the rocks show intercrystalline and intracrystalline fractures, angular to rounded particles consisting of one or more phases, mostly straight grain boundaries, but also some pressure solution rims and undulatory extinction. Equidimensional grains make up the matrix of the cataclasites. Healed fragments indicate multiple cataclasis within one cataclasite, which is visible by clasts consisting of cataclastically deformed rocks.

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### PHASES FORMATION IN THE SYSTEM WITH CALCIUM, GADOLINIUM, MANGANESE, TITANIUM, AND URANIUM OXIDES: APPLICATION TO RARE EARTH - ACTINIDE WASTE IMMOBILIZATION

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Ceramics within the compositional series  $\text{Ca}_{4-x}\text{Gd}_x\text{Mn}_2\text{Ti}_2\text{O}_{20+x/2}$  ( $X = 0, 1, 2, 3, 4$ ) and a sample with  $\text{Ca}_2\text{U}_2\text{Ti}_7\text{O}_{20}$  formulation were studied as promising matrices for immobilization of rare earth and actinide constituents of high level waste (HLW). The samples were prepared by cold pressing of oxide mixtures in pellets at 200 MPa, followed by their sintering at 1400°C or melting at 1500°C, and examined with X-ray diffraction, scanning and transmission electron microscopy. At  $x=0$  and  $x=1$  a perovskite – pyrophanite assemblage occurred. The sample with  $x=2$  consisted of murataite and perovskite. Murataite was a major phase in the sample with  $x=3$  (pyrochlore and perovskite were minor phases) and the only phase in the sample with  $x=4$  prepared under oxidizing conditions (in air). The latter was composed of two murataite varieties with seven- and five-fold fluorite unit cells. The sample with the same formulation, but synthesized under reducing conditions, contained pyrochlore as an extra phase.  $\text{Ca}^{2+} + \text{U}^{4+}$  ions heterovalent substitution for  $\text{Gd}^{3+}$  ions resulted in formation of pyrochlore as major phase. The ceramic samples corresponding to the compositional series studied are composed of murataite – perovskite and murataite – pyrochlore assemblages. Gadolinium is considered as trivalent rare earths and actinides surrogate. In the first case both phases are hosts for trivalent rare earth and actinides and these HLW

constituents are partitioned among them. In the second case murataite is the host phase for rare earths and actinides (mainly trivalent, including Pu(III), Am(III), and Cm(III)) and corrosion products (manganese, iron, aluminum) whereas pyrochlore is the host phase for rare earths and tetravalent actinides (U(IV), Np(IV), Pu(IV)). This makes the system of calcium, gadolinium, manganese, and titanium oxides prospective for immobilization of rare earth – actinide fraction of HLW.

### TEMPERATURE DEPENDENCY OF Sm, Eu, Gd, AND Ga PARTITIONING BETWEEN CLINOPYROXENE AND GARNET AND ITS POSSIBLE USE AS GEOTHERMOMETER

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During the last years, the techniques of in-situ microanalytical trace element analyses (e.g. ion microprobe or laser ablation ICP-MS) have been improved so that it becomes possible to use trace element partitioning between solid phases as a geothermometer. For this reason, the temperature dependency of Sm, Eu, Gd, and Ga partition coefficients between garnets, clinopyroxenes, and silicate melts ( $D^{\text{cpx/gar}}$ ,  $D^{\text{cpx/l}}$ ,  $D^{\text{gar/l}}$ ) were experimentally investigated using a piston cylinder apparatus. Experiments were conducted at pressures and temperatures ranging from 2 to 3 GPa and 950 to 1100°C, respectively.  $D^{\text{gar/l}}$  values vary in a wider range than  $D^{\text{cpx/l}}$  ones. In terms of the lattice strain model of Blundy & Wood (1994) this is due to the fact that the size of the unstrained lattice site  $r_0$  incorporating the rare earth elements (REE) is more variable in garnet than in clinopyroxene (Klein et al. 2000). That is, the more  $r_0$  is shifted to lower values the more the partition coefficients of a fixed cation decrease. As a result, variations of  $D^{\text{cpx/gar}}$  are mainly controlled by the garnets.  $D^{\text{gar/l}}$  values of the REE are much more sensitive to changing run conditions than those of Ga. This is also supported by the observation that strongly zoned garnets are homogeneous with respect to Ga and it can be explained by the fact that the ionic radius of Ga is very close to  $r_0$  of the lattice site in octahedral coordination in garnets and clinopyroxenes. The results reveal a negative, linear correlation between the reciprocal temperature and  $\ln D^{\text{cpx/gar}}$  at fixed pressure and an increase of  $D^{\text{cpx/gar}}$  with decreasing pressure at constant temperature. Sm partitioning shows the strongest change with temperature and pressure.

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Klein M, Stosch HG & Shimizu N, *Geochim. Cosmochim. Acta*, **64**, 99-115

# EMPG IX

## Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

### THE GARNET-SPINEL TRANSITION IN THE SYSTEM $\text{MgO-Cr}_2\text{O}_3\text{-SiO}_2$

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The transition from spinel lherzolite to garnet lherzolite is one of the most important phase boundaries in the Earth's upper mantle. For example, our understanding of the generation of mid-ocean ridge basalts requires a sound understanding of the position of the garnet-spinel transition as a function of pressure, temperature and composition.

The garnet-spinel transition is well understood in simple (e.g.  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ , c.f. Klemme and O'Neill, 2000a) and complex systems in fertile compositions (see e.g. Robinson and Wood, 1998), but there is scant information about the transition in refractory compositions. Moreover, rigorous thermodynamic modeling of spinel-garnet reactions in the upper mantle over a range of temperatures, pressures and compositions requires reliable thermodynamic data for Cr-bearing minerals such as Cr-spinels, Cr-bearing pyroxenes and Cr-bearing garnets, the latter of which are, unfortunately, rather unconstrained. The present study aims to fill this gap.

The simplest reaction describing the transition from spinel lherzolite to garnet lherzolite may be written as follows



However, the present study experimentally investigates the analogue reaction to (1) in an Al-free, but Cr-rich system, i.e.



Reversal experiments on reaction (2) were performed in a multi-anvil apparatus at pressures between 4.5 GPa and 11 GPa and at temperatures between 1200°C and 1600°C. The starting material contained all four phases that were synthesized prior to the commencement of the study. Analysis of run products with X-ray diffraction and electron microprobe showed which phase assemblage grew and which was consumed.

Whilst the garnet spinel transition in Cr-free (reaction 1) and in fertile compositions is known to have a positive Clapeyron slope (e.g. Klemme and O'Neill, 2000a, Robinson and Wood 1998), experimental results on reaction (2) seem to indicate a negative slope in pressure-temperature space at considerably higher pressures. Thermodynamic evaluation of our experimental results enable calculation of thermodynamic properties of khorringite garnets and, in conjunction with data for Cr-spinels and Cr-bearing pyroxenes (Klemme et al. 2000, Klemme and O'Neill 2000b), calculations of phase equilibria in Cr-rich compositions.

Klemme S & O'Neill HStC, *Contrib. Mineral. Petrol.*, **138**, 237-248, (2000).

Klemme S & O'Neill HStC, *Contrib. Mineral. Petrol.*, **140**, 84-98, (2000).

Klemme S, O'Neill HStC, Schnelle W & Gmelin E, *Am. Mineral.*, **85**, 1686-1693, (2000).

Robinson JAC & Wood BJ, *Earth Planet. Sci. Lett.*, **164**, 277-284, (1998).

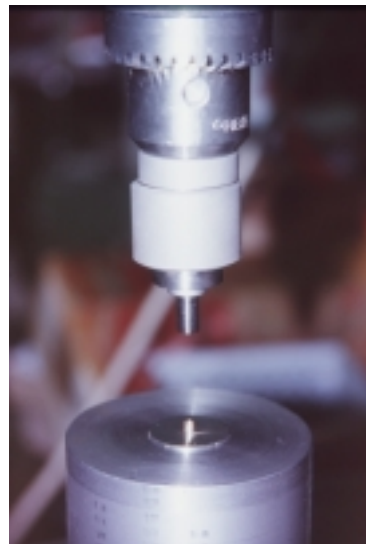
### ORBITAL HEADFORMING: A COLD FORMING PROCESS TO SEAL SAMPLE CAPSULES

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Orbital headforming is a non-impact and vibration-free cold forming process, which is widely used in industrial production. This technology can be advantageously used for sealing precious metal sample capsules for high pressure experiments. Due to the high heat input, conventional arc welding technique suffers from a high fault rate, especially if large fluid amounts should be sealed. Headforming is a cold forming process, which seals malleable metal cylinders of any size certainly and fast. The sample capsules closed in this way can be used in any kind of high pressure experiment, i.e. piston cylinder, cold seal vessel, internally heated vessel or multi anvils. Orbital headforming can be used as an alternative to conventional hammering, crimping, welding and other closing operation. Industrial orbital assembly systems are highly developed units, which are too expensive for laboratory purpose in most cases.

I present a simpler design: the capsule-closing-system (CCS) has all features of the orbital process, but runs on a simple workshop drilling machine. CCS consists of a capsule fixture and three form tools for each desired capsule diameter. The form tools are mounted off-center in a revolving chuck. The chuck and the drilling machine can be used for all desired diameters. The first tool forms the cylindrical capsule container conically without closing the capsule yet. The second tool has a flatter inner shape and seals the capsule. Finally, the third tool produces a planar surface. The capsule fixture allows a vertical adjustment of the capsule during the entire process. We run by routine gold capsules of 4 and 6 mm outer diameter, respectively. Each sealing takes about 5 minutes at a fault rate of practically zero, even if large fluid amounts are encountered. Depending on the pre-existing equipment, CCS is available from 1415 EURO up. For further information contact [www.geolab.de](http://www.geolab.de).



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### STABILITY OF SPINELLOID PHASES IN THE SYSTEM $Mg_2SiO_4$ - $Fe_2SiO_4$ - $Fe_3O_4$ UNDER UPPER MANTLE AND TRANSITION ZONE CONDITIONS

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Experiments were conducted at 4-14 GPa and 1100-1200°C in the  $Mg_2SiO_4$ - $Fe_2SiO_4$ - $Fe_3O_4$  ternary system. Mixtures of olivine<sub>ss</sub> + magnetite were used as starting materials, with olivine having  $X_{fay} = 0.1, 0.3, 0.5, 0.8$  or  $0.9$ . Particular attention was paid to the presence or absence of spinelloid III, since this polytype is isostructural with  $Mg_2SiO_4$ -wadsleyite.

Spinelloids II, III, and V are stable within the ternary system. In general the addition of Mg shifts the spinelloid stability fields towards higher pressures compared to the Mg-free system (Woodland & Angel, 2000). Spinelloid II is the first intermediate phase to appear at low pressures (~3 GPa) in Mg-poor compositions, with olivine<sub>ss</sub>+spinel<sub>ss</sub> stable in more Mg-rich compositions (e.g.  $X_{fay} \approx 0.5$  in olivine). With increasing pressure, spinelloid V effectively replaces spinelloid II between 6.5 and 7 GPa. Spinelloid III can coexist with either spinelloid II or V depending on pressure and contains less  $Fe_3O_4$  than either II or V (up to 0.94 cpfu). The most Mg-rich spinelloid synthesised to date contains 0.56 cpfu Mg and has the spinelloid V structure, which is stable up to 9 GPa. This indicates that the stabilities of the spinelloid phases are limited to the  $Fe^{2+}$ -rich half of the ternary system. In experiments with high Mg, olivine<sub>ss</sub> always coexists with a  $Fe^{3+}$ -rich spinel<sub>ss</sub>.

Magnetite-rich spinel can incorporate significant amounts of Si and Mg when coexisting with the spinelloids. However, coexistence with olivine<sub>ss</sub> in Mg-rich compositions causes a shift in the spinel composition to include a Mg-ferrite component (Si < Mg). Thus this system is pseudo-ternary since Mg substitution can be decoupled from Si in spinel. Phase relations in Mg-rich bulk compositions suggest that, in the absence of garnet and cpx, introducing even a small amount of  $Fe^{3+}$  into a depleted mantle composition could stabilize a  $Fe^{3+}$ -rich spinel coexisting with olivine.

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### HIGH-PRESSURE IR-SPECTRA AND THE THERMODYNAMIC PROPERTIES OF CHLORITOID

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Using IR radiation from a synchrotron source, high-quality absorbance spectra were obtained from polycrystalline powder of chloritoid (cld) from ambient conditions up to pressures of 10 GPa over 50 to 4000  $cm^{-1}$ . The idealized chemical composition of the chloritoid group is  $M_2Al_4O_2(SiO_4)_2(OH)_4$  where M = Fe or Mg in our experiments. All of the 42 expected fundamental IR modes were observed. These data, combined with the response of the IR bands to substitutions of Fe for Mg, and of D for H, constrained the band assignments. Heat capacity ( $C_p$ ) and entropy ( $S_o$ ) for the triclinic and monoclinic polymorphs of Fe- and Mg-cld were calculated from Kieffer-type model, using our detailed band assignments. The calculated heat capacity and entropy for the monoclinic and triclinic polymorphs differ negligibly. The results at temperatures of above 298 K are described by the following polynomial expressions in J/mol-K:  $C_p = 7.835 \cdot 10^2 - 5.170 \cdot 10^3 T^{-0.5} - 1.648 \cdot 10^7 T^{-2} + 1.934 \cdot 10^9 T^{-3}$  for Mg-cld and  $C_p = 7.848 \cdot 10^2 - 5.185 \cdot 10^3 T^{-0.5} - 1.548 \cdot 10^7 T^{-2} + 1.783 \cdot 10^9 T^{-3}$  for Fe-cld. At room temperature,  $S_o = 293$  J/mol-K for Mg-cld and 335 J/mol-K for Fe-cld. These values differ somewhat from entropy estimated from various internally consistent data bases (-3 - -9% for Mg-cld and -9 - +5% for Fe-cld). However, using our new  $S_o$  and  $C_p$  values in conjunction with the enthalpy of formation,  $H_f = -7101$  kJ/mol for Mg-cld or  $H_f = -6422$  kJ/mol for Fe-cld (estimated in this study), we can closely reproduce the experimental data for the reactions Mg-chloritoid + talc = clinocllore + kyanite (Chopin, 1985) and Fe-chloritoid = almandine + diaspore + water (Vidal et al., 1994).

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Vidal O, Theye T & Chopin C, *Contrib. Min. Pet.*, **118**, 256-270, (1994).

### PETROGENESIS OF OCEANIC PLAGIOGRANITES BASED ON NEW EXPERIMENTAL DATA OF HYDROUS THOLEIITIC SYSTEMS

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Evolved rocks composed of quartz diorites, tonalites, trondhjemites, so-called plagiogranites exist in the recent oceanic crust and are also present in the plutonic sections of most ophiolites. For their genesis at mid-ocean spreading systems, two models are under discussion: (1) Late-stage differentiation of a MORB-type melt (e.g., Dixon-Spulber and Rutherford, 1983) and (2) partial melting of pre-existing gabbros within high-

temperature shear zones (e.g., Flagler and Spray, 1991). In this study, we have applied recent experimental data of the experimental lab in Hannover to the plagiogranite petrogenesis in order to test both models. The role of water during the genesis of these rocks (presence of amphibole as mafic phase in many natural plagiogranites) was assessed by including water to the systems. Crystallization experiments were performed in a MORB system doped with different water contents at different redox conditions at 200 MPa (Berndt et al., submitted), and hydrous partial melting experiments were performed at 200 MPa on typical oceanic gabbros. For the experiments we have used an internally heated pressure vessel for high temperatures (up to 1250°C) equipped with a rapid-quench system and a hydrogen membrane for controlling the oxygen fugacity. Liquid lines of descent obtained via crystallization experiments are mainly controlled by oxygen fugacity and only to a little extent by water activity. SiO<sub>2</sub>-rich residual melts can be obtained under both oxidizing and reducing redox condition, but at least one fractionation step is required to reach plagiogranitic (in the narrower sense) residual melt compositions (SiO<sub>2</sub> > 70 wt%; Na<sub>2</sub>O = 4 wt%; K<sub>2</sub>O = 1 wt%). The experimental obtained liquid lines of descent are compared with differentiation trends of natural plagiogranitic suites. The results of partial melting experiments show that the process of re-melting of oceanic gabbros is ineffective in generation of SiO<sub>2</sub>-rich liquids.

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Dixon-Spulber S & Rutherford MJ, *Journal of Petrology*, **24**, 1-25, (1983).

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### AN EXPERIMENTAL STUDY ON THE INFLUENCE OF WATER AND OXYGEN FUGACITY ON THE DIFFERENTIATION OF A FERROBASALTIC SYSTEM (SKAERGAARD PARENTAL LIQUID): EXPERIMENTAL OUTLINE AND FIRST RESULTS

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The ferrogabbroic layered intrusion of Skaergaard/Greenland is one of the most impressive and best investigated rock suites on Earth. One of the proposed compositions of the parental liquid of the intrusion ("SC1") was used as starting material for extensive experimental studies under "dry" condition at 1 atm both in a system open (Toplis and Carroll, 1995) and close to oxygen (Lattard and Partzsch, 2001). The present study investigates the role of water under controlled oxygen fugacities on the phase relations and phase compositions in the same system. Thus, experiments with "SC1" under dry and hydrous conditions will result in an unique, system-consistent data set, well suited for testing quantitatively our ideas and models how the extensive parameters T, P, water activity, and oxygen fugacity will influence the differentiation of ferrobaltic systems. The crystallization experiments are performed at a pressure of 200 Mpa in an internally heated pressure vessel equipped with a rapid quench system. To control the oxygen fugacity, this apparatus is equipped with a Shaw membrane made of Pt for high temperatures enabling the accurate determination of the hydrogen fugacity prevailing in the vessels. Within the sample

capsule the oxygen fugacity is fixed due to the in-diffusion of hydrogen and the water equilibrium ( $H_2 + 0.5 O_2 = H_2O$ ). Therefore, oxygen fugacity is dependent of water activity in runs with water activity < 1, and the exact oxygen fugacity can be determined only after the experiment (after calculation of the prevailing water activity). To minimize the Fe-loss by diffusion into the capsule material, Au<sub>80</sub>Pd<sub>20</sub> pre-saturated in iron is used for the experiments. First results are presented.

Lattard D & Partzsch GM, *Eur. J. Mineral.*, **13**, 467-478, (2001).  
Toplis MJ & Carroll MR, *J. Petrol.*, **36**, 1137-1170, (1995).

### IN-SITU X-RAY STUDY OF (Mg,Fe)O UNDER HIGH PRESSURE AND TEMPERATURE

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Magnesiowustite, (Mg,Fe)O, is one of the major minerals in the earth's lower mantle. The decomposition of ringwoodite and the possible further transition to oxide mixtures (Saxena et al., 1996) would produce oxides in the deep mantle. The stable phases and physical properties of magnesiowustite at the lowermost mantle condition are still debated and important to investigate the dynamics and structure of the core-mantle boundary. The high pressure behaviors of FeO and MgO are quite different in both crystal structure (Fei & Mao, 1994) and electronic structure (Knittle & Jeanloz, 1986). Recently, the decomposition of (Mg,Fe)O was reported (Dubrovinsky et al., 2000). However, the phase boundary and its dependence on composition are unknown. In order to clarify these problems, we performed high pressure experiments using a diamond anvil cell with both external heating and laser heating using multi-mode Nd:YAG laser. Starting materials were synthetic (Mg<sub>x</sub>Fe<sub>1-x</sub>)O (X=0, 0.1, 0.2, 0.4, 0.6). In situ X-ray diffraction experiments under high pressure and high temperature were made at Photon Factory (BL-13B2 and BL-13A) in KEK, Tsukuba. The monochromatized X-ray with energy of about 30 KeV was collimated to 30 micron square beam. The diffracted X-ray was detected using an imaging plate. Rhombohedral distortions probably due to a magnetic transition were observed for all compositions, but the initiation pressure of the distortion has a positive dependency on the Mg composition. No further phase change or decomposition was observed up to about 100 GPa and about 800 K by external heating for (Mg<sub>0.1</sub>Fe<sub>0.9</sub>)O and (Mg<sub>0.2</sub>Fe<sub>0.8</sub>)O. However, B1 phase was observed at higher temperature condition about above 1500 K using laser heating for (Mg<sub>0.1</sub>Fe<sub>0.9</sub>)O. We have also observed B1 phase above the stability field of B8(NiAs) phase in FeO. These results indicate that the stable phase of (Mg,Fe)O have B1 structure in the lowermost mantle condition.

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Fei, Y. & Mao, H.K., *Science*, **266**, 1678-1680, (1994).

Knittle, E & Jeanloz, R, *Geophys. Res. Lett.*, **13**, 1541-1544, (1986).

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Dubrovinsky, L.S., Dubrovinskaia, N.A., Saxena, S.K., Annersten, H., *Science*, **289**, 430-432, (2000).

### EXPERIMENTAL INVESTIGATIONS ON THE ROLE OF PARTIAL MELTING DURING THE FORMATION OF HIGH-P/HIGH-T GRANULITES

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High-P/high-T granulites are a prominent rock type in the Moldanubian Zone of the Variscan Orogen in Lower Austria. These rocks are thought to have formed in a Carboniferous subduction setting at 950 - 1050°C and 15 - 19 kbar from mainly granitoid protoliths [1 and refs. therein]. During subsequent rapid exhumation, the original peak P-T assemblage garnet + ternary feldspar + quartz  $\pm$  kyanite  $\pm$  clinopyroxene was variably retrogressed. One important question with considerable petrological implications concerns the role of partial melting during the formation of the South Bohemian high-P/high-T granulites [2]. In order to place further constraints on this particular problem, piston cylinder experiments were conducted in the T-range of 800 - 1000°C and in the P-range of 12 to 16 kbar. The experimental conditions should simulate the metamorphic P-T path of these granulites, with peak conditions of 1000°C, 16 kbar and the subsequent stage of nearly isothermal compression (950°C, 14 kbar and 900°C, 12 kbar). In addition, experiments at 800°C, 12 kbar and 850°C, 16 kbar were performed to investigate the upper T-limit of biotite stability. We used a natural felsic granite gneiss as starting material with the assemblage plagioclase + K-feldspar + biotite + sillimanite + quartz which is geochemically similar to the main granulite type in South Bohemia. The experiments in the temperature range of 900 - 1000°C all yielded the assemblage garnet + ternary feldspar + quartz + melt  $\pm$  kyanite. Biotite is only stable in the experiment at 800°C and 12 kbar. The amount of melt in the 1000°C, 16 kbar experiment is approximately 20 volume% and decreases with temperature. The obtained melt is strongly peraluminous granitic in composition. Garnets are almandine-pyrope solid solutions but show unusually high Ti contents of approx. 1 - 2 wt% TiO<sub>2</sub>. Ternary feldspars are close to ab<sub>40</sub>or<sub>50</sub>an<sub>10</sub>. The high Ti-contents found in the experimental garnets is consistent with the presence of rutile exsolutions in some granulite garnets.

O'Brien PJ, Carswell DA, *Geol.Rundschau*, **82**, 531-555, (1993).  
Roberts MP, Finger F, *Geology*, **4**, 319-322, (1997).

### EXPERIMENTAL INVESTIGATIONS ON THE FORMATION OF PHOSPHORAN OLIVINE IN PARTIALLY MOLTEN GNEISSES FROM A PREHISTORIC SACRIFICIAL PLACE, TYROL, AUSTRIA

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Natural olivine with significant P<sub>2</sub> contents (>1 wt.%) is extremely rare and only known from very low fO<sub>2</sub> environments (Agrell 1998). P- and Fe-rich olivine, however, may be present in slags and is known from prehistoric to medieval smelting operations (Heimann et al., 1998). In this study we describe an occurrence of unusually P-rich olivine with up to 9 wt% P<sub>2</sub>O<sub>5</sub> from partially molten metapelitic gneisses recovered from a presumably La-Tène (450-15 B.C.) age sacrificial place in the Ötz Valley, Northern Tyrol, Austria, where ritual immolation of animal offerings took place. Thus, apatite from animal bones is the likely source of phosphorus. To place constraints on the conditions of olivine formation, 1 bar melting experiments were conducted in the temperature range 900-1300°C under oxidizing (Pt-crucible) and reducing (C-crucible) conditions. The investigated gneiss samples were collected from the immediate vicinity of the firing site and have a protolith assemblage biotite + plagioclase + K-feldspar + quartz. During partial melting, foamy patches of glass containing an assemblage olivine  $\pm$  clinopyroxene + witlockite + plagioclase formed at the surface of the rocks. In an attempt to reproduce the observed assemblages and textures, bone material was sandwiched between small slabs of gneiss. Under reducing conditions, melting starts around 900°C with the formation of small patches of eutectic melt. Complete breakdown of biotite with concomitant formation of olivine + witlockite + Ti-magnetite + K-rich melt was observed in experiments at 1000°C. At 1100°C clinopyroxene may be present as additional phase with large fractions of melt. Above 1200°C the observed assemblage is whitlockite + Ti-magnetite + quartz + melt. Significant amounts of P in olivine in the range 0.3 - 1.2 wt% P<sub>2</sub>O<sub>5</sub> were observed at 1100°C but only in the immediate vicinity of the bone layer. This confirms the supposed olivine formation mechanism of incongruent melting of biotite under reducing conditions in the presence of organic apatite and also indicates strong disequilibrium P-partitioning between olivine and melt.

Agrell SO, Charnley NR, Chinner GA, *Mineral.Mag.*, **62**, 265-269, (1998).

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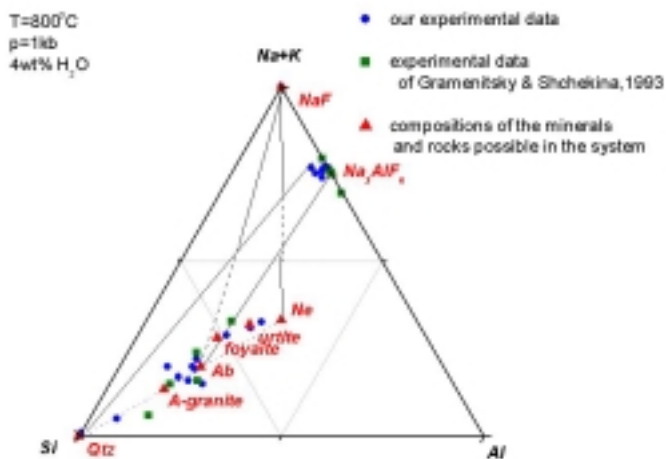
### EXPERIMENTAL INVESTIGATION OF THE MELT PHASE RELATIONS IN THE SYSTEM Na-Al-Si-O-F-H<sub>2</sub>O AT 800°C AND 1 kb

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Phase equilibrium relations have been experimentally obtained in the system Na-Al-Si-O-F-H<sub>2</sub>O at 1 kb, 800°C and water contents of 4 and 7 wt%. All experiments were performed in the Tuttle cold-seal pressure vessels inside of sealed platinum capsules. Start materials were supersaturated with the fluorine to attain the aluminosilicate and salt melts two phases equilibrium under experimental condition. The experiments were quenched and the runs products were analyzed by X-ray and Electron Microprobe Analysis. The amount of the fluorine in the aluminosilicate glass in the equilibrium with salt phase was accepted as the maximum solubility of the fluorine in the melt under experimental conditions. In the experimental products the salt melts is represented by globules, which have cryolite (Na<sub>3</sub>AlF<sub>6</sub>) or villiaumite (NaF) compositions. It is shown the nepheline-normative aluminosilicate melt coexists with villiaumite salt melt and the quartz-normative aluminosilicate melt coexists with cryolite one. In the space of (Na-Al-Si)<sub>x,y</sub>-(O-F)<sub>z</sub> triangular prism cryolite-aluminosilicate melt connods dispose over villiaumite-aluminosilicate melt ones (Figure 1).



Aluminosilicate melt in the equilibrium with two salt melts has near albite-normative composition. The solubility of the fluorine in the aluminosilicate melt is dependent on the contents of the water and silica in the system. In the nepheline-normative glass the fluorine content is about 0,5 at% in the system with 4 wt% H<sub>2</sub>O while it is about 3 at% in the system with 7 wt% H<sub>2</sub>O. The solubility of the fluorine in the aluminosilicate glasses increases gradually as the silica content is increased. In quartz-normative glasses of near-haplogranite composition fluorine contents is about 1,5 at% in the system with 4 wt% H<sub>2</sub>O and about 4,5 at% in the system with 7 wt% H<sub>2</sub>O. In extreme cases of near-silica composition of the glass the fluorine content peaks at about 6 and 14 at% in the systems with 4 and 7 wt% H<sub>2</sub>O respectively. Obtained phase relations are correlated well with the geological observational data. Cryolite is found only in the association with granitic rocks: Ivigtut (Greenland), Pitinga (Brasil), East Siberia (Russia) while villi-

aumite is only seen in the association with nepheline syenite: Lovoserskii and Khibinskii massives (Russia), Illimausak (Greenland). This work is supported by grants RFFI #00-15-98504, #01-05-64530, #01-05-64512.

### THE MECHANISMS OF FLUID MIGRATION IN LOW-PERMEABILITY ROCKS

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Rocks undergoing subduction and prograde metamorphism are subject to devolatilization reactions, fluid escape and associated compaction. High-grade metamorphic rocks are generally left with no free fluid phase or a disconnected pore space, and are impermeable to fluid flow. Fluid infiltration into such rocks during uplift and retrogressive metamorphism generally requires permeability generating mechanisms in order to reconnect the existing inclusion space or create new pore space by some deformation-related dilation process. On a large scale, the introduction of external fluids requires the presence of high-permeability channels like fractures resulted from the external stress. However, extensive interaction between the externally derived fluids and fractured rocks requires efficient mass transport away from the initial fracture into the adjacent rocks. This often occurs over distances much longer than expected from grain boundary diffusion. Here we present examples of 2 fundamentally different fluid migration mechanisms, constrained from field observations, microtextural studies and electron microprobe data. The importance of grain boundary dilation and hydrofracturing during the infiltration of non-wetting fluid is illustrated by an example of hydrated mantle-derived peridotites at the Almklovdalen, Western Gneiss Region, Norway.

Fluid migration facilitated by dilation connected to the PδV terms of overstepped metamorphic reactions is demonstrated by an example of serpentinization of a troctolite from the Duluth complex, Minnesota, USA. Results from numerical modelling of extensional microcracks in plagioclase formed due to volume change and "pressure generation" during the serpentinization of the adjacent olivine are presented.

### THE NEW LASER TIME-OF-FLIGHT MASS-SPECTROMETER FOR ANALYSIS OF GEOSAMPLE

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The new laser time-of-flight mass-spectrometer for panoramic isotopic analysis of elements in solids and powder samples (conductors, dielectrics, biological and mineralogy objects) is represented. The time of the analysis is about 10-15 minutes, an error of measurements less than 0.1%. The sensibility of is 3\*10<sup>-7</sup> %, range of mass is 1-400 a.m.u. The size of device (555\*550\*885 mm) and weight (100 kg) allow to analyze objects immediately without special preparing samples. The

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ion source uses Nd:YAG laser operating with 1064 mkm wavelength. The parameters of laser irradiation are following: 10-20 mJ pulse energy, 7 nsec pulse duration,  $(1-2) \cdot 10^9$  Wt/cm<sup>2</sup> irradiation power, 10-50 Hz pulse repetition frequency. Light optics allows laser beam to be focused into 50-70 mkm spot. Ion optics provides effective ion extraction from laser plasma, ion focusing and formation of nano-second ion packet duration. The electrostatic analyser is made in the form of cylindrical condenser. Inner and outer analyser electrodes radiuses equal 80 mm and 120 mm correspondingly. Height of analyser equals 180 mm. The special diaphragm (energy window) is installed within the analyser to decrease noise level. As a result it permits both to decrease noise level and to decrease duration of ion clouds at entrance of the detector. A new detector is used in the instrument. In fact one incorporated a couple of SEM. Each SEM is used for detecting ion packets having different intensities. Analog signals from every SEM after amplifying is digitised by a couple of 100 MHz 10 bit ADC also operation as single ADC with digital performans step of 5 ns. Both double channel mode and single channel mode can be used in the instrument. Data acquisition, accumulation and mass spectra processing is automated and carried out with the help of a Pentium-120 computer. Friendly user interface provides comfortable working condition in Windows environment. For improving accuracy of measurements authors propose to account multiply-charged ions of elements. It was introduced correction factor for avoiding discrimination of ions deferent masses. This factor includes potential of ionisation and cross-section. This innovation enables essentially to lower error.

#### THE FORMATION OF K-RICH LAVAS AND ULTRABASIC NODULES OF VOLCANO VESUVIUS ACCORDING TO THE PARAGENETIC ANALYSIS AND SOME EXPERIMENTAL DATA

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The Somma-Vesuvius volcanic complex, located east of Naples in southern Italy, is a part of Thyrreinan volcanic province. It is characterized by association of silica undersaturated and potassium rich rocks. Through plinian eruptions different nodules with pyroclastic material are carried out. In this work we consider tephrites, basanites and ultrabasic nodules, which consist of olivine, clinopyroxene, phlogopite and titanian magnetite. During study of morphological features and chemical compositions of minerals, composing products of volcanic activity of Vesuvius (ultrabasic inclusions, tephrites, basanites) some parageneses of minerals were revealed. In nodules the next parageneses were studied: olivine + clinopyroxene + shpinel; clinopyroxene + phlogopite + titanian magnetite; clinopyroxene + phlogopite + titaniferous magnetite + apatite. In lavas - olivine + clinopyroxene + titaniferous magnetite; clinopyroxene + leucite + plagioclase + titaniferous magnetite; olivine + clinopyroxene + leucite + plagioclase + titaniferous magnetite. The evolution of mineral compositions and the cause of a variety of parageneses in volcanic products were determined. The occurrence of phlogopite and leucite in volcanic products proves the magmatic evolution extended with the potassium accumulation. The content of calcium increasing in pyroxenes from the ultrabasic nodules and the constant content of calcium in pyroxenes from lavas proves the calcium enrichment of magma. According to the Korzhinsky's

theory, the activity of one basic component increasing in magma promote the activity of another basic component. We explain such evolution by the magma assimilation of crustal components, which consists of dolomites and mica shales. Our data adjust with results of determination of <sup>87</sup>Sr/<sup>86</sup>Sr ratio and other isotopic characteristics. Presence of phlogopite in nodules and leucite in lavas suggests different fluid and pressure conditions of the rock formation. It is also confirms by the results of experimental study of fluid and melt inclusions in the minerals of nodules and lavas of Vesuvius.

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#### SULPHATE-BEARING SODALITE STABILITY UNDER HYDROTHERMAL CONDITIONS AND T-X DIAGRAM OF Cl- SODALITE – NOSEAN SOLID SOLUTIONS

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Sulphur and chlorine play an important part in mineral forming fluid. Sodalites are the minerals which formation closely connected with the fluid conditions. The dependence of Cl-sodalite stability on concentration of NaCl in the fluid and temperature was studied earlier. The experiments on study of dependence of sulphate sodalite (nosean) formation on the fluid composition and temperature were desired at 600-800°C and P=2 kbar. The gel mixtures of nepheline and water solutions of Na<sub>2</sub>SO<sub>4</sub> were used as the start materials. The "large ampoule" method was used for the control of the salt concentration. On the experimental results the nosean is stable relatively nepheline at importance less concentrations of salt then Cl-sodalite. The phase diagram of Cl-sodalite – nosean system was constructed on data of the synthesis of these solid solution at the temperature 300-800°C and P=1-3 kbar. Starting material was a gel of nepheline. The composition of the sodalite solid solutions was set by a ratio (NaCl/Na<sub>2</sub>SO<sub>4</sub>) in an initial solution. The existing of wide immiscibility gap at the temperature 300-750°C for solid solutions of the (Cl,SO<sub>4</sub>-) bearing sodalites was shown. Solvus of this solid solution is nonsymmetric: at 700°C the sulphate mineral contains up to 24 mol.% of the Cl-sodalite, the chloride mineral of sodalite contains only 7 mol.% of sulphate one. The sulphur distribution between sodalite and fluid was studied at the same conditions. On the basis of the experimental data the analytical dependence for calculation of the sulphur mole fraction in mineral-forming solutions and for temperature determination using the compositions of the coexisting sodalite phases was derived. On this basis the estimation of temperatures and regime of fluids for the sodalite nepheline syenites of Lovozersky alkaline massif were conducted. *The work was supported by the RFBR grant 00-05-64680.*

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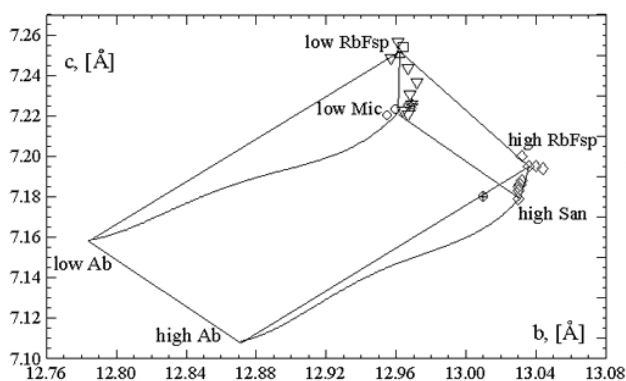
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### THE B - C DIAGRAM OF TERNARY (Na,K,Rb)- FELDSPAR SOLID SOLUTIONS

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Ten samples of order and disorder (K,Rb)- feldspars were synthesized by the method of hydrothermal recrystallization of gel mixtures and cation-exchange of natural feldspars with molten salts. The cell parameters were refined for triclinic (Rb-microcline) and monoclinic (Rb-sanidine) series. Smith (1974) proposed the diagram in coordinates of the cell parameters b and c for determination of degree of ordering of binary (Na,K)-feldspars. In the present work the similar diagram sets up for ternary (Na,K,Rb)- feldspars based on the cell parameters of synthetic (Na,K)- feldspars (Kroll et al., 1986), Rb-microcline (Pentlinghaus & Henderson, 1979), Rb-sanidine, synthesized in the present research. The compositional dependences of the cell parameters b and c of the (Na,K)- feldspars describes by the third degree expressions (Kroll et al., 1986). The compositional dependences of these parameters for order (McMillan et al., 1980) and disorder (results of the present work) (K,Rb)-feldspars are linear. The expressions of b - c parameters for other solid solutions were accepted linear. The cell parameters of different Rb- bearing alkaline feldspars are plotted on the diagram. The data on Rb- bearing microcline by present research are close to results of McMillan et al. (1980). The parameters of natural Rb- containing microclines from Red Cross Lake pegmatite (Canada), Černý et al. (1985), are similar to the results of McMillan et al. (1980) for synthetic samples and data of the present work on natural Rb- bearing microclines from massif Orlovskiy (Zabaykalye, Russia). The natural Rb-microcline (rubicline) from San Piero in Campo (Elba, Italy) (Teertstra et al., 1998) by the cell parameters gets in area of disorder (Na,K,Rb)- feldspars. The computer program was created for degree of ordering estimation of Rb- containing alkaline feldspars using composition and cell parameters data. *The work was supported by the Junior grant of RAS # 329.*



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### AN IN-SITU X-RAY DIFFRACTION STUDY OF KINETICS OF THE POST-GARNET TRANSFORMATION

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The subducted oceanic lithosphere is mainly composed of basaltic crust and the underlying peridotite layer, in which garnet and silicate spinel are the major constituent minerals, respectively, at the depth of 500-600 km. As the slab descends into the lower mantle, garnet and spinel decompose to perovskite plus aluminous phase (post-garnet transformation) and perovskite plus ferro-periclase (post-spinel transformation), respectively. Metastability and changes of microstructures in these transformations under subduction zone conditions greatly affect on dynamics of the slab in the deep mantle. In order to clarify kinetics of these transformations, we performed high-pressure and high-temperature *in-situ* X-ray diffraction experiments combined with microstructural observations of the recovered sample. Here we report results on the post-garnet transformation kinetics of pyrope.

*in-situ* X-ray diffraction experiments were carried out using sintered-diamond multi-anvil apparatus "MAX-III" installed at KEK-PF, Japan. Two pyrope garnets with different chemical compositions were used as the starting material. One is synthetic polycrystalline pyrope  $Mg_3Al_2Si_3O_{12}$ , and another is natural polycrystalline pyrope with a composition of  $(Mg_{0.72}Fe_{0.17}Ca_{0.11})_3Al_2Si_3O_{12}$ . We observed kinetics of the post-garnet transformation at 27.0-31.0 GPa and 1273-1553 K. Time-resolved X-ray diffraction profiles of the sample were taken every 10-500 seconds during the transformation.

Dissociated post-garnet assemblages do not show the lamellar growth as observed in the post-spinel assemblages (e.g., Kubo et al., 2000), which suggests that the growth requires long-range diffusion. Obtained kinetic data indicates that the growth rate is time-dependent and significantly decreases with time contrary to the post-spinel transformation (Kubo et al., 2002). Consequently, the growth in the post-garnet transformation is much slower than that in the post-spinel transformation. Differences in kinetics of these transformations might have important implications for buoyancy of the subducted oceanic crust and formation of the garnetite layer at the top of the lower mantle.

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#### ALUMINUM POSITION IN SYNTHETIC Rb-FELDSPAR AS DETERMINED BY X-RAY PHOTOELECTRON SPECTROSCOPY

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Aluminums occupying two kinds of structural sites of synthetic Rb-feldspars have been detected by Al 2 p X-ray photoelectron spectra. Chemical compositions and properties of the synthetic Rb-feldspars were characterized using classical methods: electron microprobe analysis, X-ray powder diffraction analysis and Fourier transform infrared microspectroscopy. Resultantly small amounts of H<sub>2</sub>O molecule and of excess Si and Al have been detected for all single crystals of the Rb-feldspars. Moreover the quantities of excess-Al are on average 0.044 apfu and negatively correlated with those of Rb. Inasmuch as this negative correlation suggests the presence of excess-Al occupying non-tetrahedral sites of the feldspar structures, incorporation of the “Al(Al<sub>3</sub>Si)O<sub>8</sub> molecule” into the Rb-feldspars has led to presentation of appropriate endmembers for the unusual chemical compositions. Thus the representative EPMA allow the present Rb-feldspar to be identified as the non-stoichiometric feldspar with excess of Si and Al, resulting in a unit formula of (Rb<sub>0.831</sub> Al<sub>0.125</sub> Al<sub>0.044</sub>) Al<sub>0.963</sub> Si<sub>3.037</sub> O<sub>8</sub>, where the site is occupied by H<sub>2</sub>O molecule. In order to confirm excess-Al occupying the extra-framework sites of the feldspar structure, the effect of Al-Si ordering on Al 2 p X-ray photoelectron spectra of feldspars has been examined, using a monochromatized AlK $\alpha$  X-ray source, in comparison with the Rb-feldspars and several feldspar minerals. Al 2 p XPS signals of the Rb-feldspars reveal appreciably higher energy than any others of feldspars (sanidine, orthoclase, microcline and low albite) and higher one than that of bicchulite [Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>6</sub>(OH)<sub>2</sub>], one of the exceptional minerals for the “aluminum avoidance rule”. Since the present Rb-feldspar is generally similar in Al-Si disordering to sanidine, shift of the Al 2 p X-ray photoelectron spectra toward the higher energy side provides a reasonable explanation for coexistence of the Al at extra-framework sites with the tetrahedral Al-O-Al linkage within the present Rb-feldspar.

#### CRYSTAL CHEMICAL CONTROLS ON RARE-EARTH-ELEMENT PARTITIONING BETWEEN EPIDOTE-GROUP MINERALS AND MELTS

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We have combined structural and physical data for epidote-group minerals (allanite, epidote s.s., clinozoisite and zoisite) with the elastic strain model of Blundy and Wood (1994) in order to qualitatively predict the changes of REE+Y mineral/liquid partitioning pattern with changing crystal structure. In addition, we present the first experimental data for partitioning of REE+Y between zoisite and hydrous silicate melt. Comparison of the predicted partitioning pattern with our new experimental zoisite/melt partitioning data and natural allanite/melt partitioning data suggests that REE+Y are preferentially incorporated into the A2 site of epidote-group minerals and that mineral/melt partitioning patterns are mainly controlled by the size and shape of the A2 site of these minerals. As a result all epidote-group minerals are expected to strongly fractionate the LREE from the HREE in mineral-melt systems. The moderately compatible behaviour of LREE and MREE in zoisite suggests that melts generated in the presence of zoisite are highly LREE and MREE depleted. In contrast, the available data for partitioning of REE between epidote-group minerals and fluids show no or little agreement with predicted REE partitioning pattern and suggest that fluid composition and oxidation state are likely to have a strong effect on the REE partitioning pattern. However, both mineral/melt and mineral/fluid partitioning data reveals that charge balancing mechanisms may exert important controls on absolute D<sub>REE+Y</sub> values for epidote-group minerals. The elastic properties of the allanite and zoisite A2 site, obtained by fitting our new and existing mineral/melt partitioning data for trivalent cations to the elastic strain model of Blundy and Wood (1994), indicate that the bulk elastic properties of epidote-group minerals are dominantly controlled by the large cation sites.

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#### DEFECT MICROSTRUCTURES AS A GENETIC FINGERPRINT OF DIAMONDS

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Diamonds occur in a great variety of natural environments such as ultra-high pressure metamorphic belts, kimberlite pipes, impact craters, and meteorites. These different occurrences of

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diamonds reflect formation by various mechanisms, as diverse as crystallization from melt, vapour condensation, and solid-state transformation. Therefore it seemed possible that the defect microstructures of diamonds provide a fingerprint to their genesis. To test this hypothesis, we have conducted a TEM study on diamonds from the following sources: (i) metamorphic diamonds from Kokchetav and Erzgebirge, (ii) impact diamonds from Ries and Popigai craters, and (iii) kimberlitic diamonds from various pipes. The microstructure of meteoritic diamonds was extensively studied by Dalton et al. (1996).

The metamorphic diamonds observed occur primarily as inclusions in the container mineral garnet. Particularly the diamonds from Erzgebirge are surrounded by other minerals such as intercalated sheet silicates, apatite, anatase, quartz, and plagioclase. The diamonds usually exhibit octahedral faces, occasionally with skeletal morphology. Most importantly, the microstructure of these diamonds is absolutely defect-free. This contrasts with observations on diamonds from all other sources.

Kimberlite diamonds usually contain dislocations, especially in the presence of tiny inclusions which possibly act as dislocation sources during the rapid ascent within a pipe. Impact diamonds are pervaded by numerous twin bands. These bands are inherited from precursor graphite that, prior to transformation, was deformed by shock compression. Presolar diamonds occurring as inclusions in meteorites contain interconnected stacking faults and microtwins (Dalton et al., 1996), which indicates condensation from vapour.

In conclusion, the present microstructural comparison of diamonds from various environments reveals structural and textural characteristics indicative of the geological process that produced them. Detailed TEM studies may thus provide profound insights into the origin of natural diamonds, even if the diamonds occur as loose grains in placer deposits.

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### STABILITY OF PICOILMENITE FROM KIMBERLITE (PHYSICO-CHEMICAL MODEL AND EXPERIMENT)

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Stability of metastable picroilmenite in case of varying P-T parameters and the fluid regime is discussed. Method of physico-chemical modeling of geochemical systems (Karpov et al., 1997) and experimental study of retrogressive metasomatism are used for this purpose. Stability of picroilmenite under equilibrium conditions in the temperature range from 400 to 1000°C and pressure from 1 to 50 kbar was considered. Fluid phase was given by water and carbonic acid in proportion H<sub>2</sub>O/CO<sub>2</sub> -39.08, 3.9 and 2 in amounts from 1.5 to 3-weight%. The modeling of the picroilmenite stability demonstrated its stability in hydrous systems. Decomposition of picroilmenite in the presence of carbonic acid into carbonate-rutile or carbonate-rutile-perovskite (with CaO in the system) associations is noted. Under conditions of higher oxygen fugacity and CO<sub>2</sub> content in fluid phase the picroilmenite serves as a pecu-

liar buffer in conservation of diamond. The range of diamond stability in kimberlite system significantly increases at expense of redox reactions in picroilmenite structure (variation of FeO/Fe<sub>2</sub>O<sub>3</sub> and Mg/Fe ratios) and binding excessive CO<sub>2</sub> into carbonate. Experimentally, chemical zoning expressed in obvious change of its composition from the center of grain to its periphery forms during reaction of substitution of picroilmenite at T=800°C and P= 2000 atm and the fluid of C-O-H system: 1) decrease of TiO<sub>2</sub> and Fe<sup>++</sup>, 2) sharp increase of Fe<sup>+++</sup> oxide and oxides of Al, Mg and Cr. Change of oxygen regime of kelyphitization is following by oxidation from FeO to Fe<sub>2</sub>O<sub>3</sub> which may enter into structure of modified ilmenite or forms its own titanomagnetite phase. The work was supported by the RFBR, grant # 01-05-65269

### OXYGEN FUGACITY BUFFERING WITH CO<sub>2</sub>/H<sub>2</sub> MIXTURES BETWEEN 700° AND 1200°C

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Gas mixing techniques are among the most versatile methods for the control of oxygen fugacity at low pressure. CO<sub>2</sub>/H<sub>2</sub>, CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O mixtures can reliably buffer *f*O<sub>2</sub> above 1200°C, whereas below this temperature deviations from calculated fugacities are frequent. These differences are caused by incomplete equilibration within the gas phase, thermal partitioning of the reactants, inaccuracies in flow and temperature control, differences in experimental conditions, configuration factors, etc.

Performances are strongly influenced by the experimental set-up and discrepancies between individual authors are often due to the lack of standardization: careful calibrations which take in consideration all parameters affecting the fugacity in the T-*f*O<sub>2</sub> regime of interest are crucial to properly control the run conditions in any furnace.

Extended calibration work was carried out on a classical gas-mixing furnace (GMF) and on a High-Temperature Diffraction (HTD) camera which was equipped with a CO<sub>2</sub>/H<sub>2</sub> mixing system in order to do *in-situ* high temperature analysis under controlled atmosphere.

The iron-wüstite buffer was used as calibration couple: for the GMF quenched samples were analyzed by Raman Spectroscopy and XRD, while the HT-diffractometer was calibrated directly monitoring the buffer reaction: in both cases the observed fugacities are more reduced than expected and present the largest deviations at 800°C.

To verify if these results could be extrapolated in a different fugacity range, we calibrated the wüstite-magnetite buffer too: the deviations are comparable in the HTD but significantly larger in the GMF.

The effects of flow reduction and of the presence of platinum as catalyst were evaluated, both to investigate the crossed influence of slow kinetics and thermal segregation, and to try to minimize the deviations: the kinetic problem is predominant and the catalytic solution is especially effective in the GMF.

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For the furnace set-up, the influence of the use of a sample container was tested. Interestingly, the atmosphere within a crucible is significantly more oxidized than in the free gas stream and therefore gets closer to the thermodynamically expected one.

### TOWARDS A THERMODYNAMIC DATABASE FOR PHOSPHATE MINERALS: ELASTIC PROPERTIES OF MG-PHOSPHATES AND PHASE RELATIONS IN THE SYSTEM $MgO-Al_2O_3-P_2O_5-SiO_2-H_2O$

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Although less common in nature than other phosphates like apatite, Mg-phosphates are useful petrological indicators owing to their numerous polymorphic relations. Despite the wide range of other applications (in the cement and fertilizer industry, in medicine), very few thermodynamic data are available, even in as simple a system as  $MgO-P_2O_5-H_2O$ : calorimetric data exist only for farringtonite ( $Mg_3(PO_4)_2$ ), a low-pressure anhydrous Mg-phosphate (Oetting and McDonald, 1963). On the other hand, the phase relations between farringtonite and its high-pressure polymorph Mg-sarcopside, and between the  $Mg_2PO_4OH$  polymorphs ( $\epsilon$ - $Mg_2PO_4OH$ , holtedahlite, althausite and hydroxywagnerite) as well as the stability field of phosphoellenbergerite ( $(Mg_{1-x}, [X]_x)_2Mg_{12}P_8O_{38}H_{8+4x}$ , x about 0.1) have already been experimentally studied (Brunet et al., 1998). However, because of the lack of sufficient 'anchor' phases with well-defined thermodynamic properties, no thermodynamic data could be extracted for Mg-phosphates in the system  $MgO-P_2O_5-H_2O$ .

Through consideration of silica or alumina as additional components, we were able to study two reactions involving three known solid phases and a single 'unknown' phosphate: the reaction P-ellenbergerite + quartz = Mg-sarcopside + talc +  $H_2O$  has been bracketed between 575 and 600°C near 9 kbar and between 18 and 20 kbar at 775°C, and althausite + corundum = Mg-sarcopside + spinel +  $H_2O$  between 800 and 820°C near 9 kbar. Combined and tested for compatibility with existing phase-equilibrium data, they allow extraction of thermodynamic properties for most Mg-phosphates. Actually, a more rigorous treatment requires consideration of elastic properties. Therefore, compressibilities and thermal expansions of wagnerite, farringtonite, Mg-sarcopside and P-ellenbergerite were determined up to 55 kbar, 900°C using a multi-anvil apparatus at the HASYLAB-DESY synchrotron facility (Hamburg).

Extension of this system to additional components involving well-characterised mineral phases like apatite -  $Ca_5(PO_4)_3OH$ , berlinite -  $AlPO_4$ , or lazulite -  $MgAl_2(PO_4)_2(OH)_2$  (Schmid-Beurmann & Brunet, this meeting) provides us with a thermodynamic database, allowing the calculation of phase relations for most phosphates in metamorphic rocks.

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### THE T- $X_{ps}$ DEPENDENCY OF THE ISOSYMMETRIC DISPLACIVE PHASE TRANSITION IN SYNTHETIC $Fe^{3+}$ -Al ZOISITE: A POWDER X-RAY DIFFRACTION AND TEMPERATURE DEPENDENT INFRARED SPECTROSCOPY STUDY

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Rietveld refinements based on powder X-ray diffraction patterns of synthetic  $Fe^{3+}$ -Al zoisite [ $Ca_xAl_2Al_{1-x}Fe^{3+}_xSi_3O_{11}(O/OH)$ ] in the compositional range of 0.0 - 0.14  $X_{ps}$  [ $X_{ps} = Fe^{3+}/(Fe^{3+}+Al-2)$ ] yield two zoisite modifications (I and II) with the following lattice parameters: zoisite I:  $a$  [Å] =  $-3.72 \cdot 10^{-2} X_{ps} + 16.1913$ ;  $b$  [Å] =  $6.43 \cdot 10^{-2} X_{ps} + 5.5488$ ;  $c$  [Å] =  $3.43 \cdot 10^{-2} X_{ps} + 10.0320$ ;  $V$  [Å<sup>3</sup>] =  $11.4 \cdot X_{ps} + 901.3$ , and zoisite II:  $a$  [Å] =  $-8.26 \cdot 10^{-2} X_{ps} + 16.2061$ ;  $b$  [Å] =  $8.14 \cdot 10^{-2} X_{ps} + 5.5486$ ;  $c$  [Å] =  $1.18 \cdot 10^{-1} X_{ps} + 10.0263$ ;  $V$  [Å<sup>3</sup>] =  $19.3 \cdot X_{ps} + 901.6$ . The lattice parameters show discontinuities at  $X_{ps} = 0.05$  between zoisite I and II. The Rietveld refinements suggest that the phase transition between zoisite I and II is isosymmetric and displacive. The dependency of this phase transition on temperature and composition has been determined by temperature dependent infrared spectroscopy. Spectra were recorded in 20°C-steps in the temperature interval -170 to 250°C. Because the zoisite II structure is more flexible than the zoisite I structure, the positions of the IR-bands display a stronger temperature dependency of zoisite II than of zoisite I and the transition from zoisite I to II is mirrored by discontinuities in band-position in response to temperature. These discontinuities between zoisite I and II are best displayed by the OH-band at approx. 3150  $cm^{-1}$  and by two bands at approx. 909 and 950  $cm^{-1}$ . The data indicate that zoisite II is the high temperature form and that the critical temperature of the phase transition is negatively correlated with the iron content in zoisite according to the equation  $T_c = 65 - 900 \cdot X_{ps}$  [°C], with  $\Delta T_c = \pm 35^\circ C$ .

### MELTING OF PERIDOTITE UNDER LOWER MANTLE CONDITIONS

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Peridotite phase relations and mineral-melt partitioning along the mantle solidus are required in order to understand the earliest differentiation of the Earth's mantle, which may have occurred during the crystallization of a magma ocean. In this study melting experiments are being performed on synthetic mantle peridotite doped with a selection of 21 trace elements to determine melting temperatures and partitioning relations between crystals and melt at conditions applicable to the lower mantle. Melting experiments are being performed in the 22-28 GPa pressure range in a multi-anvil apparatus using 10/4 and 7/3 (octahedral edge length/anvil truncation length in mm) pressure cell configurations with  $LaCrO_3$  heaters and axially inserted WRe thermocouples. The phases are analyzed by scan-

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ning electron microscopy and electron microprobe. Several peridotite compositions with differing degrees of fertility have been examined.

We have performed experimental runs in both Re and graphite capsules to investigate the influence of oxygen fugacity on the phase relations of minerals such as magnesiowüstite, perovskite and garnet, which can dissolve significant amounts of ferric iron. Experiments performed in Re capsules and in graphite, (which imposes a lower  $fO_2$  than Re), yielded different coexisting phases under identical subsolidus conditions of 23 GPa and 2200°C. Garnet, magnesiowüstite and magnesium silicate perovskite were observed in the Re capsule whereas no evidence was found for perovskite in the graphite capsule which has transformed to diamond during the run. This implies that there may be a perovskite stabilizing effect resulting from higher  $fO_2$ .

### STRUCTURAL CHANGES IN CALCINED $NH_4$ -CHABAZITE

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The hydrogen form of natural chabazite obtained through deammoniation of  $NH_4$ -chabazite at calcination up to 400°C is characterized by acid catalytic properties (Beyer et al., 1977). To investigate the overall structure persistence during formation of H-chabazite the samples of  $NH_4$ -exchanged natural chabazite  $Ca_{1.63}Na_{0.16}K_{0.12}[Al_{3.77}Si_{8.26}O_{24}]12.75H_2O$  (Khilok River, Transbaikalia) calcined under vacuum shallow-bed conditions at 100°, 250°, and 400°C and rehydrated in air were studied by X-ray diffractometry and IR spectroscopy. The intensity of X-ray diffraction peaks decreases at 250° when deammoniation starts to proceed, and slight amorphization occurs at 400° when the almost fully protonated structure is formed. The parameters of rhombohedral unit cell slightly decrease at 250°; at 400° the contraction of the unit cell volume achieves 1.8% compared to the initial  $NH_4$ -chabazite. The extent of the volume contraction is comparable with that observed in natural chabazites when passing from medium to high-silica varieties (Passaglia 1975). The changes in the framework IR spectrum are more noticeable compared to structural data. The high-frequency shift of the main framework T-O stretching mode near 1000  $cm^{-1}$  is observed start from early stage of  $NH_3$  removal and achieves 60  $cm^{-1}$  in hydrogen chabazite. The frequency of this mode is known to be proportional to the fraction of Si-O bonds (Si/Al ratio) in the zeolite framework (Pichat et al., 1975). Thus we may suppose that the Si/Al ratio in the chabazite framework increases during calcination of its  $NH_4$ -form, in agreement with our X-ray diffraction data. The dealumination of the framework may result, analogously to observations in other zeolites, from partial hydrolysis of the framework aluminum by residual water and protons formed after removal of ammonia (Weeks et al., 1975; Shannon et al., 1985). If so, the amount of catalytically active hydroxyl groups produced at deammoniation is likely to be less than that expected from an "ideal" structure of hydrogen chabazite.

Further high-resolution <sup>27</sup>Al NMR study will permit to analyze the extent of dealumination and the nature of non-framework Al species formed at calcination of  $NH_4$ -chabazite.

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### HEAT CAPACITIES AND DERIVED THERMODYNAMIC PROPERTIES OF GLASSES AND LIQUIDS IN THE SYSTEM $Na_2O-B_2O_3-SiO_2$

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The wide range of applications of borosilicates, from laboratory glassware to nuclear waste disposal is well established. Yet, comparatively few studies have been done on the thermochemical properties of this system. However, these measurements are badly needed to determine entropies of melts, and especially to understand the relative importance of the contributions to the entropy stemming from thermal vibrations and temperature-induced structural changes. The heat capacities ( $C_p$ ) of four sodium borosilicate glasses have been measured from 15 K to the temperature of the glass transition using an adiabatic calorimeter, a differential scanning calorimeter and an ice calorimeter using the drop method. Results shows that there exist deviations of  $C_p$  from an ideal-solution model with oxides as component in the system  $Na_2O-B_2O_3-SiO_2$ . This nonideality may be related to B-coordination differences between pure  $B_2O_3$ , where boron is essentially three coordinated by oxygen atoms, and investigated glasses, where boron is distribute in various species ( $BO_4$ ,  $BO_{3A}$ ,  $BO_{3S}$ ); on the other hand, these deviations could be also associated with peculiar interactions between B and Si. Results allowed to determine the partial molar heat capacities of boron and sodium oxides in the silica-rich part of this system in the glass state. Drop calorimetry has been used to measure the  $C_p$  of the liquids in this system. At the glass transition, the  $C_p$  of liquids is from 18 to 30% higher than that of glasses. The  $C_p$  of sodium borosilicate liquids has a markedly non-linear composition dependence and shows negative temperature dependences. These anomalous variations could be associated with peculiar interactions between B and Si. Implications to the derived entropy and configurational properties will be discussed.

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### PHASE RELATIONS OF HYDROUS MID-OCEAN RIDGE BASALT WITH IMPLICATIONS FOR LOWER MANTLE MINERALOGY

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Subduction of oceanic lithosphere into the deep Earth's interior is supposed to create chemical heterogeneity in the lower mantle. It was found recently, that anhydrous basalt have different melting temperature and density changes with depth relative to peridotite (Hirose et al., 1999). Study of water-bearing basalt might be also important for identification of possible hydrous phases in the basaltic composition, changes in phase transitions, and seismic anomalies. Phase relations in the hydrous MORB were determined at 18-25 GPa and temperature range between 1000 and 2400°C. There were no dense hydrous phases, which are stable in the MORB at 18-25 GPa. We observed the expansion of stability field of Al-rich perovskite and NAL-phase (Miura et al., 2000; Mijajima et al., 2001) to the lower pressures. Al-rich perovskite was observed below 1400°C at 25 GPa, whereas in anhydrous experiments it is stable above 27 GPa at 1400°C. NAL-phase occasionally stable at 20-25 GPa and temperature below 1200°C. At the higher temperature, NAL-phase is replacing by CAS-phase. We have supposed influence of water on stability field of the perovskite and provided additional experiments on water solubility in Al-rich perovskite in the Fe-bearing and Fe-free systems. FTIR data suggest that Al-perovskite can contain about 100-200 ppm H<sub>2</sub>O. In the MORB composition, lawsonite and phengite are stable up to 12-13 GPa under slab conditions (Schmidt and Poli, 1998). At the higher pressure, distribution of water to the MORB components is very restricted. Trace amount of water can be stored in garnet, stishovite (Bolfan-Casanova et al., 2000), and perovskite. Therefore, MORB cannot be considered as important water carrier to the lower mantle. We ascertain that water in the MORB can evaluate local variations in the density anomalies at the top of the lower mantle.

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### DIAMOND GENESIS: EXPERIMENTAL SOLUTION

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Disclosing the chemical conditions of diamond formation in the Earth's mantle is the key to solution of the problem of diamond genesis. Based on mineralogical evidence, it is suggested that the primary fluid (Schrauder & Navon, 1994) or sulphide (Bulanova, 1995) inclusions in diamonds from

kimberlite deposits may be alternatively considered as parental growth media. Successful experimental programs on diamond syntheses in multicomponent carbonate - silicate - carbon (Litvin & Zharikov, 2000) and sulphide - carbon (Litvin et al., 2002) systems properly accounting for the natural fluid and sulphide prototypes are realized.

Diamond synthesis at 5.5 - 8.5 GPa in carbonate - silicate ("fluid") and sulphide melts oversaturated with dissolved carbon is the direct evidence of the high efficiency of both the natural parental media for diamond formation. The experimental carbonate - silicate melts similar to the natural ones belong to the multicomponent system K<sub>2</sub>O - Na<sub>2</sub>O - CaO - MgO - FeO - Al<sub>2</sub>O<sub>3</sub> - TiO<sub>2</sub> - P<sub>2</sub>O<sub>5</sub> - SiO<sub>2</sub> - Cl - CO<sub>2</sub> - H<sub>2</sub>O - C. The experimental sulphide - carbon melts much like to the natural ones belong to the system Cu - Fe - Ni - S - C. In either case, physicochemical mechanism of diamond formation is conceptually identical and controlled by PTN - diagram of carbon oversaturation for the relevant system (N = dissolved carbon concentration in melt). Diamond formation in the carbonate - silicate (carbonatite) and sulphide solvents is characterized by multitude spontaneous nucleation. Numerous octahedron - shaped crystals, spinel - law twins, and oriented crystalline aggregates are formed. Crystal morphological and physical properties of the carbonatite - synthetic and sulphide - synthetic diamonds show their similarity to natural diamonds.

Thus, existence of two types of natural diamond - producing media in the Earth's mantle conditions is experimentally established and agrees with mineralogical data for syngenetic inclusions in natural diamonds. It seems reasonable to say that the bulk of natural diamonds was crystallized rather in silicate - rich carbonatite melts with dissolved carbon than in sulphide ones. Nevertheless, the true chemistry of the parental media for natural diamonds can result from specialized mineralogical tests.

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### Cr<sub>2</sub>O<sub>3</sub>: THE UNFORGETTABLE BUT FORGOTTEN OXIDE IN MANTLE PARTIAL MELTING PROCESS

**Xi Liu & Hugh H.StC. O'Neill**

Chromium is a highly compatible element and its importance to melting phase relations may not be obvious from the study of the melts themselves. Therefore, direct partial melting experiments are highly desirable. No any systematic work, however, has been done and chromium has been forgotten.

To investigate the chromium effect on mantle partial melting, piston-cylinder experiments have been carried out at 11 kbar in the model mantle system CMAS-Cr<sub>2</sub>O<sub>3</sub>. Previous experiments using traditional experimental technique were not successful due to some special chemical behaviours of this model mantle system: 1) Chromium has variable valance states and oxygen fugacity is critical to the experiments; 2) Partial melting along the solidus in the spinel peridotite stability field is isobarically

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pseudo-invariant; 3) Melt composition becomes increasingly picritic and quench crystallisation more serious with increasing Cr/(Cr+Al) ratio.

In order to circumvent these problems, we used some new experimental techniques and took new experimental rationale to carry on the study. Recent experiments are successful and suggest that: 1) Chromium dramatically changes the compositions of the pyroxenes, the major contributors to the mantle melting process. 2) Chromium raises the solidus of system CMASCr. The solidus increases are not linear with the Cr/(Cr+Al) ratio in the bulk compositions but are very strong at low Cr/(Cr+Al) ratios, very weak at median Cr/(Cr+Al) ratios and very strong again at high Cr/(Cr+Al) ratios. 3) Partial melting reaction in system CMASCr is totally different and spinel joins forsterite to be in a reaction relation with melt. 4) A wide range of melt composition is observed. As the Cr/(Cr+Al) ratio in the bulk composition increases, melt becomes less An-normative but more En-normative

### ACCURATE DETERMINATION OF THE SOLIDUS OF SIMPLIFIED SPINEL LHERZOLITE IN THE SYSTEM CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) AT 11 KBAR: TRADITIONAL AND NEW EXPERIMENTAL TECHNIQUES

**Xi Liu & Hugh H.StC. O'Neill**

The solidus of simplified spinel lherzolite in system CMAS at 11 kbar were determined by traditional forward partial melting experiments (TE), sandwiched K<sub>2</sub>O-doping forward partial melting experiments (SKE) and reversal experiments (RE). All experiments indicate the solidus is 1320°C, 30 degrees lower than the literature data (Presnall et al., 1979).

The TE bracketed the solidus between 1300°C and 1310°C. Considering the water influence, we believe the solidus would be higher.

The SKE took new experimental techniques. In these experiments, a glass layer of melt composition was put between two layers of crystalline mixture. The composition of the glass came from Walter & Presnall (1994) and 1%, 3% or 10% K<sub>2</sub>O was added in. In system CMAS, melt coexists with Fo+Sp+Opx+Cpx only at one single temperature at any specific pressure. The introduction of K<sub>2</sub>O split the temperature point into a temperature interval and the assemblage of Fo+Sp+Opx+Cpx+Melt was achieved. In order to overcome the water problem, outside buffer Fe<sub>2</sub>O<sub>3</sub> was exploited. The K<sub>2</sub>O content of the melts in those experiments displaying Fo+Sp+Opx+Cpx+Melt was extrapolated back to 0 K<sub>2</sub>O and the solidus, 1319°C, was reached. Following the same principle, the glass composition at the solidus was derived from the collected phase composition data of those experiments.

The RE demonstrated that the melt composition derived from the SKE is indeed multiply saturated by Fo, Sp, Opx and Cpx and the solidus is around 1320°C.

The data collected in the SKE are combined with some literature data to generate an empirical geothermometer.

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### THERMODYNAMICS AND CRYSTAL CHEMISTRY OF Al SUBSTITUTED HEMATITE AND GOETHITE

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Synthetic samples of goethite-diaspore (FeOOH-AlOOH) and hematite-corundum (Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>) solid solutions were investigated using high-temperature oxide-melt calorimetry and Rietveld refinement of X-ray diffraction powder patterns. The mixing enthalpies are positive (~10 kJ/mol at X<sub>Al</sub> = 0.2) and of comparable magnitude, when normalized per one cation. The equilibrium solubility of corundum in hematite and diaspore in goethite at 298 K is negligible. The enthalpies of mixing in the hematite-corundum solid solution series show no temperature dependence between 298 and 1000 K. The excess enthalpies of mixing are too large to reproduce the experimental phase diagram (Muan and Gee 1956), unless excess entropies in the solid solution are considered. The thermodynamics of variable ordering schemes of composition FeAlO<sub>3</sub> was explored by static lattice energy calculations, using program GULP (Gale 1997). The calculations, in qualitative agreement with the calorimetric results, show that the disordered (corundum-like) configuration is highest in energy. Ordered (ilmenite- and LiNbO<sub>3</sub>-like) configurations are somewhat more stable in terms of energy but they lack the configurational entropy, and therefore are not observed in the system. The excess volume of mixing is positive for Al-hematite but almost ideal for Fe-corundum. Moreover, the degree of deviation from Vegard's law for Al-hematite depends on the thermal history of the samples. Introduction of Al into the hematite structure causes varying distortion of the hexagonal network of oxygen ions while the position of the metal ions remains intact. Distortion of the hexagonal network of oxygen ions attains a minimum at a composition Fe<sub>0.95</sub>Al<sub>0.05</sub>O<sub>3</sub>. The excess volume of mixing in the goethite-diaspore solid solution is positive. The observed degree of Al substitution in natural goethite and hematite is probably controlled by nucleation pathways and slow kinetics of transformation to the stable phase assemblage rather than thermodynamic properties of the solid solutions.

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### ZIRCONOLITE: EXPERIMENTS ON THE STABILITY IN HYDROTHERMAL FLUIDS

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As a principal host for actinides and certain fission products (e.g., REEs (rare earth elements)), zirconolite is a major constituent of Synroc. Hydrothermal experiments were carried out with various fluids over a range of temperatures at 50 MPa to study the corrosion behavior of zirconolite. Experiments were performed in a closed system with single-phase, polycrystalline zirconolite-2 M, doped with REEs, Hf and U as actinide analogues and/or neutron absorbers.

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Results show that zirconolite is not corroded at temperatures below 250°C, but revealed various degrees of alteration at higher temperatures. In acidic environments (HCl, H<sub>3</sub>PO<sub>4</sub>), corrosion is weak up to 500°C, but more pronounced above that temperature, and various TiO<sub>2</sub> phases, including rutile and anatase, are observed as alteration products. In a basic environment (NaOH), on the other hand, zirconolite shows increasing degrees of corrosion up to 500°C. At this temperature, zirconolite breaks down to perovskite and calzirtite. At a higher pressure (200 MPa), the breakdown products are perovskite and baddeleyite [1].

All data indicate that the corrosion and formation of secondary phases is strongly dependent on time, temperature, pressure and ionic strength and composition of the fluid. Although our results obtained by electron microscopy document zirconolite breakdown in certain environments they provide clear evidence for retention of most of the actinide analogues and neutron poisons by the breakdown phases and their fractionation. However, these phases thus act as secondary waste form. These data are essential for the assessment of the long-term behavior of zirconolite-based nuclear waste forms in final repositories.

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### MOVING BEYOND THE PRESSURE AND TEMPERATURE LIMITS OF COMMON HYDROTHERMAL DIAMOND ANVIL CELLS

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Hydrothermal diamond anvil cells (HDACs), and especially the Bassett-type cell (Shen et al., 1992), are today's most powerful tools for in situ high-pressure research on fluids. However, the hydrothermal design restricts their use to generally less than approx. 22 kbar and 1000°C. Even near these maximum conditions experiments are difficult. One major problem is the use of three independent screws to adjust anvil positions, such that relative tilting of the opposing anvils is difficult to avoid. Thus pressure distribution on the gaskets is inhomogeneous, leading to their deformation and movement. To counteract this, most users predeform the gasket to harden the material and ensure a sealed sample chamber. However, it becomes difficult to optimize the gasket thickness for specific pressures.

To overcome these limitations, we have developed a new type of HDAC based on a hollow single-screw structure, i.e. two threaded opposing platen enclosing the diamond anvils on adjustable seats between them. After the usual adjustment and loading of the sample volume, the cell is pressurized by screwing the upper and lower platen together, ensuring precisely uniaxial pressures and avoiding inhomogeneous gasket flow. Gaskets can now be ground to defined thicknesses optimized to the pressures to be reached (e.g. 70 µm for pres-

ures up to 45 kbar at 850°C). In addition, a new buffering mechanism compensates for thermal expansion, avoiding rapid increase of effective pressure on the gaskets at high temperatures. With the new HDAC technology we have studied wollastonite solubility rates in H<sub>2</sub>O up to 45 kbar, crossing the wollastonite I - wollastonite II transition. Similarly, we have investigated the solubility rate of SiO<sub>2</sub> up to 40 kbar, crossing the quartz-coesite transition. In both cases the solubility rate is lower for the higher-pressure phase. Interestingly, coesite grows from independent nuclei whereas wollastonite II nucleates in and grows from the wollastonite I crystal. In contrast to low pressures, wollastonite dissolves congruently at pressures over 8 kbar.

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### DECOMPRESSION EXPERIMENTS AS AN INSIGHT INTO ASCENT RATES OF SILICIC MAGMAS

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We performed decompression experiments in order to simulate the ascent of silicic magmas within a volcanic conduit. The main processes occurring during magma ascent are volatile degassing and crystallization of microlites, which characteristics and kinetics are crucial for the understanding of the diversity of eruptive styles (i.e., plinian versus pelean) observed for island arc volcanoes. The experiments were performed in hydrothermal cold-seal pressure vessels equipped with a rapid-quench device at 860°C, NNO+1, H<sub>2</sub>O-saturation, and pressures ranging from 150 to 1700 bars. The starting material was a synthetic glass powder representing the rhyolitic composition of the interstitial glass of the Soufriere Hills andesite, Montserrat. Isobaric experiments (duration of 7 days) provided the phase assemblage, composition, volume proportion, size distribution, and number density, as well as the melt H<sub>2</sub>O content (or solubility) in equilibrium. Two sets of decompression experiments were realized, a) from 1500 to 500 bars within 15 days to 6 seconds, referred to as the plinian decompressions and b) from 500 to 150 bars within 1 month to 15 seconds referred to as the pelean decompressions. The results suggest that complete degassing is achieved within decompression durations >1 min. However, for decompression rates >1000 bar/min that may only prevail during plinian eruptions, the degassing process is incomplete. Comparing the phase assemblage (titano-magnetite, plagioclase, orthopyroxene, melt) and composition at equilibrium with the minerals in the decompression charges highlights nucleation time-lags and incomplete chemical re-equilibrations to the final pressures. The investigation of the crystal size distributions and number densities reveals that the dominant crystallization process upon decompression is characterized by growth of existing crystals

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during the plinian decompressions, whereas nucleation of new minerals is the favoured crystallization process during the pelean decompressions.

#### THE SYSTEMS $\text{PbO-Al}_2\text{O}_3\text{-SiO}_2$ (PAS) AND $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ EXTENDED TO $\text{PbO}$ AND $\text{Cr}_2\text{O}_3$ (PMASCr) AT 1 ATM: INVESTIGATIONS ON PHASE RELATIONS AND POSSIBLE APPLICATIONS TO THE MATERIAL SCIENCES

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Although Pb has been an important commodity, not only as alloy but also as mineral (silicate) in the glass industry, little petrological information is available on silicate systems in the presence of Pb. Investigation in these systems may of interest in the field of material sciences and for facing environmental problems involving heavy metal pollution. We started the study of phase relations in the systems  $\text{PbO-Al}_2\text{O}_3\text{-SiO}_2$  (PAS) and  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  extended to  $\text{PbO}$  and  $\text{Cr}_2\text{O}_3$  (PMASCr) at 1 atm, in open conditions and between 950° and 1350°C. Phases were characterized by means of XRPD and electron microprobe. Outside the Pb-rich portion (glass production), the PAS system is virtually unknown: after Pb-feldspar synthesis, charges with compositions lying along the Pb-feldspar-mullite join were run to start exploring the Al-rich portion of the system (where the fluxing effect of Pb is less striking), and to start defining the stability field of Pb-feldspar. In the PMASCr system we investigated the fluxing effect of Pb on a typical system widely employed in igneous petrology of mafic rocks and in the production of ceramic refractories. At the same experimental conditions as above, we ran charges with bulk compositions corresponding to the association of Pb-feldspar and spinel with variable Cr:Al ratio. We studied phase relations and Cr, Al and Pb partitioning in associations dominated by Pb-feldspar plus Cr-rich spinel and eskolaite-corundum s.s. in subsolidus conditions, and dominated by Cr-rich phases (spinel, eskolaite) and Cr-poor Pb-rich glass in case of crystallization from liquid. The study of such systems may have interesting applications for planning inertization and, possibly, recycling of highly toxic, heavy metal-bearing industrial wastes. The choice of (a) Pb and Cr, and (b) feldspar and spinel structures is related, respectively, to composition of real wastes, and to the strong resistance to leaching shown by the relevant structures.

#### STRUCTURAL CHANGE OF WATER WITH SOLUTES AND TEMPERATURE UP TO 100°C IN AQUEOUS SOLUTIONS AS REVEALED BY ATR-IR SPECTROSCOPY

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In order to study structural changes of water in the presence of several solutes together with its change with temperature up to 100°C, the ATR-IR spectra of aqueous solutions were measured by using a newly developed heatable ATR cell. Pure  $\text{H}_2\text{O}$ ,  $\text{NaCl}$  and carbonate solutions were used as representative geofluids.

The O-H stretching bands showed systematic changes with increasing solute concentrations. ATR-IR difference spectra from pure water indicated the increase or decrease of different band components with varying hydrogen bond distances. By using 4 Gaussian components at around 3550, 3400, 3230 and 3080  $\text{cm}^{-1}$  the OH bands can well be reproduced. The water structure can therefore be represented by 4 different water clusters having different mean hydrogen bond distances. The relative intensities of these 4 components vary systematically with concentration of dissolved species in aqueous solutions at room temperature.

From the spectra of  $\text{NaCl}$  solutions, the water clusters are considered to be de-polymerized by the insertion of  $\text{Na}^+$  and  $\text{Cl}^-$ . On the other hand, for the carbonate solutions, the water clusters are considered to be polymerized by the insertion of carbonate anion.  $\text{NaCl}$  solutions show less polymeric so that "softer" natures, while carbonate solutions present more polymeric so that "harder" ones.

By measuring IR spectra of these aqueous solutions in a heated ATR cell,  $\text{Na}_2\text{CO}_3$  1 M solution conserves above polymeric "hard" nature up to 100°C. On the other hand, less polymeric "soft" nature of  $\text{NaCl}$  solutions becomes attenuated at higher temperatures because of the de-polymerization of pure water itself.

These in-situ observations on aqueous solutions are generally in agreement with the wetting characteristics of  $\text{NaCl}$ -rich and  $\text{CO}_2$ -rich fluids and provide physicochemical bases for evaluating real natures of fluids in the earth.

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### MELTING EQUILIBRIA OF THE $\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{K}_2\text{Ca}(\text{CO}_3)_2$ SYSTEM MODELING A SOURCE COMPOSITION OF CARBONATE - SILICATE DIAMOND - BEARING ROCKS OF KOKCHETAV MASSIFF (P = 7 GPa)

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Experimental studies of melting relations of the system diopside  $\text{CaMgSi}_2\text{O}_6$  - pyrope  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  -  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  were carried out at 7 GPa to explore the version that carbonate - silicate diamond - bearing rocks of Kokchetav metamorphic complex have magmatic origin. The rocks are composed of dolomite, clinopyroxene and garnet (Perchuk et al., 1995). The carbonate  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  (=KCC) was used due to the composition is most representative for primary fluid inclusions in natural diamonds (Schrauder & Navon, 1994) and the carbonate melt is effective medium for diamond crystallization (Litvin et al., 1999). The studies of melting equilibria of the system were carried out in the diopside70KCC30 - pyrope70KCC30 join at 7 GPa and the temperature - composition phase diagram is constructed. Clinopyroxene and garnet are the liquidus phases. In the course of melting, homogeneous carbonate - silicate melts are formed. The melts are quenched as phlogopite - forsterite - carbonate intergrowths of dendritic structure. No evidence of the effect of carbonate - silicate liquid immiscibility was recognized. The melting of the system is eutectic and controlled by the pseudoinvariant equilibrium  $\text{Cpx} + \text{Grt} + \text{carbonate} = \text{liquid}$  (1250°C at 7 GPa). Subsolvus assembly is represented by clinopyroxene, grossular - pyrope garnet and carbonates.  $\text{K}_2\text{O}$  content in clinopyroxene is negligibly small in contrast to the similar system diopside - grossular -  $\text{K}_2\text{Mg}(\text{CO}_3)_2$  (=KMC). For the system in the diopside30KMC70 - grossular30KMC70 join,  $\text{K}_2\text{O}$  content in clinopyroxene is more than 4,5 wt.% (Matveev et al., 1998). Diamonds were synthesized with the use of  $(\text{Di}_{25}\text{Py}_{25}\text{KCC}_{50})_{60}$  - graphite<sub>40</sub> mixture at 7 - 8 GPa. It can be seen that the natural diamond - bearing carbonate - silicate assembly is reproducible in high - pressure experiment. This provide new essential grounding in the magmatic version of diamond genesis in Kokchetav - type deposits. Support: grant 01-05-64775 of RFBR.

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### FERROPERICLASE FROM THE LOWER MANTLE: OXYGEN FUGACITY AND DIAMOND GENESIS

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The discovery of diamonds from the lower mantle has raised many questions about their origin and the information they provide regarding the composition, mineralogy and dynamics of the lower mantle. One parameter which has remained elusive is oxygen fugacity, despite its obvious influence on many properties and processes that occur in that region. Previous work has established that a significant proportion of iron in the dominant lower mantle phase, magnesium silicate perovskite, is oxidised, but that this is a consequence of the crystal chemistry of the perovskite structure, and does not reflect conditions of oxygen fugacity. We have therefore focused our attention on ferropericlase, which has been found in abundance in diamonds from the lower mantle. We examined a suite of inclusions from Kankan, Guinea that had already been interpreted on the basis of chemistry and mineralogy to have originated in the lower mantle. Moessbauer spectroscopy was used to determine iron oxidation state, and showed that the relative abundance of ferric iron was consistent with oxygen fugacity conditions higher than iron metal equilibrium. This is supported by previous observations of a ferrite phase within ferropericlase inclusions from Sao Luiz, Brazil. On the basis of the present evidence combined with previous studies of lower mantle diamonds and their inclusions, we suggest that lower mantle diamonds formed near the interface of oxidised subducted oceanic crust and reduced primitive lower mantle.

### HIGH-Ca PRIMITIVE LIQUIDS: PARTIAL MELTS OF CLINOPYROXENE-RICH CUMULATES?

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Primitive CaO-rich melts have been documented in many geodynamic settings including mid-ocean-ridges, back-arc basins, oceanic islands and volcanic arcs (e.g., Schiano et al., 2000, Sigurdsson et al., 2000). The high CaO contents (up to 19wt%) and CaO/Al<sub>2</sub>O<sub>3</sub> ratios (up to 1.7) of these melts cannot be explained by lherzolite melting under anhydrous or hydrous conditions. Lherzolite melting involving CO<sub>2</sub>-rich fluids (Schmidt et al., 2001) produces high-CaO/Al<sub>2</sub>O<sub>3</sub> liquids, however, requires significant amounts of CO<sub>2</sub> and does not reproduce CaO-rich nepheline-normative liquids in arcs.

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High-pressure liquidus experiments were performed on two hypersthene-normative and ne-normative CaO-rich compositions in order to characterize their liquidus phases and P-T conditions of equilibration. For both compositions, saturation with a wherlitic (ol+cpx) assemblage occurs at the liquidus, but orthopyroxene is never a liquidus phase. At first sight, these results suggest that CaO-rich liquids represent primary melts of wehrlites. Equilibration conditions of the two end-members are very different: 1.2 GPa and 1410°C (unrealistic in almost any environment) for the hy-normative high-Ca liquid, 0.3 GPa and 1250°C for the ne-normative one.

For the hy-normative end-member, our results are consistent with Kogiso and Hirschmann (2000) wehrlite melting experiments. The high temperatures needed are problematic as a particularly high mantle potential temperature (e.g. Iceland) would be necessary. Other possibilities are significant amounts of H<sub>2</sub>O or wherlite assimilation by picritic magmas rather than melting. Ne-normative high-CaO liquids have not yet been reproduced experimentally. These liquids occur only in island arcs, thus partial melting experiments were conducted on amphibole-bearing cpx-ol arc cumulates (e.g. Himmelberg & Loney, 1995). Partial melts of such cumulates at 0.5-1.0 GPa are similar to typical high-CaO ne-normative liquids, thus placing their origin in ultramafic cumulates at the basis or within arc crust. Furthermore, the presence of amphibole lowers melting temperatures to more realistic values (e.g. ≤ 1220°C at 5 kbar).

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### EXPERIMENTAL STUDY OF THE KELYPHITIZATION PROCESS OF GARNETS IN KIMBERLITES

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In order to elucidate the mechanism of the kelyphitic rims origin and to refine P-T conditions of their formation we have conducted an experimental study of the kelyphitization of garnets of various composition in synthetic and natural kimberlite matrix in the temperature range from 500 to 800°C and pressure from 500 to 2000 atm involving the fluid of the C-O-H system with various component contents. Comparative analysis of kelyphitic formations obtained after garnets of pyrope series showed that one can form compositionally different kelyphites by varying the composition of enclosed matrix and the fluid regime. It should be noted that kinetics of transformation of mineral phases is determined by the fluid which is in equilibrium with kimberlite matrix. Compositionally different kelyphitic rims from amphibole-pyroxene, amphibole-spinel-forsterite-pyroxene in kimberlite free system in the presence of water; from spinel-forsterite, forsterite-spinel-magnetite with compositionally different synthetic kimberlite to spinel-monticellite-clintonite-periclase

kelyphitic rims formed after garnets in the system with natural monticellitic kimberlite. Size of zones at pressure of 2000 atm and temperature of 800°C for fluid with 95% of H<sub>2</sub>O+2.5% CO<sub>2</sub>+2.5% O<sub>2</sub> and experiment duration of 360 hours is equal to 0.4 mm. Increase of the duration to 720 hours gives its rise up to 0.85 mm. Garnet kelyphitization at temperature below 800°C does not practically take place. Thus, the rim size is 0.01 mm at 700°C and the experiment duration up to 360 hours. Increase of CO<sub>2</sub> up to 50% in the fluid does not give a remarkable change of the obtained mineral phases, it influence only the kinetics of transformation.

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### REVISED THERMODYNAMIC PROPERTIES OF KYANITE, ANDALUSITE AND SILLIMANITE

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We propose a revised set of the thermodynamic properties of the Al<sub>2</sub>SiO<sub>5</sub> polymorphs (kyanite, andalusite, and sillimanite). Our results were obtained by a simultaneous co-processing of the experimental data on the heat capacity in the temperature range from 5 to 1000 K (Robie and Hemingway, 1984; Hemingway et al., 1991; Todd, 1950), relative enthalpy from 400 to 1600 K (Pankratz and Kelley, 1964) and volume at temperature from 289 to 1300 K and at pressures from 0 to 58 kbar (Skinner et al., 1961; Winter and Ghose, 1971; Ralph, 1984; Hemingway et al., 1991; Comodi et al., 1997; Yang et al., 1997; Grevel et al., 1998).

In this study the Mie-Grüneisen equation from Dorogokupets (2000, 2001) was used, in which the thermal part of the free energy was expressed in the Bose-Einstein formalism of Kut'in and Pyadushkin (1998) and an intrinsic anharmonic term. Cold pressure was expressed by the third-order Birch-Murnaghan equation, and the intrinsic anharmonicity parameter was assumed to depend on volume. Generally, the model describes the experimental data extremely well.

Calculated standard entropy for kyanite, andalusite, and sillimanite are equal to 83.19, 92.29 and 95.76 J/(mol K), respectively. Calculated entropy for kyanite and andalusite are higher than the entropy reported by Robie and Hemingway (1984). It was probably resulted from the fact that smooth data for heat capacity (Robie and Hemingway, 1984, Table 4, 5) compared to initial ones (Robie and Hemingway, 1984, Table 1, 2) are lower by 1%.

The thermodynamic functions of kyanite, andalusite, and sillimanite derived in this study do not lead to any essential modifications of the phase diagram Al<sub>2</sub>SiO<sub>5</sub>, however they could influence the thermodynamics of the aluminum silicates which connect with Al<sub>2</sub>SiO<sub>5</sub> polymorphs via phase relations.

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### IN-SITU INVESTIGATION OF CRYSTALLISATION OF STEEL SLAG USING HIGH TEMPERATURE X-RAY DIFFRACTION AND DIFFERENTIAL THERMAL ANALYSIS

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The physical properties of the slag, such as for rocks, are controlled by chemistry and more important by mineralogy. The mineralogy of the slag, however, also strongly depends on the cooling history. Steel slag has an averaged composition of about 45 wt% CaO, 20 wt% FeO, 15 wt% SiO<sub>2</sub> and between 5 and 10 wt% MgO and MnO. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> are present in amounts < 5 wt%. Most abundant mineral phases found in solid slag are magnesio-wuestite ([Fe,Mg]O), lime (CaO), srebrodolskite (Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>), larnite (Ca<sub>2</sub>SiO<sub>4</sub>), hatrurite (Ca<sub>3</sub>SiO<sub>5</sub>) and iron. The order of crystallisation depends on the chemical composition of the slag and is difficult to investigate on quenched samples because of rapid crystallisation. The main goal of this study was to validate the calculated order of crystallisation based on thermodynamic models assuming a simplified chemistry, using real slag in experiments. The crystallisation of molten steel slag has been investigated using High Temperature X-ray Diffraction (HT-XRD) and Differential Thermal Analysis (DTA) between temperatures of 1000°C and 1500°C. All experiments were conducted under an inert gas atmosphere to prevent further oxidation of the slag. Molybdenum was used as material for DTA crucibles and for heating strips for HT-XRD because Pt is not suitable due to the high Fe-content of the slag. Although Mo should be inert against steel slag according thermodynamic calculations it partially dissolved in the slag during the experiment. Nevertheless, the DTA analysis show exothermal reactions at 1520°C, 1395°C, 1345°C and 1100°C which correspond to the crystallisations of wuestite, hatrunite, larnite and srebrodolskite, respectively identified by HT-XRD. The temperatures, however, do not completely agree with the calculated crystallisation temperatures probably due to the incorporation of Mo. A sharp maximum in DTA curve at 1415°C correspond to crystallisation of a Mo-Fe alloy.

### FILLING CHRYSOTILE NANOTUBES WITH METALS

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Chrysotile is a sheet silicate (Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) forming nanotubes with similar radial dimensions as multi-walled carbon nanotubes (MWCNTs) e.g. 5 nm inner diameter and 20 nm outer diameter. Chrysotile nanotubes are considerably longer (up to few millimeters) compared to carbon nanotubes. Chrysotile, however, is an insulating material and is unstable at higher temperatures. As predicted by Dujardin et al. (1994)<sup>1</sup> injection of molten metals with liquid-vapor surface tensions higher than 100-200 mN/m into nanotubes has been proved to be possible by applying an outer pressure. Hg nanowires as long as few hundred nanometers have been created by this

means at room temperature. Pb and Sn nanowires were produced by means of high pressure and high temperature piston-cylinder experiments (10 Kbar, 440°C). The evolution of the morphology of the chrysotile nanotubes with increasing temperature is a crucial factor for the injection of liquid metals into the tubes. The thermal behavior of chrysotile has, therefore, been studied using IR spectrometry, XRD, TEM and DTA-TGA analysis. IR spectrometry studies show that metastable dehydration of chrysotile starts at 470°C. The kinetics of the structural water release depends strongly on the temperature. At 700°C total dehydroxilation is observed after 30 min; for lower temperatures this process can take as long as one day. XRD studies of chrysotile heated at 700°C during 30 min indicate that complete dehydroxilation leads to the development of an amorphous state, but TEM imaging show that the tubular structure is still present at that temperature. Between 700°C and 850°C transformation to forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) of the amorphous tube-walls takes place and the nanotube collapse to a polycrystalline fiber. This phase transformation is coherent with the maximum of the exothermal peak at 820°C visible in the DTA analysis. This thermal stability limits dictate the choice of materials that can be introduced into the tube through a melt phase.

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### ELASTIC PROPERTIES OF CORDIERITE: FIRST RESULTS FROM RUS AND STATIC COMPRESSION MEASUREMENTS

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The orthorhombic framework silicate cordierite, Mg<sub>2</sub>Al<sub>3</sub>(AlSi<sub>5</sub>O<sub>12</sub>), has been subject to numerous experimental studies, in particular focussing on the Al,Si ordering and the storage of volatiles such as CO<sub>2</sub> and H<sub>2</sub>O. Although the majority of the physico-chemical properties of cordierite is well documented, reliable data for its mechanical properties are rare. Here we report first results of elasticity measurements at room temperature using the resonant ultrasound spectroscopy (RUS) technique, complementary to a study of isothermal static compression as carried out by means of single-crystal diffraction in a diamond-anvil cell.

Our single crystal elastic constants agree well with the values recently obtained by Brillouin spectroscopy [1]; the bulk modulus was found to be 130.7(3) GPa. The close relationship between the structures of beryl and cordierite is clearly reflected by the pseudo-hexagonal character of the elastic anisotropy, i.e. C<sub>11</sub><sup>a</sup>C<sub>22</sub><sup>a</sup> > C<sub>33</sub><sup>a</sup>. Due to the incorporation of Al into the structure, the mean elastic stiffness of cordierite is about 27% smaller compared to beryl.

The high pressure experiments up to 1.0 GPa were carried out using water as hydrostatic pressure medium. The high-precision P-V data reveal two transition points at critical pressures of 0.210(5) GPa and 1.01(3) GPa with the first, weak transition being apparently second-order in character. In contrast, the second transition is accompanied by a significant volume discontinuity, as previously reported [2]. Both transitions reveal small, but detectable elasticity anomalies showing typical softening on approaching the transition pressures. The

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compressibility according to a second-order Burch-Murnaghan equation of state result in  $K_r=124.0\pm 3.4$  GPa for the low-pressure polymorph ( $P<0.21$  GPa), and  $127.7\pm 1.2$  GPa considering coupling [3] through Landau theory across the first transition. [1] Toohill, Siegesmund, Bass (1999) *Phys. Chem. Min.* **26**: 333-343. [2] Mirwald, Malinowski, Schulz (1984) *Phys. Chem. Min.* **11**: 140 [3] Tröster, Schranz, Miletich (2002) *Phys. Rev. Lett.* **88**: 055503

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### EVOLUTION OF FIBER TEXTURE IN A DIFFUSION-CONTROLLED REACTION RIM

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Diffusion-controlled growth of reaction rims is, at given P, T, and fluid composition, determined by grain boundary diffusion coefficients and the availability of grain boundaries, i.e. grain size. We studied, how the fiber thickness in wollastonite rims grown around quartz grains in calcite matrix evolves during rim growth.

The reaction rims were synthesized at 850, 900, and 950°C at 100 MPa CO<sub>2</sub> pressure. TEM samples were cut using the Focused Ion Beam technique. Rim texture was determined from dark field and bright field images. Wollastonite crystallizes fibrous at the qz-wo interface and granoblastic at the wo-cc interface. The fiber thickness decreases with time, i.e. there is continuous nucleation. The nucleation rate decreases with increasing temperature. During growth of each rim it decreases with  $t^{1/2}$ , i.e. it is proportional to the propagation rate of the qz-wo interface. The mean fiber thickness at the qz-wo interface decreases with  $t^{1/4}$ .

A model explaining the textural evolution is suggested. The rims crystallize in diffusion gradients between the two interfaces whereby grain boundary diffusion of the SiO<sub>2</sub> component is rate-limiting. Fiber thickness evolves due to grain-scale diffusion gradients within the qz-wo interface. These microscale diffusion gradients must exist between the center and edge of each wollastonite fiber tip and are induced by the volume increase during wollastonite crystallization at the qz-wo interface.

Fiber texture is common in metamorphic wollastonite and other reaction rims. Understanding the textural evolution might reveal kinetic information about their diffusion-controlled growth history.

### TITANIUM-CARRIER OXIDE MINERALS: A COMPARATIVE STUDY OF ILMENITE AND RUTILE BY X-RAY ABSORPTION SPECTROSCOPY

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Ilmenite (FeTiO<sub>3</sub>) and rutile (TiO<sub>2</sub>) are widespread accessory minerals in many igneous and metamorphic rocks and with economic importance as titanium ores.

The trigonal crystal structure of ilmenite (hematite-type) may be described in terms of a distorted hexagonal closest packing of oxygens parallel to (0001) with cations occupying 2/3 of the available octahedral interstices (site symmetry 3) in a honeycomb pattern that repeats along [0001]. The layer sequence provides a tetrahedral cationic environment to the anions (positional symmetry 1). The tetragonal structure of rutile is based on a peculiar eleven-neighbours packing of oxygens with cations occupying also octahedral interstices (symmetry *mmm*) that share opposite edges to form chains along the *c*-axis. Oxygens are surrounded by three cations each forming isosceles triangles on {110}.

An X-ray absorption spectroscopy (XAS) study would probe the electronic structure of oxygen (*K*-edge), titanium and iron (*L*-edge) in these minerals and provide an insight on the influence of Fe<sup>2+</sup> vs. Ti<sup>4+</sup> on O<sup>=</sup> coupled with oxygen site geometry plus symmetry. As the electronic transitions are governed by the dipole rule, L<sub>2,3</sub>-edges in 3d transition metals would reflect *d* and *s* unoccupied states (de Groot et al., 1990) whereas the *K*-edge of oxygen would display transitions to *p*-like unoccupied states (Kurata et al., 1993).

XAS experiments were performed at BESSY synchrotron facility in Berlin (Figueiredo and Mirao, 2002). Interpretation of O 1s spectra within a Full Multiple Scattering (FMS) approach applying the FEFF program (Ankudinov et al., 1998; Rehr and Albers, 2000) indicated oxygen electronic structure is neither sensitive to the geometry of coordination polyhedron nor to the presence of iron as coordinating cation, or, alternatively, that both effects compensate in the overall details of O *K*-edge. The fine structure of XAS spectra will be discussed in terms of transitions from O 1s to O 2p orbitals hybridised with metal *d*-orbitals and the crystal field splitting of *d* orbitals in transition metal ions reflecting distortions of oxygen octahedra.

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### FLUIDS AT ULTRA-HIGH PRESSURE METAMORPHIC CONDITIONS - AN EXPERIMENTAL STUDY ON SYSTEMS OF NATURAL ROCK COMPOSITION

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To understand the rheological behaviour of deeply subducted continental crust, experiments on fluid distribution at conditions typical for ultra-high pressure metamorphism were performed using a piston-cylinder apparatus. Starting materials are specimens of S-type granitic biotite-phengite-gneiss and pyrope-quartzite, both from the Dora Maira Massif (Western Alps, Italy), and diamond-bearing garnet-mica-gneiss with granodioritic bulk composition from the Erzgebirge (Germany). Bulk water contents are 0.8 to 15 wt.%. Samples are pressurised to 2.5 GPa, heated to 1000°C, and held at these conditions for one day. The pressure is then raised to 3.5 GPa, followed by cooling at different rates to various end temperatures; some samples are annealed for up to several days. Finally, the runs are quenched by a sudden drop in temperature, whereby the ultra-high pressure fluid forms a hydrous silicic glass.

Microfabrics are analysed by SEM, reliable chemical compositions are determined by a special EMP measurement method. In the granitic system with 2.8 wt.% bulk water content, the volume proportion of the quenched fluid quantified by digital image analysis decreases almost linearly from about 70 vol.% (1000°C) to 50 vol.% (900°C) and 11-15 vol.% (700°C). The fluid quenched at temperatures of 1000 to 800°C is a homogeneous glass with a water content of up to 10 wt.%. At 700°C, the glass contains 10 to 15 wt.% water and is crowded with bubbles formed by demixing of an aqueous solution upon quenching. Demixing is also observed for the garnet-mica-gneiss, with a water content of the glass phase of about 20 wt.%. In the pyrope-quartzite, in contrast, only a few droplets of silicic glass indicate a demixed hydrous solution with a low dissolved silica content. With cooling, the fluid becomes enriched in potassium and sodium and concomitantly depleted in silicon and aluminium in all rock compositions.

### SWELLING-SHRINKAGE KINETIC OF BENTONITE MX80

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The swelling- shrinkage kinetic of an industrial Bentonite (MX80) was investigated using a new technique of Electron Microscopy (ESEM) coupled to a Digital Image Analysis Program (Visilog). This expansive clay was characterized by several analytic tools (ICP-AES, SEM, STEM, RXD, etc.), before the new technique was applied.

The swelling -shrinkage was directly observed at high magnification and at different stage of relative humidity in an Environmental Scanning Electron Microscope (ESEM). Nine wetting/drying cycles were performed in the sample. Each cycle was performed at different relative humidities (55, 60, 65,70,75,80,85,90, and 95%).

A Digital Image Analysis program was used to determine swelling-shrinkage. This method consists in estimating the percent augmentation of the surface as a function of time ( $S=[(S_t-S_r)/S_r]*100$ ).

Finally, we tested two swelling-shrinkage kinetic models for the experimental data; the first one, a hyperbolic model normally reported in the literature, and the second, is based on a linear kinetic equation of the first order ( $dS/dt=k(S_M-S)$ ).

The results presented show that both models fit well with the experimental data. However, at low humidities the basic linear model fits better with the experimental data, and close to 100% the hyperbolic model fits better.

### THE ROLE OF CATION SATURATION IN THE WATER SORPTION OF THE BENTONITE (MX80)

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The potential of water sorption and swelling-shrinkage in the expansive clays is practically defined by the nature of the inter-lamellar cations. The purpose of this paper is to estimate the effect of the cation saturation ( $Mg^{++}$ ,  $Ca^{++}$ ,  $Li^+$ ,  $Na^+$  and  $K^+$ ) in the bentonite (MX80). The bentonite was treated with concentrated solutions (1N) of sodium, calcium, magnesium, potassium and lithium chlorides. This treatment was made three times with constant agitation during one hour. After, the clay was washed three times for each case. The scanning transmission electron microscopy (STEM) and ICP-AES were used to verify the efficiency of the cation saturation.

Finally, two techniques were employed to estimate the effect of the cation saturation in the bentonite: the first one uses an isothermal system of water adsorption where the relative humidity is controlled by a supersaturated salt solution. In the second, an environmental scanning electron microscopy (ESEM) coupled to a digital image analysis program were used to estimate of swelling- shrinkage kinetic.

The results show that cation saturation with lithium and sodium have the largest potential of water adsorption and swelling. In addition, we observe that the swelling kinetic is very complex in the initial stage.

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### A NEW METHOD TO COMPUTE FLUIDS SATURATION IN C-H-O-S-SILICATE MELT SYSTEMS

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We developed a method to calculate equilibrium between a C-O-H-S fluid phase and a silicate melt based on a previous model for the saturation of H<sub>2</sub>O-CO<sub>2</sub> fluids (Papale, 1999) and on a thermochemical approach for calculating sulfide and sulfate solubilities of simple and complex melts. In particular, this second approach combines the Toop-Samis polymeric model with the Flood - Grjotheim theoretical treatment of silicate melts (Ottonello et al., 2001; Moretti, 2002). Moreover, fugacities in the gaseous phase are computed through the SUPERFLUID code (Belonoshko et al., 1992). The C-H-O-S saturation model allows determining the partition of H<sub>2</sub>O, CO<sub>2</sub>, and S between silicate melt and coexisting fluid, and the composition of the fluid phase in terms of H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S, as a function of pressure, temperature, volatile-free liquid composition, oxygen fugacity, and total amount of volatile components in the system. For the sake of simplicity, we assumed that no reduced or oxidized sulfur-saturated solid or liquid phases nucleate or separate from the liquid-gas system. Minima in sulfur solubility as a function of oxygen fugacity are depicted, in good agreement with theory and experiments. Applications are given for rhyolitic and basaltic melts with various oxygen fugacities in the range NNO±2, and pressure from a few hundred MPa to atmospheric. The developed model accounts for the reciprocal effects of volatiles on their saturation contents, and the complex relationships between the saturation surface of a multicomponent fluid and the liquid composition, volatile abundance, P-T conditions and oxidation state.

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### THERMAL STABILITY OF THE OH-SUBSTITUTION AND THE ANOMALOUS BIREFRINGENCE IN Ca-GARNETS

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The origin of anomalous birefringence in Ca-garnets is in focus of scientific interest. Although some causes of birefringence such as OH substitution, long-range cation ordering, strain and exsolution were suggested [1,2,4,5] contribution of each mechanism into observed optical patterns is not clear and a quantitative model for co-existing mechanisms has to be constructed.

Micro-IR absorption spectra of three andradite-grossular garnets from Malian skarns with birefringence up to 0.015 were studied. The samples were also characterised by EPMA, SC-XRD, reflection IR and micro-Raman techniques [3]. Samples reveal macroscale (yellow or green core with 0.3-0.7 at. Fe/Al and brown or dark-green rim with 0.5-1.5 at. Fe/Al and 0.2-0.6 at.% Ti) and microscale (due to oscillations of Al/Fe ratio) inhomogeneity. Two patterns of birefringence can be recognized: (a) with "high" values (0.001-0.015; often oscillatory) in rim and sometimes in core zones; (b) lamellar or wavy (<0.001) in core zones. Three samples were annealed in the air at different temperatures between 500 and 1150°C for total 430, 69 and 20 hours.

The results are:

1) structural hydroxyl groups cause from 5 to 10 spectral bands between 3500 and 3700 cm<sup>-1</sup>;

2) OH concentration correlates with Fe,Ti-contents (the integral intensity rises in 2-4 times from core to rim, the intensities of distinct bands may change not uniformly);

3) neither absolute nor relative values of birefringence correlate with OH content;

4) "a"-pattern of birefringence disappears during annealing, it proceeds much more rapidly in rims; "b"-pattern is stable;

5) bands vanish with different kinetics, low-frequency bands are more stable.

One can suppose that:

1) "a"-type birefringence is due to the ordering in octahedral sites, whereas "b"-type is controlled by the strain;

2) OH substitution furthers "re-symmetrisation" of the garnet structure;

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### SIMULTANEOUS XRD AND ELASTIC PROPERTY MEASUREMENTS IN A MULTI-ANVIL DEVICE

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A key question to all high pressure research arises from the reliability of pressure standards. There is some indication and discussion of an uncertainty of 10-20% for higher pressures in all standards. Simultaneous and independent investigation of the dynamical (ultrasonic interferometry of elastic wave velocities) and static (XRD-measurement of the pressure-induced volume decline) compressibility on a sample reveal the possibility of a standard-free pressure calibration and, consequently an absolute pressure measurement.

Ultrasonic interferometry is used to measure velocities of elastic compressional and shear waves in the multi-anvil high pressure device MAX80 at HASYLAB Hamburg enabling simultaneous XRD and ultrasonic experiments. NaCl was used as pressure calibrant after Decker (1971). From the ultrasonic wave velocity data we calculated the compressibility of NaCl. The results were compared with data of static compression experiments up to 5 GPa, published by Bridgman (1940). In the range between 1 and 3.5 GPa our velocity-based data correspond within  $\pm 1\%$  precision to the static compression data. Furthermore the pressure revealed according to Decker (1971) is in accordance to our standard-free pressure calibration within the uncertainty of the experiment.

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### MINERALIZATION OF ALPINE FISSURES AS A FUNCTION OF CONTINENT-CONTINENT COLLISION IN THE CENTRAL ALPS

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Fluid evolution and mineral precipitation were studied in several hundred Alpine fissures of the Central Alps. The methods applied include microthermometry, micro-Raman spectroscopy, K/Na thermometry, stable isotope and x-ray analyses.

Close to the peak of the late Tertiary event Alpine fissures were opened by compressional tectonics caused by continent-continent collision. Fluids entered the growing fissure systems and fissure wall rock were leached. Dissolved minerals were transported into the fissure systems where they precipitated. Fissure mineral assemblages evolved, from north to south, as a function of the chemical composition of the host rock, the increase in temperature and the change in fluid composition.

During retrograde conditions the Adriatic promontory of the African plate was thrust beneath the European continent causing thickening, exhumation and extension. As a consequence repeated fluid pressure drops and channelized fluid flow through the massifs and nappe systems occurred. The fissure minerals were no longer in equilibrium with the CO<sub>2</sub>-enriched fluids and reacted to a late carbonate dominated assemblage with siderite, ankerite, phengite and rutile (MULLIS et al., 1994). Meteoric water infiltrated to depths exceeding 10 km (MULLIS et al., 2001). Enormous amounts of silica were dissolved and precipitated as needle and split-growth quartz.

The alteration of the surrounding rocks and the precipitation of quartz and other minerals was modeled with the newly developed program THERIAQ for a well studied Alpine fissure from Zinggenstock in the Aar Massif (Mullis, 1996; Mullis and de Capitani, 2000). The calculations begin with the computation of the chemical equilibrium for a given bulk composition. The chemical potentials are used to calculate the composition of an aqueous solution in equilibrium with this assemblage. The alteration is modeled by subtracting the dissolved components from the bulk composition and re-calculating a new buffered assemblage.

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### IN SITU XAFS STUDY OF THE EFFECT OF WATER ON LOCAL STRUCTURE AROUND TRANSITION METALS IN SILICATE MELTS

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XAFS (X-ray Absorption Fine Structure) spectroscopy has been used to investigate the effect of water on the atomic environment of transition metals in silicate melts in situ. We present Ni K-edge XAFS results obtained at high-temperature (up to 1100°C) using a platinum heating wire furnace, and at high-temperature / high-pressure (HP-HT; up to 900°C / 1.2 GPa) using a diamond anvil cell (Bassett type). The HT XANES (X-ray Absorption Near Edge Structure) were collected on ID26 at the ESRF (Grenoble, France) and the HP-HT XANES were collected on PNC-CAT beamline at APS (Chicago, USA).

We first performed HT measurements on NS3 glass containing 2 wt.% Ni and 8 wt.% water. XANES and pre-edge analysis show that nickel is 5-coordinated in the melt state (910°C). But after quench, XANES resemble to that for an anhydrous NS3 sample (NIR experiments are underway to identify water speciation in these samples). Then, another sample (a NS3 glass containing 3.5 wt.% Ni and water saturated) was studied under HP-HT conditions. XANES spectra for the melt phase in situ (870°C / 1.14 GPa) suggest that Ni(II) is 4-5 coordinated. Close to T<sub>g</sub> (769°C / 975 MPa), a highly structured XANES appears, which resemble to that of internally heated pressure vessel (IHPV) quenched glasses, for which we show (Farges et al., 2001) that a nepouite-related nanophase has nucleated. However, after the in situ quench, the XANES corresponds to that for a nanophase-free hydrated NS3 glass with 6-coordinated Ni(II).

Our result show that quench rates are critical on the synthesis of water-bearing glasses in IHPV devices and that in situ experiments are needed to infer robust structural information on transition elements in water-bearing melts under geochemical conditions. In HP-HT melts, the effect of water on the speciation of Ni(II) is not as strong as previously thought.

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## PHASE EQUILIBRIA OF H<sub>2</sub>O-UNDERSATURATED ANDESITE LIQUIDS AT HIGH PRESSURE

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Andesite is the most common erupted lava type in subduction-related magmatic arcs and a variety of processes have been invoked to explain their genesis [1,2]. Water has proven to be one important variable in the formation of andesites, and their phenocryst assemblage contain potentially important clues regarding H<sub>2</sub>O undersaturated high pressure fractionation and may provide insights into crystallization processes in the deep crust. Here we explore the effects of temperature and variable water content on the phase relations among garnet, plagioclase and amphibole in andesite liquids at high pressure using crystallization experiments on H<sub>2</sub>O undersaturated compositions. Experiments were performed on a synthetic andesite composition that was derived by a series of fractional crystallization experiments of a primary hydrous picrite [3]. H<sub>2</sub>O content was varied by mixing variable proportions of a dry and H<sub>2</sub>O-bearing powder of the same composition, which resulted in an initial H<sub>2</sub>O content between 4 and 8 wt%. To minimize Fe-loss, iron pre-saturated Au<sub>90</sub>Pd<sub>10</sub> inner capsules were used for the hydrous piston cylinder experiments. The capsule was placed into an outer Pt capsule with the same powder as inside the inner capsule. With this design the H<sub>2</sub> diffusion out of the capsules was minimized while maintaining relatively oxidizing conditions around the NNO buffer. Run times varied between 100 and 170 hours. Our preliminary results indicate that in T-X

H<sub>2</sub>O space at constant pressure amphibole-in has a positive slope, while plagioclase-in is negative. Clinopyroxene is stable over the whole range of temperatures and H<sub>2</sub>O contents examined. In addition to clinopyroxene, amphibole±magnetite are the liquidus phases at high H<sub>2</sub>O contents, while garnet was the liquidus phase at relatively low H<sub>2</sub>O content. The main compositional effects of increasing the H<sub>2</sub>O content in the liquid at constant temperature is to stabilize an iron oxide to higher temperatures and to increase the Mg/Fe ratio in crystallizing amphibole and clinopyroxene. This suggests that oxide-bearing hornblendites which are common in many calc-alkaline gabbroic differentiates in xenoliths and exposed sections of deep island arc crust only form at relatively high magmatic water, while garnet- and clinopyroxene-bearing rock types form at lower H<sub>2</sub>O content.

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## MELT PHYSICS AND CHEMISTRY

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Important aspects of structure and properties of natural magmatic liquids may be examined in appropriate portions of the system MO<sub>n/2</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, where M = Na, K, Mg, Fe<sup>2+</sup>, and Ca. The anionic structure of their melts and glasses to temperatures at or exceeding those of natural magmatic liquids is described in terms- of simple structural units (Q-species) characterized by their individual number of bridging oxygen per tetrahedrally coordinated cation (Si<sup>4+</sup> and charge-balanced Al<sup>3+</sup>). These units are linked via their nonbridging oxygens between the metal cation(s).

The equilibria among these units 2Q<sup>n</sup>⇌Q<sup>n-1</sup>+Q<sup>n+1</sup> are functions of metal/silicon ratio, electronic properties of the metal cation, Al/Si, and temperature. For binary compositions relevant to natural magmatic systems, n=1. With n=1, ΔH for the reaction decreases from ~0 to -30 kJ/mol with increasing melt polymerization (NBO/T) within the NBO/T-range of most natural magmatic liquids. The ΔH is negatively correlated with Al/(Al+Si) and positively correlated with Z/r<sup>2</sup> of the metal cations.

The relationships between bulk composition, temperature, and structure can be employed to describe physicochemical properties of melts in terms of temperature- and composition-dependent Q-speciation. Examples of such relationships include activity-composition relations among Q-species, and relationships between speciation and melt properties such as configuration entropy and heat capacity. There is a linear relationship between the log γ<sub>i</sub> (activity coefficient) and log X<sub>O<sub>i</sub></sub> (mol fraction of species, i). By combining structural data with available information of configurational heat capacity, C<sub>p</sub><sup>config</sup>, values of C<sub>p</sub><sup>config</sup> for individual Q-species, C<sub>p</sub><sup>config</sup>(Q<sup>i</sup>), can be extracted. The C<sub>p</sub><sup>config</sup>(Q<sup>i</sup>)-values do not depend on metal cation properties. That information, in turn, can be used to calculate C<sub>p</sub><sup>config</sup> from the structure of silicate melts and also aid in estimating the viscosity of silicate melts at magmatic temperatures.

### SOLUBILITY OF ALKALI AND ALKALINE EARTH ALUMINOSILICATE COMPONENTS IN AQUEOUS FLUIDS IN THE LOWER CRUST AND UPPER MANTLE PRESSURE AND TEMPERATURE RANGE

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The solubility of Na- and Ca-aluminosilicate components in aqueous fluids in the 1000°-1400°C and 0.8-2.0 GPa temperature- and pressure-range, respectively, has been determined along each of the joins  $\text{CaSi}_4\text{O}_9$  -  $\text{Ca}(\text{Ca}_{0.5}\text{Al})_4\text{O}_9$  and  $\text{Na}_2\text{Si}_4\text{O}_9$  -  $\text{Na}_2(\text{NaAl})_4\text{O}_9$  with 0, 3, and 6 mol%  $\text{Al}_2\text{O}_3$ . The solubility,  $X_{\text{H}_2\text{O}}^{\text{fluid}}$ , ranges from 0.5 to 20 mol% depending on temperature, pressure, and bulk composition. Its temperature dependence is linear and ranges between 0.7 and  $4.2 \cdot 10^{-3}$  mol%/°C depending on pressure. The pressure-dependence of silicate solubility is also positive but non-linear. The solubility decreases with increasing  $\text{Al}_2\text{O}_3$  content.

The aluminosilicate solubility along the join  $\text{CaSi}_4\text{O}_9$  -  $\text{Ca}(\text{Ca}_{0.5}\text{Al})_4\text{O}_9$  was fitted to the expression:  $X_{\text{silicate}}(\text{mol}\%) = -2.6 - 0.20 \cdot X_{\text{Al}_2\text{O}_3}(\text{mol}\%) + 0.002 \cdot T(^{\circ}\text{C}) + 0.86 \cdot P^2(\text{GPa})$ . Along the  $\text{Na}_2\text{Si}_4\text{O}_9$  -  $\text{Na}_2(\text{NaAl})_4\text{O}_9$  join, the solubility is 2-3 times greater and is more sensitive to temperature, pressure, and  $\text{Al}/(\text{Al}+\text{Si})$ ;  $X_{\text{silicate}}(\text{mol}\%) = 1.9 - 1.3 \cdot X_{\text{Al}_2\text{O}_3}(\text{mol}\%) + 0.008 \cdot T(^{\circ}\text{C}) - 13 \cdot P(\text{GPa}) + 7.3 \cdot P^2$

The partial molar volume of  $\text{H}_2\text{O}$  in both Na- Ca-silicate-saturated aqueous fluids,  $V_{\text{H}_2\text{O}}^{\text{fluid}}$ , ranges between ~17 and ~27  $\text{cm}^3/\text{mol}$  depending on pressure, temperature, and compositions. The molar volume of silicate-saturated aqueous fluid is nearly identical to  $V_{\text{H}_2\text{O}}^{\text{fluid}}$  because  $\text{H}_2\text{O}$  is the dominant component.

The isochors of both Na- and Ca-aluminosilicate-saturated aqueous fluids differ from those of pure  $\text{H}_2\text{O}$  and also differ from each other. For Ca-aluminosilicate fluids, pressure-difference at given temperature ranges between 5 and 10% in the 0.8-2.0 GPa and 1000°-1400°C pressure- and temperature-range. For comparison, in the Na-aluminosilicate-saturated fluids, this difference is between 5 and 30% depending primarily on fluid density and pressure. This difference between the Na- and Ca- system reflects the different solubility of Ca- and Na-silicate in aqueous fluids.

### <sup>1</sup>H MAS NMR STUDY OF WATER SOLUBILITY IN ENSTATITE

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An exact determination of the solubility of water in nominally anhydrous minerals is a prerequisite for understanding water storage in the earth's mantle. Large discrepancies were reported between the study of Kohn (1996) using <sup>1</sup>H MAS NMR and other studies using infrared spectroscopy. Keppler and Rauch (2000) suggested that this was because of differences in starting materials for experiments, and because of adsorption of water onto the powders used in NMR measurements. In order to resolve this discrepancy, a series of enstatite

synthesis experiments were carried out at 900-1100°C and 1.5-2.5 GPa in the presence of 0.5-31 wt% excess water. The <sup>1</sup>H MAS NMR spectra shows up to 5 peaks, 4 peaks are very sharp (peak center 1.1, 4.7, 5.6, 7.4 ppm) and 1 peak is very broad and asymmetric (3.3 ppm). This is in contrast to the observation of a single broad component in a recent study (Keppler and Rauch 2000). The broad peak increases with increasing water in the bulk composition as well as with P and T. No systematic differences were observed between different types of starting materials, and no evidence was found to suggest that adsorption of water is a serious problem. The sharp peaks were assigned to OH point defects (5.6 and 7.4 ppm), water in fluid inclusions (4.7 ppm), and OH from amphibole lamella in the enstatite structure (1.1 ppm). The broad peak at 3.3 ppm is very typical for water (OH and H<sub>2</sub>O) in glasses and gels, which occurred as quench phase in our runs. Using heat treatments up to 700°C, all peaks disappeared except the OH point defect peaks. It revealed that the main reason for discrepancies of water determination using the NMR method was caused by additional contributions of the overlapping quench-phase water peak with peaks from OH point defects. This can be controlled by an appropriate choice of temperature and bulk water concentration in the sample. About 200 ppm water at 1100°C and 1.5 GPa and 300 ppm water at 900°C and 2.5 GPa was determined for enstatite if only the point defect peaks were considered. This is in good agreement with results using the IR method.

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### MELTING PHASE RELATIONS IN THE SYSTEM Fe-FeO AT 15-25 GPa

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High-pressure phase relations in the system Fe-FeO has primary importance in understanding the constitution of the planetary core. Ringwood and his coworkers determined the melting phase relation of the Fe-FeO system to 15 GPa and concluded that the liquid immiscibility (which is predominant at 1 atm experiments) disappears at 15 GPa and above 2100°C (Ohtani & Ringwood, 1984) Kato & Ringwood, 1989; Ringwood & Hibberson, 1990). We revisited the system with similar experimental technique (multi-anvil press, 10 and 7 mm MgO octahedral pressure medium (for 15 and 25 GPa, respectively), LaCrO<sub>3</sub> heater, mixed Fe-FeO powdered specimen, and Al<sub>2</sub>O<sub>3</sub> capsule). Although our run products showed textures similar to those previously reported, we reached very different conclusion. Using alumina content as an indicator, coexisting Fe and FeO melts before quenching and FeO dissolved from molten Fe-rich melt during quenching are clearly distinguished. Using the new textural criteria, the solubility of FeO in molten Fe liquid is less than 10 mol% in the temperature 2000 to 2300°C at 15 GPa. The critical point of Fe-FeO liquid immiscibility at 15 GPa must reside at much higher temperature than Ringwood proposed (ca. 2100°C, Ringwood & Hibberson, 1990). The experiments at 25 GPa are in progress and it has been demonstrated that the solubility of FeO in molten Fe is much expanded at this pressure.

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### FLUID HETEROGENIZATION PROCESS IN EPITHERMAL Au-Hg DEPOSITS

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Thermodynamic modeling (using CHILLER program) of Au and Hg behaviour at 250-50°C in heterogenous fluid of the same composition as real ore-forming fluids, shows that boiling of fluids with separation of gas phase ( $H_2O > CO_2$ ) brings to transition of sufficient part of mercury in gas phase as HgO gas and removal it from the solution (70% at 250°C, up to 90% at 300-350°C). It's in conformance with really observed Hg distribution between gas phase and solution in recent geothermal systems. During isothermal heterogenization of the solution, deposition of the first portion of gold occurs due to transition of some part  $H_2S$  in the gas phase, pH increasing (owing to  $CO_2$  degassing) and as a result deposition of adular. It's also in a agreement with often observed forming of gold + quartz + carbonate paragenesis at deep horizons of volcanogenous-hydrothermal Au-Hg deposits - at the level of boiling of ore-forming solution. After heterogenization and precipitation of some part of gold, enough quantity of Au remains in the solution ( $n \cdot 10^{-6}$  mol) that deposits under subsequent temperature decrease up to 150°C. Thus, heterogenization of ore-forming solutions has very important consequences for ore deposition: 1) Hg transition in vapor-gas phase which is able to migrate independently, may explain isolated position of cinnabar mineralization relatively of Au-Hg deposits; 2) boiling of fluids explains the position of quartz-adular-carbonate veins with Au in deepest horizons of Au-Hg deposits; 3) an increase of pH (owing to  $CO_2$  degassing) and concentration of solutions (loss of  $H_2O$  solvent) that provides stability of hydrosulfide Au-complexes and creates conditions for Au transport using such solutions to the lower temperature areas (down to 150°C). This study is supported by Russian Foundation (grant 01-05-65096).

### THE HIGH-PRESSURE $P_2/c$ - $C_2/c$ PHASE TRANSITION FOR THE CMS ( $CaO$ - $MgO$ - $SiO_2$ ) CLINOPYROXENE

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A high pressure  $P_2/c$  -  $C_2/c$  phase transition for a synthetic iron-free clinopyroxene with composition  $Ca_{0.15}Mg_{1.85}Si_2O_6$  was observed at 5.2 GPa and at room temperature by single-crystal X-ray diffraction. The unit-cell parameters were

measured from atmospheric pressure up to 5.5 GPa. Data collections of five  $b$ -reflections ( $h + k = \text{odd}$ ) and five  $a$ -reflections were done at each pressure step to follow the evolution of the intensity ratio ( $I$ ), in order to characterise the transition. This phase transformation is first order in character with no hysteresis. At the transition pressure, the  $b$ -reflection intensities disappear and a strong decrease of unit-cell parameters ( $a$  decreases by 3.4%,  $c$  by 4.4%,  $\beta$  by about  $6^\circ$  and  $V$  by 6.4%) has been observed.

Ca-free clinoenstatite (Angel and Hugh-Jones, 1994) shows the same first order character, very similar  $V/V_0$  step associated with the transition and a similar transition pressure during decompression, i.e.  $P = 5.3$  GPa. For clinoenstatite, however, a significant hysteresis is present (between 7 and 5.3 GPa). Substitution of a small amount of Ca into the clinoenstatite structure, hence, eliminates the hysteresis of the phase transformation, suggesting that it might facilitate the nucleation of one structure from the other during the first-order transition process. At higher Ca content ( $Ca_{0.50}Mg_{1.50}Si_2O_6$  (Tribaudino et al., 2001) smearing of the unit-cell parameters was observed during the phase transition, which might be explained by a possible interaction with the strain associated with compositional modulation.

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### XANES AND RAMAN SPECTROMETRY ON GLASSES AND CRYSTALS IN THE CAS SYSTEM

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Calcium aluminate and aluminosilicate glasses are attractive materials for a wide range of technical applications due to their highly refractory nature, their excellent optical and mechanical properties. The  $CaO$ - $Al_2O_3$ - $SiO_2$  system (CAS) is remarkable since glasses with very few  $SiO_2$  content can be synthesized, contrary to alkali or Mg aluminosilicate glasses. We have synthesized more than 40 different glasses in the CAS system using quenching method and 6 glasses in the CA system using laser heating. These glasses were studied using a Raman spectrometer T64000 from Jobin-Yvon-Dilor company and using X-ray absorption spectroscopy at Si, Al, Ca K edges the SA32 and D44 ligne in LURE. Cormier et al (2000) have shown from X-ray and neutron diffraction that aluminium is in 4-fold coordination in this ternary system. We present Raman and XANES data obtained at room temperature for these glasses. On the join  $SiO_2$ - $CaAl_2O_4$  glass, we observe a decrease in Raman intensity with increasing  $CaAl_2O_4$  content for all the bands. In particular, we observe a sizeable decrease in intensity for the T4 band near  $1150\text{ cm}^{-1}$  assigned to T-OO in T4 units. This decrease suggests that aluminium substitutes preferen-

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tially to Si<sup>4+</sup> in the fully polymerized structural units TO4 according with Neuville and Mysen (1996). On the join SiO<sub>2</sub>-Ca<sub>3</sub>Al<sub>2</sub>O<sub>7</sub> (R=CaO/Al<sub>2</sub>O<sub>3</sub>=3), the band intensities decrease with decreasing SiO<sub>2</sub>, which can be interpreted as a substitution of Si by Al in T4 units with other substitution of Si by Al in T3 units. From the Xanes spectra, we can conclude that: - Al is in tetrahedral site in different Q species in all the CAS system. - Ca is in octahedral site in all the CAS system, with a decrease of the site distortion as SiO<sub>2</sub> content increases. Finally, the anomalous behavior for the viscosity and glass transition properties in the low silica glasses can be explained by the presence of Al in Q3 species at high CaO content.

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### LIQUIDUS ASSEMBLAGES AND PARENTAL MELTS OF SAO MIGUEL AND PICO, AZORES ISLANDS: MAGMATIC INCLUSIONS STUDY

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The Azores volcanic chain is frequently attributed to melting of an underlying hotspot, but others have suggested the Azores result from the melting of a 'wet-spot'. We have made a melt inclusion study of two islands in the Azores, Sao Miguel and Pico to investigate the melting process and ultimately address the role of water in the formation of the lavas. There are significant major element differences between lavas of Sao Miguel and Pico. At the same MgO, Sao Miguel lavas are richer in TiO<sub>2</sub>, FeO\*, MnO, K<sub>2</sub>O, Ca/Al and poorer in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O relative to Pico. These differences are possibly compatible with smaller degrees of melting beneath Sao Miguel or the involvement of different sources or melting conditions beneath the two islands. In order to address these questions we present preliminary compositional data of liquidus assemblages and parental melt petrology for Sao Miguel and Pico islands lavas. Crystallization temperatures and compositions of melts determined from homogenization/quenching experiments of melt inclusion in olivine phenocrysts Fo 89.5-77 for Sao Miguel and Fo 86-74 for Pico range from 1330° to 1125°C (MgO = 15 - 5 wt.%) and from 1230° to 1100°C (MgO = 8.5 - 3.5 wt.%), respectively. Parental melt compositions of Sao Miguel and Pico demonstrate the same difference observable from lava compositions. Modeling the results show that more cooler and differentiated parental melt of Pico could not result from olivine or clinopyroxene crystallization from Sao Miguel parental melts. This suggests that differences in source compositions beneath the islands, not greatly evident in isotopic compositions strongly influence the composition of melts produced. The role of water may thus be possibly implicated.

### INFLUENCE OF MELT COMPOSITION ON THE MOBILITY OF CARBON DIOXIDE AND IMPLICATIONS FOR THE DIFFUSION MECHANISMS

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Carbon dioxide is the second most abundant volatile in terrestrial magmatic systems after water. The knowledge of the influence of melt composition on CO<sub>2</sub> diffusion is crucial for understanding the CO<sub>2</sub> diffusion mechanisms, degassing processes of magmas, and volatile fractionation. Recently, Sierralta et al. (manuscript submitted to Am. Mineral.) have demonstrated a significant increase of CO<sub>2</sub> diffusivity with increasing Na<sub>2</sub>O content and thus progressive depolymerisation in the system NaAlSi<sub>3</sub>O<sub>8</sub> (Ab) + nNa<sub>2</sub>O (n = 0-7 wt%) at 1523 K and 0.5 GPa. We performed additional CO<sub>2</sub> diffusion couple experiments in this system at 1373-1623 K and 0.5 GPa to obtain the activation energies. Furthermore, we performed CO<sub>2</sub> diffusion couple experiments in the system Ab70SiO<sub>2</sub>30 (in wt%) at 1423-1613 K at 0.5 GPa. The one dimensional CO<sub>2</sub> concentration-distance profiles were monitored using micro IR spectroscopy. An error function was fitted to the symmetrical profiles to obtain diffusion coefficients of bulk CO<sub>2</sub>. In the case of Ab + nNa<sub>2</sub>O melts the activation energies decrease from 194 kJ mol<sup>-1</sup> in Ab melt to 123 kJ mol<sup>-1</sup> in Ab + 2.58 wt% Na<sub>2</sub>O, and to 110 kJ mol<sup>-1</sup> in Ab + 6.87 wt% Na<sub>2</sub>O. In contrast to this behaviour the CO<sub>2</sub> diffusion coefficients in Ab70SiO<sub>2</sub>30 melt and thus the activation energy are virtually identical within error to fully polymerised Ab composition in the investigated temperature range. During diffusional processes in the melt, the equilibrium between the CO<sub>2</sub> species (molecular CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup>) is locally maintained. The equilibrium concentrations are not quenchable to room temperature (Porbatzki and Nowak, 2001; Nowak et al., manuscript submitted to Am. Mineral.). However, we can extract some qualitative information on the CO<sub>2</sub> diffusion mechanism. The dependence of bulk CO<sub>2</sub> diffusion coefficients over the range of composition studied may reflect two effects: (1) changing CO<sub>2</sub> speciation in the melt and (2) changes in the individual diffusion coefficients of molecular CO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> with composition.

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### NEW INSIGHTS INTO CARBON DIOXIDE SPECIATION IN SILICATE GLASSES AND MELTS

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Next to H<sub>2</sub>O, CO<sub>2</sub> is the second most abundant volatile in terrestrial magmas. CO<sub>2</sub> plays an important role in the petrogenesis of silica-undersaturated peralkaline magmas at mantle depth, in the evolution of oceanic basalts, and in the degassing

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processes of magmas. The knowledge of the CO<sub>2</sub> speciation in silicate liquids is crucial for understanding the CO<sub>2</sub> dissolution mechanisms, the diffusion mechanisms, and the degassing processes. Using IR spectroscopy, we investigated the speciation of CO<sub>2</sub> in albitic and synthetic iron free dacitic glasses by heating the glasses below the glass transition temperature ( $T_g$ ) in the temperature range 673-973 K at 0.5 GPa for 48 h and rapidly quenching. Our study demonstrates that in contrast to recent suggestions, the equilibrium of the CO<sub>2</sub> species reaction  $\text{CO}_2 + \text{O}^{2-} = \text{CO}_3^{2-}$  in silicate glasses/melts shifts towards molecular CO<sub>2</sub> with increasing temperature. The CO<sub>2</sub> species concentrations and an ideal solution model were used to determine equilibrium constants for the homogeneous species reaction. We derived the thermodynamic quantities  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction, assuming that the species concentrations reflect those at experimental temperatures ( $\Delta H^\circ = -12 \pm 2 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = -23 \pm 3 \text{ J mol}^{-1}\text{K}^{-1}$  for albitic composition;  $\Delta H^\circ = -29 \pm 2 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = -32 \pm 3 \text{ J mol}^{-1}\text{K}^{-1}$  for dacitic composition). An estimate of the relaxation time of the albitic network structure based on viscosity data gives 126 yr at 773 K and 7.7 m.y. at 673 K. This is far above the heating duration of 48 h. Nevertheless, we observe a significant change in CO<sub>2</sub> speciation even at 673 K in the albitic glass. We conclude that in contrast to the H<sub>2</sub>O species reaction the relaxation of the CO<sub>2</sub> speciation is decoupled from the network structure relaxation of the melt/glass. The CO<sub>2</sub> molecule attached to a bridging oxygen to form carbonate (Kohn et al., 1991) can explain the observed change of CO<sub>2</sub> speciation below  $T_g$ . The CO<sub>2</sub> species reaction involving attachment and deattachment of CO<sub>2</sub> molecules from bridging oxygens does not affect the highly polymerised rigid glass network structure.

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### THE EFFECT OF FeO ON THE SULFUR CONTENT AT SULFIDE SATURATION (SCSS) OF SILICATE MELTS

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At low oxygen fugacities sulfur dissolves in silicate melts as S<sup>2-</sup> by replacing O<sup>2-</sup> on the anion sublattice, as described by the reaction:  $\text{S}^{2-} + 1/2 \text{O}_2 = \text{O}^{2-} + 1/2 \text{S}_2$  suggesting the relationship:  $\log C_s = \log [\text{S}] + 1/2 \log f_{\text{O}_2}/f_{\text{S}_2}$  (1) where [S] is the sulfide content and  $C_s$  is the "sulfide capacity" of the melt, analogous to an equilibrium constant.  $C_s$  is a very strong function of the FeO content of the melt. For most geological applications, the main question of interest is at what point a magma becomes saturated in immiscible sulfide. The equilibrium between silicate and FeS-rich immiscible sulfide melts can be described by the reaction:  $\text{FeO}_{\text{silicate}} + 1/2 \text{S}_2 = \text{FeS}_{\text{sulfide}} + 1/2 \text{O}_2$  For which:  $-\Delta G/2.3RT = \log a(\text{FeS}) - \log a(\text{FeO}) + 1/2 \log f_{\text{O}_2}/f_{\text{S}_2}$  (2) Subtracting (1) from (2) to eliminate  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$  gives:  $\log [\text{S}]_{\text{SCSS}} = \Delta G/2.3RT + \log C_s + \log a(\text{FeS}) - \log a(\text{FeO})$  (3) where  $[\text{S}]_{\text{SCSS}}$  is the "Sulfur Content at Sulfide Saturation". The interesting feature of eqn. (3) is that it shows that the SCSS of a silicate melt depends on its FeO content from two different terms, namely  $\log C_s$  and  $\log a(\text{FeO})$ . The former term has a positive slope versus FeO and dominates at high FeO, whereas the  $\{-\log a(\text{FeO})\}$  term has a negative slope versus FeO, and should dominate at low FeO. The net result is that  $[\text{S}]_{\text{SCSS}}$  should show an asymmetric U-shaped dependence on FeO. To

test this experimentally, we have equilibrated a series of haplobasaltic silicate melts with FeO varying from 0.7 to 30 wt% with immiscible FeS liquid, at 1400°C and 15 kb in the piston-cylinder apparatus, using Re and Pt/graphite capsules. The results confirm the asymmetric U-shaped dependence, with the minimum in SCSS occurring at 4 wt% FeO.

### COMPOSITION OF THE EARTH'S MANTLE

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The composition of the Bulk Silicate Earth (BSE) can be constrained from cosmochemical arguments. The material forming the terrestrial planets derived from a reasonably homogenous solar nebula (whose composition is that of the Sun), but modified by i) various volatility-related chemical fractionation processes, ii) possible fractionation of the major elements Mg and Si, and iii) a cosmochemical metal/silicate fractionation. Superimposed on this was the second, more important, metal/silicate fractionation that resulted in core formation. Further loss of volatile elements may have accompanied accretion and/or formation of the Moon. This complexity means that while it is reasonable to assume that Refractory Lithophile Elements (Ca, Al, Ti, REE, U, etc.) occur in the BSE in solar relative abundances, the abundances of siderophile and volatile elements, and of Mg and Si, must be established empirically. This cannot be done in isolation from an understanding of the structure and evolution of the mantle, which understanding in turn depends on knowing the BSE composition. Hence the problem is decidedly non-linear.

Geophysical observations (densities, seismic velocities, etc.) establish the main features of the Earth's structure, but cannot be converted to composition unambiguously. The abundances of incompatible siderophile and volatile trace elements can be obtained from geochemical arguments, e.g., by identifying constant element ratios in basalts. But the concentration of a major element in a partial melt depends on its chemical potential rather than its concentration in the source, hence inferring mantle abundances of the major elements requires direct study of mantle peridotite. However, all mantle peridotites are victims of a complex history that includes the development of modal inhomogeneity on the cm to 10 m scale, as well as prior episodes of melt extraction, refertilization and metasomatism. The modal inhomogeneity in mantle samples is sometimes overlooked, but may be important in understanding upper mantle processes as well as in reconstructing the BSE composition.

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### PHASE COMPOSITIONS, ELEMENTS PARTITIONING AND LEACH RESISTANCE OF CERAMICS WITH ZIRCONOLITE-PEROVSKITE FORMULATIONS

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Phase compositions, elements partitioning and leach resistance of ceramics in system:  $\text{CaO-Gd}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-ZrO}_2$  along compositional line: zirconolite – gadolinium aluminate with perovskite structure ( $\text{CaZrTi}_2\text{O}_7\text{-GdAlO}_3$ ) are of great importance to select ceramic waste forms for immobilization of a long-lived (rare earth – actinide – zirconium) fraction of high level waste (HLW). We studied ceramics in the series:  $(1-x)\text{CaZrTi}_2\text{O}_7\text{-}x\text{GdAlO}_3$  which were prepared by cold pressing at 200 MPa pre-treated/activated oxide mixtures followed by sintering at 1400 or 1500°C for 5 hours. The samples obtained were examined by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive system (SEM/EDS). Leach resistance was measured using a PCT test. XRD patterns of the samples sintered at both 1400 and 1500°C are very similar. XRD patterns for the sample with  $x=0$  (nominal composition  $\text{CaZrTi}_2\text{O}_7$ ) are typical of zirconolite-2 M variety. The samples with  $x=0.25$  are composed of major zirconolite. The amount of perovskite structure phase is negligible (the strongest peak at 0.271 nm). The samples with  $x=0.5$  consist of major zirconolite and minor perovskite, moreover rare grains of hibonite/lovingite are also present. Prevalence of zirconolite (~70-75%) over perovskite phase (~20-25%) is due to features of elements partitioning among the phases. Zirconolite ( $\text{Ca}_{0.36}\text{Gd}_{0.60}\text{Zr}_{1.12}\text{Ti}_{1.40}\text{Al}_{0.47}\text{O}_7$ ) is capable to incorporate Gd and Al in more extent than perovskite ( $\text{Ca}_{0.64}\text{Gd}_{0.34}\text{Ti}_{0.73}\text{Al}_{0.26}\text{O}_3$ ). At  $x=0.75$  only perovskite content becomes approximately equal to zirconolite and XRD pattern for perovskite phase comes nearer to typical of  $\text{GdAlO}_3$ . Average zirconolite and perovskite compositions are  $\text{Ca}_{0.24}\text{Gd}_{1.00}\text{Zr}_{0.93}\text{Ti}_{1.21}\text{Al}_{0.60}\text{O}_7$  and  $\text{Ca}_{0.31}\text{Gd}_{0.64}\text{Ti}_{0.43}\text{Zr}_{0.06}\text{Al}_{0.55}\text{O}_3$ , respectively. For all the samples studied Gd (trivalent actinides surrogate) and Zr (tetravalent actinides surrogate) leach rates were found to be lower than  $10^{-4}$  g/(m<sup>2</sup>·day) that is typical of zirconolite-perovskite ceramics.

### PHASE TRANSFORMATIONS IN GARNETITE: PRELIMINARY RESULTS FROM LONG DURATION EXPERIMENTS IN MULTIANVIL APPARATUS

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Geophysical data and modelling of mature subduction zones strongly support the occurrence of temperatures less than 1000°C within subducting slabs at mantle transition zone depths. Despite the relevance of this low temperature region most available experimental data on the transformation from eclogite to garnetite, and from garnetite to perovskite-bearing assemblages are restricted to temperatures higher than 1200°C and run durations to a maximum of a couple of hours. Low

temperature experiments in MORB composition performed by Okamoto & Maruyama (2001), as well as experimental data in model systems by Gasparik (e.g. 1996) reveal complexities in such transformations which include the occurrence of Na-rich pyroxenes and/or garnets, the presence of Al-rich and Ca-rich silicates. Long duration experiments (up to ca. 150 hrs) were performed in a multianvil apparatus in order to clarify phase transformations in garnetite facies metamorphism of basaltic systems. 10 mm octahedra, 32 mm cubes with 4 mm TEL, calibrated using Bi, GaAs at room temperature, and coesite/stishovite,  $\text{Mg}_2\text{SiO}_4$  at 1000°C and 1200°C. Different experimental setup (including different gasketing) were tested to achieve stability in long duration experiments. Two bulk compositions representative of the compositional variability within modern oceanic crust (from basalt to troctolite) were modeled in the system  $\text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3 + \text{SiO}_2$  (NCMAS) and NCMAS + FeO. Gels and glasses were used as starting materials. Pressure conditions investigated in preliminary experiments presented here range from 10 to 20 GPa and temperatures from 900 to 1200°C. At ca. 16 GPa in the system NCMAS+FeO garnet, clinopyroxene, an Al-rich phase and stishovite are present. In the NCMAS system, garnet and a MgAlSi phase were recognized, but clinopyroxene is absent. Various structures were found for Al-rich phases (Akaogi, et al. 1999; Irifune and Ringwood, 1993; Hirose et al. 1999); however, it has never been reported  $P <$  lower than 24 GPa in a multi-component system of basaltic bulk.

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### MINERAL CHEMISTRY AND DENSITY OF SUBDUCTED OCEANIC CRUST IN LOWER-MANTLE CONDITIONS

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High-pressure phase equilibria studies provide important constraints on the mineralogy and composition of the earth's interior. However, most of these experimental studies have concentrated upon the magnesium-rich simple system. The attention given to investigating multicomponent systems at very high pressures ( $> 30$  GPa) has been small, by comparison. It is generally acknowledged that the phase change of the basaltic crust plays significant role in mantle dynamics. In the present study, the cell parameters of minerals in the basaltic composition have been determined by a laser-heated diamond anvil cell technique and in situ X-ray method at the synchrotron beam line BL10XU, SPring-8 (Ono et al., 2002). The MORB composition crystallized into an assemblage of Mg-perovskite + Ca-perovskite + stishovite + aluminous phase. This result is generally consistent with those of Kesson et al. (1994), who examined the quenched samples by transmission electron microscopy. The estimated densities of MORB were denser than those of the seismic observations (e.g. PREM). Therefore, the oceanic crust may subduct into the base of the lower

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mantle. In previous studies (Kesson et al, 1998; Ono et al., 2001), it was proposed that the density profile of MORB is expected to intersect the average mantle density in the lower mantle. The density crossover indicates that the subducted slab may stagnate in the lower mantle. Although the mineral volumes were directly determined using in situ X-ray methods in this study, the thermoelastic parameters of minerals of simple compositions were used to estimate the mineral volumes in the previous studies. Therefore, the compositional effect of the thermoelastic parameters (Andraut et al, 2001) should be considered to investigate the densities of high pressure minerals in the multicomponent systems.

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### STABILITY OF Ca - Mg GARNETS AT P=2.5 GPa: AN INSIGHT

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Some experiments in a piston-cylinder apparatus at P=2.5 GPa and T from 800 to 1500°C were performed in order to constrain the P-T stability conditions of Ca-Mg garnets. Starting materials used were a mixture of chemical reagents or of chemical reagents + natural grossular with bulk compositions corresponding to *py25 gr75* (*py*=pyrope; *gr*=grossular) and *py40 gr60*. The products obtained in the whole T range were constituted mainly of pyroxenes with composition lying on the diopside - CaTschermak join. Nonetheless, euhedral garnets up to 80 µm in size and with a pyrope content up to 10 mol.% were also present among the products of the *py25 gr75* runs at all T and of the run performed at the lowest T (800°C) using *py40 gr60* starting material. Variable amounts of glass were also ubiquitous.

These experimental results show that under the investigated P-T conditions mixed pyrope-grossular garnets are not stable with respect to a clinopyroxenes containing mixture, at least in the middle part of the join. In fact, the stability of the nesosilicates is limited by the presence of pyroxenes whose crystallisation is exclusive when relatively Mg rich starting materials are used. On the other hand, in agreement with the intrinsic stability of Ca-Mg garnets, some evidences in literature indicate that a wider solubility among pyrope and grossular can be attained either at higher pressures and/or at lower temperatures where the reduced Al-Si vicariance inhibits pyroxene crystallisation, thus enhancing garnets stability.

In order to increase the maximum pyrope content in grossular, in some runs the investigated system was chemically complicated adding Cr and Na (5 wt.% of oxides) to the *py25 gr75* starting material. While the pyrope contents of garnets from Cr-

doped charges are in the range 12-14 mol.%, the presence of Na did not affect the chemical composition of garnet but stabilised melilites and merwinites.

### DEPROTONATION AND ORDER-DISORDER REACTIONS AS A FUNCTION OF TEMPERATURE IN A PHENGITE 3T (CIMA PAL, WESTERN ALPS) BY NEUTRON DIFFRACTION AND MÖSSBAUER SPECTROSCOPY

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Neutron powder-diffraction (at 293, 423, 573, 673 and 873 K and again at 293 K; ISIS, HRPD) and Mössbauer spectroscopy data were collected on the title phengite. It has composition  $(K_{0.94}Na_{0.02})\Sigma 0.96 (Al_{1.43}Mg_{0.33}Fe_{0.25})\Sigma 2.01 (Si_{3.47}Al_{0.53})\Sigma 4O_{10}(OH)_2$  and occurs with an almost isochemical  $2M_1$  polytype in a metamorphic dyke formed in the Sesia zone at quartz-eclogite-facies conditions (T ~ 850 K and P ~ 16-18 kbar; Ivaldi et al., 2001). Order is observed at room temperature in both tetrahedral (Si fully occupies T1) and octahedral (Al almost fills M2) sites. Upon heating, deprotonation, partial Fe oxidation and inter-site cation re-ordering reactions take place. The neutron data show a partial loss of protons upon heating and, together with the Mössbauer data, supports the existence of a reaction  $2(OH)^- + 2Fe^{2+} \rightarrow 2O^{2-} + 2Fe^{3+} + H_2$  paralleled by a re-ordering of the octahedral cations. Precisely, Al moves by (0.1 atoms from M2 to M3 site, and is replaced by Mg and Fe; Fe<sup>2+</sup> and Fe<sup>3+</sup> occupy different M-sites, whereas Fe<sup>2+</sup> was partitioned on two sites before heating (one site shared with Fe<sup>3+</sup>).

The cation ordering in the tetrahedral and octahedral sites confirms neutron-diffraction results obtained by Pavese et al. (1997, 2000, 2001) on a phengite 3T from the coesite-bearing outcrop of the Dora Maira massif. The absence of a similar deprotonation process in the Fe-bearing  $2M_1$  phengite studied in a similar neutron-diffraction experiment by Pavese et al. (1999) may be tentatively related to the presence of only one independent occupied M-site in the monoclinic polytype. Whereas a different re-ordering of the (oxidised) octahedral cations can balance a proton loss in 3T, the constraint disorder of these cations in  $2M_1$  makes deprotonation (actually dehydroxylation) a phase-transition process (Comodi & Zanazzi, 2000; Guggenheim et al., 1987).

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### FORMS OF TRANSFER OF AG AND SB AT THE Ag-Sb HYDROTHERMAL DEPOSITS

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Antimony is important ore-forming element of the Ag-Sb deposits of economic interest. Antimony in the ores is precipitated not only as sulfides (stibnite), but as sulfosalts of Cu, Ag, Pb (tetrahedrite, chalcocite, gudmundite) and native antimony. The presence Sb and Ag in Ag-Sb deposits pose a problem of coexistence of these elements in hydrothermal solution. To solve this problem, the calculations performed for thermodynamic data base forming separately for Ag and Sb. Thermodynamic parameters are calculated for different Sb complexes (chloride, hydroxide, sulfide and mixed) at 25-250°C on the base of analysis of literature information on solubility of stibnite in water solution. Major chemical forms of Sb in concentrated and diluted chloride solutions are: chloride –  $\text{SbCl}_4^-$ , sulfide –  $\text{SbS}_2^-$ ,  $\text{Sb}_2\text{S}_4^{2-}$ ,  $\text{HSb}_2\text{S}_4^-$ , hydroxide –  $\text{Sb}(\text{OH})_3$ , and mixed  $\text{SbCl}_3(\text{OH})^-$  complexes. Computer modeling data obtained suggest high Ag and Sb solubility in concentrated chloride solutions (up to 50-100 g/kg); main Ag species in these solutions are chloride complexes, which change each other during evolution of hydrothermal fluid ( $\text{AgCl}_4^{3-} \rightarrow \text{AgCl}_3^{2-} \rightarrow \text{AgCl}_2^-$ ). Considerable differences in the composition of fluids, their evolution in space and time determine different behavior of Ag and Sb in hydrothermal process, forms of migration and factors of deposition of different mineral parageneses. Main factors of formation of different Sb mineral parageneses are: the ratio of the major ore elements in solution (changing during ore-forming process), and red-ox conditions of ore deposition depending on localization of siderite veins in deep levels of the deposit. We interpret that these mineral parageneses are the products of single ore-forming process with different ore types forming on different deep levels of the deposit. Work is supported by the Russian Foundation (grant No 02-05-64795).

### KINETICS OF THE COESITE-QUARTZ TRANSITION: APPLICATION TO THE EXHUMATION OF ULTRA-HIGH PRESSURE ROCKS

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The survival of coesite as inclusions in ultra-high pressure (UHP) metamorphic rocks has important implications for the exhumation process of subducted rocks. The Pressure-

Temperature-time (P-T-t) paths of these UHP units during their ascent to the Earth's surface must allow the survival of this relict mineral. Thus, we have studied *in situ* the kinetics of the coesite-quartz phase transition by X-ray diffraction, in the 2.1-3.2 GPa, 500-1010°C pressure-temperature range. Analysis of the kinetic data within the Cahn's model (model of nucleation and growth at grains boundaries) shows that prograde and retrograde reactions have different kinetics. The quartz->coesite transformation is one order of magnitude faster than coesite->quartz. Reactions proceed by high nucleation rates, so that the overall kinetics are controlled by growth processes. Growth rates are calculated by fitting the data to the Turnbull's equation. For the coesite->quartz transition, growth rates display an exponential dependency on temperature. This enables us to calculate the activation energy for transition: 163 kJ.mol<sup>-1</sup>. This kinetic law, associated with an 'inclusion in a host' elastic model, enables to follow the size of a coesite grain during exhumation. Retromorphosis percentages calculated from the exhumation paths of three UHP units: Monts du Lyonnais (French Massif Central), Dora Maira (Western Alps) and Kaghan Valley (Pakistan), are in agreement with those measured on natural samples. These models show also that above 400°C retromorphosis is mainly controlled by the 'pressure vessel' role of the host mineral, whereas kinetics is the controlling factor below this temperature. Finally, the influence of the P-T paths shape and exhumation rates upon the transformation percentage has been tested in order to use the retromorphic rate of natural samples for P-T-t paths construction.

### UNIQUE GAS HIGH PRESSURE APPARATUS TO STUDY FLUID - MELTS AND FLUID - SOLID - MELTS INTERACTION WITH ANY FLUID COMPOSITION AT TEMPERATURE UP TO 1400°C AND AT PRESSURES UP TO 5 kb

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A unique gas high pressure apparatus have been recently developed to study of the rheological and physical-chemical properties of fluid-bearing melts as well as the fluid - melts and fluid - solid - melts interaction at the temperature up to 1400°C and at the pressure up to 5 kbars. An apparatus involves a vertically or horizontally working internally heated vessel (IHPV) and a two-stage system for compressing vessel gas (high purity Ar). The IHPV is equipped with internal device of Persikov (1991) which was now modified. The device involves both a special piston-cylinder type separator-equalizer which ensured gradient-free Ar pressure on the fluid and on melted or solid sample and a sample holder (molybdenum tube); the free volume of this tube is filled by sapphire cylinder which is placed into sealed Pt capsule when H<sub>2</sub>O or CO<sub>2</sub> are used as fluid phase. The separator-equalizer was located in the cold zone of the IHPV outside from the furnace and the sample holder was located in the hot zone of the furnace, where the thermal gradient could be minimized to less than 5°C by adjusting the two windings of the furnace. Temperature was recorded by three sheathed platinum-rhodium or tungsten-rhenium thermocouples accurate to less than ~ 5°C, calibrated at 1 kbar Ar pressure against the melting point of Au. Pressure was recorded by a Bourdon-tube gauge accurate to ~ +1%.

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Experiments can be really conducted with any fluid composition such as Ar, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>O-CO<sub>2</sub>, H<sub>2</sub>O-H<sub>2</sub> mixtures as well as with any gas mixtures and with any aqueous solutions. The inner surface of the sample holder was covered by Pt when a water- or CO<sub>2</sub>-bearing fluids are used in the experiments.

Using this apparatus, the viscosity of silicate and carbonated melts under high CO<sub>2</sub>, Ar and water pressures as well as of the mafic silicate melts - dolomite xenoliths interaction under Ar, CO<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub>-H<sub>2</sub>O mixtures pressures up to 4 kbars and in the temperature range from 1000° to 1350°C have been recently studied.

(This work was supported by the RFBR, grant No 00-05-64413)

### THE HIGH CO<sub>2</sub>, Ar AND H<sub>2</sub>O PRESSURE EFFECTS ON MELT VISCOSITY IN THE JOIN Ab - Di - Na<sub>2</sub>CO<sub>3</sub> IN A WIDE TEMPERATURE RANGE FROM T<sub>m</sub> TO T<sub>g</sub> AT FLUID PRESSURES UP TO 4 Kbars

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A unique gas high-pressure viscometer and a creep apparatus have been used to study the viscosity of near-liquidus and supercooled silicate melts in the join Ab - Di - Na<sub>2</sub>CO<sub>3</sub> in a wide temperature range from 490°C to 1400°C at atmospheric and under high CO<sub>2</sub>, Ar and H<sub>2</sub>O pressures up to 4 kbars.

New peculiarities of the rheology and structure of silicate and carbonated melts have been established. The viscosity of all studied melts regularly and dramatically decreases with increasing of melt basicity, temperature, water pressure and the amount of chemically dissolved water (hydroxyl OH<sup>-</sup>) and carbon dioxide (CO<sub>3</sub><sup>2-</sup>) which are stabilized into melts structure under high H<sub>2</sub>O and CO<sub>2</sub> pressures. For example, the viscosity of near-liquidus melts at T=1300°C and P=1 kbar decreases from 7.94E+05 poises (polymerized albite melt, 100NBO/T = 0.35) to 31.6 poises (depolymerized Ab<sub>35</sub>Di<sub>35</sub>NaC<sub>30</sub> melt, 100NBO/T = 153). The viscosity of supercooled melts of the same compositions decreases from 1.0E+13 to 1.99E+05 poises, respectively (T= 800°C, P = 1 atm).

The temperature dependence of viscosity of all investigated melts in high-temperature range (1100° - 1400°C) is Arrhenian with a constant value of preexponent constant in Arrhenius-Frenkel equation. This provided new values of activation energy of viscous flow - an important rheological and structural-chemical parameter. The low-temperature data as well as the temperature dependence of viscosity in full temperature range (490°C - 1400°C) have been fitted with the empirical Tammann-Vogel-Fulcher equation. The viscosity and glass transition temperature of all studied melts dramatically decrease with the addition of water (hydroxyl OH<sup>-</sup>) and carbon dioxide (CO<sub>3</sub><sup>2-</sup>) This effect decreases with increasing melt

basicity or degree of depolymerization. The same effects of chemically dissolved water and carbon dioxide on melts viscosity in high temperature range have been established.

The viscosity of all melts studied slightly decreases with increasing of Ar and CO<sub>2</sub> pressures (just a few tens%) but extremely large decreases under high water pressure especially for polymerized melts. Depolymerized compositions show much smaller, but still significant, decreases. For example, the viscosity of albite melt decreases by about three order of magnitude and the viscosity of depolymerized Ab<sub>25</sub>Di<sub>75</sub> melt decreases by about one order of magnitude under P=1 kbar and at T=1300°C.

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### THE EFFECTS OF PERALKALINITY ON THE STRUCTURAL ENVIRONMENT OF Nb AND Ta IN SILICATE GLASSES

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Niobium and Ta, elements increasingly sought after for their use in the aerospace and electronic industries because of their high superconductivity and resistance to corrosion, are important elements in many granitic and alkaline igneous rocks. In order to help elucidate the processes by which Nb and Ta are concentrated into economically-viable deposits, we must first understand their crystal chemistry, in particular their role in the magma from which they are derived. The local coordination environments of Nb<sup>5+</sup> and Ta<sup>5+</sup> in seven synthetic and natural glasses, along with a suite of model compounds, have been studied, for the first time, by X-ray Absorption Fine Structure (XAFS) spectroscopy. High-resolution Nb K-edge and Ta LIII-edge data were collected at the Stanford Synchrotron Radiation Laboratory (Stanford University, USA) at ambient temperature and pressure. Data were collected for both natural volcanic glasses (e.g. rhyolite, pantellerite and trachyte) and a suite of water-saturated haplogranitic glasses synthesized at 800°C and 2 kbars. Compositions of the synthetic glasses range from peralkaline (alkalinity index, AI, = (Na+K)/Al = 1.56) to peraluminous (AI = 0.82) with Nb contents ranging from 1300 to 12000 ppm and Ta contents ranging from 1755 to 10400 ppm. In addition, XAFS data were collected on selected natural Nb- and Ta-bearing oxides and silicates with well-characterized crystal structures to be used as model compounds for interpretation of the XAFS glass data. Results suggest that Nb and Ta behave similarly to Zr in glasses. XAFS features at the Nb K-edge and Ta LIII-edge suggest that both elements reside predominantly in 6-coordinated sites, in agreement with coordinations observed in the model alkali niobosilicate minerals. The local structure around Nb and Ta in the natural volcanic glasses is similar to that observed in the compositionally-similar synthetic glasses. In addition, the local distortion environment around Nb appears to be positively correlated with peralkalinity such that increased site distortion is observed with increasing alkali content (increasing AI). These structural para-

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meters will be further used, in conjunction with geochemical and petrological evidence, to discuss the crystal-chemistry of Nb and Ta in magmatic systems.

### THE SOLUBILITY OF Pt IN LIQUID Fe-SULFIDES

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The partitioning of Pt between liquid sulfides with approximately stoichiometric FeS and PtFe alloys was experimentally studied. Experiments were conducted in corundum crucibles enclosed in sealed quartz vials heated to 1100, 1200 and 1300°C. Run products, PtFe-alloys and sulfides exsolved to FeS and PtFe-alloys, were analyzed with the electron microprobe (EMP). In sulfides with S, ranging from >45 to 53 atm%, PtS appears to be the stable Pt-species. Metal/sulfide weight ratios of Pt between 3 and 1400 were found. By recalculating the data to unit Pt-activities in metal surprisingly constant Pt contents in sulfides were found. Thus  $0.25 \pm 0.22$  at% Pt, or  $0.53 \pm 0.22$  wt% Pt can be dissolved at unit Pt-activity in liquid sulfides, independent of temperature. At lower S-contents Pt-metal and/or PtFe-alloys dominate the Pt-species in sulfides. A comparison of Pt solubilities in sulfides with Pt solubilities in silicates allows the calculation of sulfide/silicate partition coefficients,  $D_{\text{sil/sul}}(\text{Pt})$ . By dividing the solubilities in sulfides obtained here with those in silicates as measured by Borisov and Palme (1997) yields very high  $D_{\text{sil/sil}}(\text{Pt})$ , around  $5 \cdot 10^9$  at 1100°C,  $10^9$  at 1200°C and ca.  $4 \cdot 10^8$  at 1300°C. These partition coefficients are much higher than those experimentally determined. The most likely reason is the formation of Pt-rich micronuggets observed in the experiments of Borisov and Palme (1997) and Ertel et al. (1999). Because Pt or PtFe-alloys are present in partition experiments but generally not in natural environments it is likely that the experimentally determined sulfide/silicate partition coefficients cannot be applied to natural systems.

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Ertel W, O'Neill HStC, Sylvester PJ, & Dingwell DB, *Geochim. Cosmochim. Acta*, **63**, 2439-2449, (1999).

### PHYSICAL PROPERTIES AS METRICS OF WELDING INTENSITY

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Welding intensity in pyroclastic deposits represents the aggregate effects of emplacement temperature and overlying load. However, vertical profiles of welding intensity contain implicit information on welding processes, including rheological properties of pyroclastic deposits. Ultimately, the geometry of these profiles can be inverted to establish both the mechanisms and timescales of welding processes. Here we compare a variety of physical properties as metrics of welding intensity. Our samples (n=100) derive from 4 drill cores (19-22 m) through Unit 4 of the Tshirege Member of the Bandelier tuff (Broxton

and Reneau, 1995). Each sample was measured for density and porosity and select samples were measured for point load strength (PLST) and uniaxial compressive strength (UCS) (Fig. 1). Eccentricity and orientation of populations of pumice clasts and shards in individual samples were also measured as estimates of integrated strain. The individual metrics show systematic variations with depth. Density, strength (UCS and PLST), and shard alignment show well-developed coincident maxima at 3-6 m (15% to 30%) above the base; porosity values define a minima at the same position. To a first order, each metric records the same peak in welding intensity, although gradients in metrics show subtle differences that must relate to the welding process. Density is the best for first order quantification (convenient and precise) but can be adversely affected by variations in crystal content. Rock strengths (PLST and UCS) are also effective in mapping welding intensity. PLST is easily done in the field and relates to the more rigorous UCS by a simple conversion factor (~9.62). Fabric measurements of pumice and shards are time consuming but give an unambiguous record of integrated strain and directly relate to viscous deformation processes. Ongoing analysis is focused on identifying and interpreting differences in gradients of welding inten-

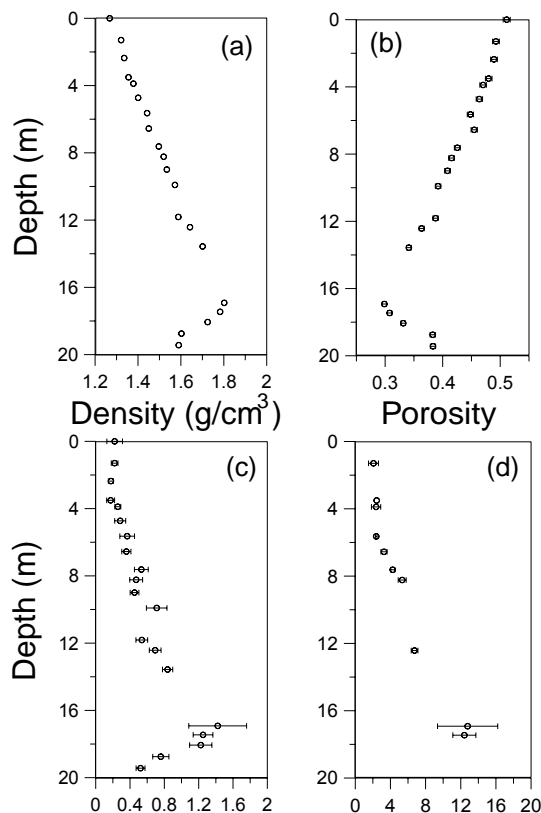


Figure 1: Metrics versus depth in selected drill core. All uncertainties based on replicate measurements: a) uncertainty ( $2\sigma$ ) smaller than symbols; b) and c) uncertainty  $2\sigma$ ; d) uncertainty  $1\sigma$ .

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### THE RHEOLOGY OF WELDING: INSIGHTS FROM EXPERIMENTAL DEFORMATION STUDIES

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The rheological behaviour of pyroclastic deposits during welding is incompletely understood and is based on a surprisingly small number of experimental studies (Table 1). In this paper, we review results from these pioneering studies and present new experimental results obtained from the Large Sample Rig (LSR) at the University of British Columbia. These results represent the first attempt to provide constitutive relationships for the compaction and welding of hot pyroclastic mixtures. Previous experimental studies by Friedman et al. (1963) and Bierwirth (1982) used well-controlled experimental conditions. Experiments were run on small (1 cm thick) samples of ash/crystal mixtures under constant load. They established minimum welding temperatures between 600 and 700°C under maximum loads of 3.6 MPa (36 bars). Both studies produced interesting but scattered results. The data have been used in subsequent modeling of welding processes (Riehle, 1995). However, these data are not sufficiently comprehensive, nor coherent enough to fully describe the rheology of these pyroclastic mixtures. Our goal is to provide constitutive relationships between material properties, temperature, load and strain rate for pyroclastic material undergoing welding. In addition, we will establish the deformation mechanisms and geometric changes accompanying the welding process. The experimental work at UBC uses a constant-displacement-rate rig with a sample size of 5 cm x 10 cm. Our preliminary experiments use homogenous glass beads, volcanic ash, and cores of pumiceous dacite. Temperatures utilized for our experiments range from below, at, and above calorimetric glass transition temperatures. From these experimental results we intend to develop a rheological model that will: a) predict distributions of welding in pyroclastic deposits; b) establish timescales and temporal relationships of cooling, welding, compaction and devitrification of pyroclastic deposits; and c) permit reconstruction of paleothicknesses of pyroclastic deposits.

Table 1: Summary of previous experimental welding studies (see references).

Reference	Size <sup>1</sup> (mm)	# <sup>2</sup>	$\Delta T^3$ (°C)	$\Delta Load$ (MPa)	Pfluid (MPa)	$\Delta t^4$ (hrs)	$T_{min}^5$ (°C)
Taneda (1957)	*	*	600-1200	0.1-0.5	Dry	1.0-1.5	920
Smith et al (1958)	5 x 10	*	535-735	0.7-3.7	0.4-2.1	10-120	<535
Boyd (1961)	2 x 4	12	550-740	2.8-5.2	hydrous	72-430	590-620
Friedman et al (1963)	5 x 10	27	400-850	1.5-3.6	0-6.9	10->1000	635
Yagi (1965)	3 x 15	23	580-622	none	0.3-2	16-45	585
Bierwirth (1982)	9 x 22	*	650-800	0.72-3.6	hydrous	17-70	650
This study (projected)	50 x 100	>25	400-750	---	0-1.5	1.0-24	<600

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Yagi, K, *Bulletin of Volcanology*, **29**, 559-572, (1965).

### CHARACTERIZATION OF TRACE Nd AND Ce SITE PREFERENCE AND COORDINATION IN NATURAL GARNETS: A COMBINED X-RAY DIFFRACTION AND HIGH-ENERGY XAFS STUDY

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The identification of the crystal-chemical parameters controlling trace-element partitioning between minerals and silicate melts is a topic of remarkable interest. Garnets represent an important group of rock-forming minerals in this regard, able to incorporate several trace elements commonly used in geochemical modeling. For these reasons, aluminosilicate garnets have received much attention, regarding either their complex crystal-chemistry, or thermodynamic properties, or trace-element behaviour. Despite the importance of the geochemical behaviour of REE in garnets, little work has been done to decipher their site preference and local coordination in trace or minor amounts. Conventional diffraction methods cannot provide direct information at such low concentration levels. In this work natural melanite garnets from carbonatitic rocks have been studied by a multi-technique approach based on both experimental (chemical, diffractometric and spectroscopic) methods and full-multiple scattering calculations of the X-ray absorption near edge structure. In particular, the site location and geometry of trace amounts of neodymium (from 176 to 1029 ppm) and cerium (791 ppm) in natural garnets have been studied by fluorescence-detected X-ray Absorption Fine-Structure Spectroscopy (XAFS) at high energy. The measurements, done at both Nd K- (43569 eV) and Ce K- (40443 eV) edges, demonstrate that, in all the samples, the trace elements are located in the dodecahedral X site. The local geometry around the two rare earth elements is compatible with their ionic radius and is compared with that of Ca, the major element at the X site, as determined by single-crystal X-ray diffraction data. This work represents the first example of direct investigation of trace-level REE coordination in natural garnets, and confirms the great relevance for the Earth Sciences of the use of fluorescence XAFS at high energy.

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### GENESIS OF THE POLLYMETALLIC ORE DEPOSIT GHEZURI, ROMANIA - CONCEPTUAL MODEL

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The geologic features of the mineralized structure Ghezuri suggest a hypoabasic intrusion represented by microdiorites with pipes intruded in the microgranodioritic porphyritic volcano. Related to it, a lead-zinc mineralization vein system has been formed. The geologic and metallogenetic context allowed the development of the following metallogenetic scenario (Buia, 1998): During the end of pontian a subvolcanic body has been intruded along a faulty structure concordant to the NNW-SSE direction. Lately, it has been penetrated by a microdioritic intrusion related to postmagmatic fluid mineralizations containing mineralizers (OH<sup>-</sup>, H<sub>2</sub>O, CO<sub>2</sub>, HCl) migrating upwards along the two faults. In the meantime, the three water types (metamorphic, connate and meteoric) have been circulated. The hydrothermal solutions generating the polymetallic deposits from Ghezuri have an important content in connate water. The intense vaporization of the fractures and aquifers water increased the external pressure, suppressing the internal one. Due to these conditions, the water from the surrounding strata is absorbed by the ascending magma. The water takes from the magma and the surrounding rock components that are deposited lately. The mixture occurred probably on the upper parts, at the level of the sedimentary intrusion, between the intrusive microgranodioritic body and the hyaloandesitic pyroxenic lava flows, fact argued by the massive galena deposition below this level. During the primary state, the internal pressure of the lava and the separate solution is greater than the external pressure, so the infiltrating water can not penetrate the magma. The main deposition mechanism of the elements from solutions is represented by filling the vacuoles, the metasomatism being active only in the contact zones. The reaction of the mineralizing solution with the host rocks produced the saturation and the deposition of the metallic components. The Ghezuri mineralization, by its characteristics can be grouped in the epithermal type mineralization, the law-sulphidation facies, with basic metals and silver sulphides, formed at high temperatures (Popescu, 1885).

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### ULTRASONIC EXPERIMENTS IN AN INTERNALLY HEATED GAS-PRESSURE VESSEL UNDER ELEVATED P-T CONDITIONS

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Dehydration reactions and partial melting are important to understand geodynamic processes and the evolution of the Earth's crust. Ultrasonic experiments are used to study these processes in the laboratory under in-situ conditions. Both, dehydration reactions and partial melting often occur at temperatures and pressures exceeding the limits and conventional ultrasonic experiments. We will present an experimental setup to determine sound wave velocities of rocks at elevated pressures and temperatures, especially designed to measure sound wave absorbing materials, such as partially molten rocks. The sample size for ultrasonic experiments is predefined by the grain size of the sample and the wavelength of ultrasonic waves. The wavelength should be at least 3-5x of the maximum grain size and the diameter of the sample should be at least 2.5 times of the wavelength. The absorption of ultrasonic waves strongly increases with increasing frequency. As a consequence, low frequencies are required to study sound-wave velocities of strongly absorbing materials. However, at low frequencies bigger samples are a prerequisite to measure P-wave velocities. An internally heated gas-pressure vessel (Harwood) for pressures up to 1 GPa is modified to measure simultaneously P- and S-wave velocities on cylindrical samples with a diameter of 29.5 mm and a length of 25 mm. To avoid uncontrolled degassing, the sample is encapsulated in a Ni- or Ni-alloy tube. Transducers are glued on ceramic buffer rods at their cold-ends. Sound velocities were deduced from travel-times measured both in pulse echo and pulse transmission mode. The measuring scheme allows correcting for the temperature and pressure depending travel-time through the buffer rods. We will present experimental results up to 1 GPa and temperatures exceeding 900°C. Some data on amphibolites and serpentinites will be discussed.

### PHASE TRANSITION IN THE MINERAL TITANITE CaTiOSiO<sub>4</sub> UNDER HIGH PRESSURE - A X-RAY SINGLE CRYSTAL STUDY BETWEEN 1 BAR AND 10 GPa

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The monoclinic mineral titanite is a common accessory in many acid and intermediate igneous rock, gneisses, mica schists and amphiboles. The structure of titanite is characterized by corner-linked chains of TiO<sub>6</sub> -octahedra parallel to [100] connected via isolated SiO<sub>4</sub> -tetrahedra. CaO<sub>7</sub> polyhedra build chains along [101]. The octahedral Ti atoms show typical out-of-center distortions. Its behavior under high pressure can give information about the driving forces of the phase transition in ABOCO<sub>4</sub> silicates. The behavior of titanite under high pressure has been studied up to 7 GPa and 850 K with powder diffraction, respectively (Angel et al., 1999; Bismayer et al., 1999;

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Kunz et al., 2000) and several phase transitions were found. The structure remains monoclinic but changes from  $P2_1/a$  to  $A2/a$  at 3.6 GPa.

Here we present evidence for a new  $A2/a - A\bar{1}$  phase transition at around 10.5 GPa. At this pressure the cell metric decreased to the following values:  $a = 6.829(4)\text{\AA}$ ,  $b = 8.594(2)\text{\AA}$ ,  $c = 6.352(1)\text{\AA}$ ,  $\alpha = 90.18(2)^\circ$ ,  $\beta = 112.78(2)^\circ$ ,  $\gamma = 89.70(2)^\circ$  and  $V = 343.7(2)\text{\AA}^3$ .

Structure refinement results of high-pressure X-ray single crystal studies from ambient conditions to 10 GPa will be presented. In addition, we compare the titanite results to the phase transition in the topological identical malayaite  $\text{CaSnSiO}_4$  at 5 GPa, where a similar phase transition has previously been observed (Rath et al., 2002).

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### ELASTICITY OF SODIUM-RICH MAJORITE

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Majoritic (aluminum-deficient) garnet is a major component of the upper mantle and the Transition Zone. Therefore the knowledge of the elasticity of majoritic garnets is extremely important for understanding the composition and behaviour of this region, as well as subduction-related processes. The variation of elastic properties within the pure Mg pyrope - majorite solid solution is well constrained. However, the effect of large cations on the elasticity of majorite-garnet solid solutions is poorly determined, even though large cations such as Na and Ca are important constituents of any realistic petrologic model of the Earth's mantle. In particular, oceanic crust subducted to transition zone depths will transform to an assemblage in which Na-rich majorite is an abundant phase.

Here we present the first Brillouin measurements on the elasticity of majorite with a composition on the enstatite-jadeite join. A polycrystalline sample with a composition of 50 mol% enstatite - 50 mol% jadeite (En50-Jd50) was synthesised in a large volume press at 22 GPa and 2000°C at the Center for High Pressure Research, Stony Brook. An x-ray spectrum of the sample indicated the presence of a majorite phase only, and no peaks of a second phase were observed.

The bulk modulus ( $K_s = 171.6(35)$  GPa) of En50-Jd50 majorite is characteristic of other majorites and aluminous garnets, indicating that the bulk modulus is remarkably insensitive to

composition. However, the shear modulus increases significantly with increasing Na content, reaching a value of 103.5(20) GPa for En50-Jd50 majorite. This shear modulus is over 20% higher than the shear modulus of En100 majorite. An analysis of available elasticity data on pyroxenes and majorites indicate that the shear velocity jump associated with the pyroxene-majorite transition will dramatically increase with increasing jadeite content of the system.

### NETWORK MODIFIER AND TRACE ELEMENT DIFFUSION IN DIOPSIDE LIQUID AT HIGH PRESSURE

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Many models of core formation in the early Earth have assumed the presence of a global magma ocean, which would have allowed chemical equilibration between metal and silicate to depths of up to 1000 km. The kinetics of equilibration would depend to a large extent on the transport properties of the silicate and metal liquid systems, for example, ionic diffusion and viscosity. It has been previously proposed that the diffusion of network modifying ions and trace elements in silicate liquids will be inhibited by pressure. Ca and Mg self-diffusion and Co and Ni trace element diffusion in diopside ( $\text{CaMgSi}_2\text{O}_6$ ) liquid have been determined at high pressure. Diffusion couples enriched in  $^{44}\text{Ca}$  and  $^{25}\text{Mg}$  and doped with trace quantities of CoO and NiO were pressurised and heated in a multianvil apparatus. Experimental charges were subsequently analysed by ion microprobe at the University of Edinburgh and the resulting profiles fitted using a non-linear least-squares approximation for self-diffusion between two finite bodies. Quantitative results for all elements from 4 to 8 GPa confirm a negative activation volume of  $-2\text{ cm}^3/\text{mol}$  and preliminary results indicate a continued increase in diffusivity to 15 GPa. This behaviour is in contrast to that of network forming ions Si and O, which show a positive activation volume to 10 GPa after which there is a change of slope and an increase in diffusivity to 17 GPa. It can be concluded that there is little diffusive coupling in diopside liquid, in this pressure range, between the network formers and modifiers or between the network formers and trace elements Co and Ni.

### RHEOLOGICAL CONSTRAINTS ON MELT MIGRATION

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The chemical differentiation of the Earth is related to flow of melts through rocks transporting heat and material and altering composition. Interpreting geochemical analyses of rocks depends on how the composition of the melt is affected by the migration processes. Substantial experimental effort was invested into constraining theoretical models of the relationships between deformation and melt extraction by laboratory studies on permeability and matrix rheology of partially molten aggregates. From an experimental point of view, migration of basic melts in the upper mantle largely responsible for the formation of oceanic crust at mid-ocean ridges is distinct from

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transport of felsic magmas involved in the development of continental crust. The pore space of partially molten peridotites is regular and interconnected. Constraints on the relationship between permeability and porosity/melt fraction can be derived from theoretical models that assume equal-sized, texturally-equilibrated grains. In contrast, the partial melt resides in irregular, often angular and isolated pockets in granites. For fluid-filled aggregates, strength depends on effective pressure, the difference between matrix and pore fluid pressure. Permeability determines whether a constant pore pressure can be maintained during deformation. Compaction rates measured for partially molten peridotites at controlled melt pressure provide estimates of the permeability and bulk viscosity of the Earth's upper mantle that can be used to calculate compaction length, the characteristic length scale of continuum mechanical models. Triaxial deformation experiments on partially molten peridotites revealed that shear viscosity experiences a modest reduction for melt fractions  $<0.05$ . The reduction is significantly greater at larger fractions related to excessive, loading-related wetting of two-grain boundaries. At the comparatively lower solidus temperatures of granites, feldspar deforms by a combination of brittle processes and low-temperature plasticity. Consequently, dilation rate becomes important leading to a rate dependent critical melt fraction.

#### HIGH PRESSURE PHASE RELATIONS AND PHYSICAL PROPERTIES OF MATERIALS IN THE EARTH'S MANTLE

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Phase relations are essential for understanding of the structure of planetary interiors and the differentiation of planetary bodies. The knowledge of the stable phases and of their elastic properties allows to decipher the seismic profile of density, compressional and shear wave velocities in terms of the constitutive mineralogical and liquid phase assemblages and to constrain the bulk chemistry and thermal state, provided the physical properties of interest are measurable under the relevant conditions. Over the past three decades, there have been a lot of improvements in that research field that now allow to measure or simulate the structure and properties of geomaterials at high pressures and temperatures. We focus here on developments in experimental techniques for in situ measurements applied to systems allowing to predict the mineralogical composition of the Earth's mantle.

Examples are given to show that integrated studies of a given material (major ferro-magnesian silicates, carbonates) with room-temperature X-ray diffraction for equation of state determination (RTEoS), HP-HT EoS determinations, HP-HT Raman spectroscopy and vibrational modeling of the thermal contribution to EoS and free enthalpy, allow to completely describe its thermodynamics and to model its phase relations. The required degree of precision for accurate modeling in the mantle pressure range is discussed in order to emphasize the new developments required in physical property measurements at HP-HT.

#### ROLE OF Si/Al RATIOS ON THE CELL PARAMETERS OF SYNTHETIC LEUCITE ANALOGUES

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The aim of this work was to evaluate the role of Si/Al ratios on the cell parameters of synthetic leucite analogues: analcime ( $\text{NaAlSi}_2\text{O}_6\text{H}_2\text{O}$ ), pollucite ( $\text{CsAlSi}_2\text{O}_6$ ) and Rb-leucite ( $\text{RbAlSi}_2\text{O}_6$ ). This study was based on systematic investigations of the variation of Si/Al ratios on stability domains of leucite analogues and the deviation from stoichiometric Si/Al ratio in the analcime – pollucite and analcime – Rb-leucite solid solutions. On analcime, cell parameters are indirectly related to the Si/Al ratios. Analcimes with  $\text{Si/Al} < 2.0$  presented nepheline like addition phase, even though at analcimes with  $\text{Si/Al} > 2.0$ , albite was detected. In leucite analogues, cell parameters are independent of Si/Al ratios. At  $600^\circ\text{C}$  - 5.5, 2.0, 1.0 kbar, all pollucites studied yield a similar value of cell parameter. Cs-nepheline was observed like subordinated phase on  $1.15 < \text{Si/Al} < 1.7$  pollucites and quartz on  $2.69 < \text{Si/Al} < 3.0$  pollucites. On Rb-leucite, at 3.5 kbar -  $600^\circ\text{C}$  and  $900^\circ\text{C}$ , all  $1.15 < \text{Si/Al} < 2.67$ . Rb-leucites presented identical cell parameters. An Rb-feldspar phase co-exist with the Rb-leucite for  $\text{Si/Al} \sim 2.12$  until  $\sim 2.67$ . The Rb-feldspar presented the same cell parameters than the natural Rb-feldspar, rubicline (Teerstra et al., 1998). Analcime – pollucite Si/Al ratios yielded a significant deviation from 2.0 stoichiometric value, and could reach 2.41 with increasing amounts of Cs in the join. However, analcime – Rb-leucite Si/Al ratios are not affected by the variation of amounts Rb. At both solid solutions, the cell parameters decrease with the increase of heavy cations amounts. In analcimes S sites are filled up by Na, while they are void in leucite analogues. T sites Al occupation is linked to the occupation of S sites, then only analcimes presented a direct relationship between Si/Al ratios and cell parameters.

Teerstra DK, Cerny P, Hawthorne FC, Pier T, Wang L-M, Ewing RC, 1998. Rubicline, a new feldspar from San Piero in Campo, Elba, Italy. *Am. Mineral*, **83**, 1335-1339.

#### CRYSTALLISATION PROCESSES OF CALCIUM ALUMINOSILICATES NEAR THEIR GLASS TRANSITION

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Although crystallisation in silicate melts has been the subject of numerous studies, the chemical and structural factors affecting nucleation and crystallisation are still poorly understood, in particular at temperatures below the solidus. In order to assess the fundamental controls affecting the kinetics of crystal nucleation/growth and phase composition below the solidus, we have undertaken a systematic study of crystallisation in calcium aluminosilicate liquids just above their glass transition. A wide range of composition has been studied with silica

content from 33 to 70 mol%, principally along two joins with molar  $\text{CaO}/(\text{CaO}+\text{Al}_2\text{O}_3)$  of 0.78 and 0.52. Typically, samples have been heated for 3 to 24 hours, between 30 and 100K above their glass transition. We have determined textures, compositions and unit-cell parameters of the crystalline phases over a wide range of length scales, using optical and electron microscopy (SEM, TEM), Electron microprobe, X-ray diffraction (XRD) and raman spectroscopy.

The results show that in the majority of cases the first phase to crystallise is not the liquidus phase but may be one of the solidus phases. With the exception of compositions close to 'anorthite', the Si/Al ratio of the first phase to precipitate is as close as possible to that of the parent liquid, consistent with the rapid diffusion of Ca compared to that of Si and Al (Gruener et al., 2001). Different mechanisms of crystallisation have been observed, including isochemical crystallisation of metastable phases, and fine scale intergrowth of (often highly substituted) stable phases. A schematic map of the compositional domains in which different low-temperature crystallisation processes occur will be presented. Furthermore, the kinetics of crystallisation are found to be decoupled from viscosity, despite the fact that diffusion and viscosity are commonly key parameters in theories of crystal growth and further work to understand these results is in progress.

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### KINETIC CONTROL ON LIQUID COMPOSITION AND PHASE RELATIONS FROM COOLING EXPERIMENTS ON STROMBOLI LAVAS (AEOLIAN ISL., ITALY)

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Cooling experiments performed at  $P=1$  atm.,  $T$  in the liquidus-solidus region and  $f\text{O}_2 = \text{NNO}$ , on 4 Stromboli lava samples ( $\text{SiO}_2 = 50.0\text{-}54.4$  wt%) of CA, HK-CA, SHO, KS affinity put in evidence the kinetic control, due to the different melt viscosities, on phase relations and on the evolution of the experimental liquids. Starting compositions, in form of finely ground powders, have been firstly raised to superliquidus temperatures ( $>1230^\circ\text{C}$ ) for three hours, then cooled at  $900^\circ\text{C}/\text{h}$  or  $1^\circ\text{C}/\text{h}$  respectively to the experimental temperature keeping a final isotherm of at least 36h and finally quenched.

The effect of the two different cooling gradients was to produce a unique liquid line of descent for each starting composition with modest compositional gaps between fast and slow cooling rates, gradually increasing at lower temperatures. Additional records of metastable equilibria due to the differential liquid

cooling rate come from phase relations and phase compositions. In the slow cooling rate runs the usual crystallisation sequence is given by plag- cpx- ol-(pig). Pigeonite is absent in the natural starting compositions but it crystallizes in the CA sample across both cooling gradients. In the HK-CA sample pigeonite crystallizes before olivine and Ca-clinopyroxene in the slow cooling rate runs, being absent in the fast gradient ones. As expected, both SHO and KS samples do not show this phase. In CA and HK-CA composition, clinopyroxene shows a remarkable temperature dependence but it does not vary significantly in the two series of experiments. On the contrary, clinopyroxene from SHO and KS samples shows a narrow compositional range.

Other experiments are in progress to compare these data with those obtainable through thermodynamic calculations that express the real conditions of thermodynamic equilibria. In any case it is evident that the kinetic control affects, in some compositions, the pigeonite stability. By calibrating opportunely this effect it is possible to gain some indication on the magma ascent speed and therefore on the volcanic hazard.

### EXPERIMENTAL DETERMINATION OF ZIRCON-GARNET-MELT TRACE ELEMENT PARTITIONING AND ITS APPLICATION TO DATING

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Garnet is the mineral most used for thermobarometry, whereas zircon is a widely used chronometer: the relative timing of their growth is thus an important information for P-T-time reconstruction. We aim to determine the coexistence of zircon and garnet by trace element partitioning.

We carried out piston cylinder experiments at conditions of  $P = 20$  kbar and  $T = 750\text{-}1050^\circ\text{C}$  in the system  $\text{Na}_2\text{O-K}_2\text{O-CaO-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . The starting material has been doped with Zr and trace elements (P, Ba, Y, Hf, REE, Th and U) and contains 8-10%  $\text{H}_2\text{O}$ . The run products include 50-90% of hydrous granitic melt, 5-20% of garnet, ca. 3% of zircon and additional phases such as allanite, staurolite, micas, pyroxenes, quartz and monazite. We were able to produce large (up to several  $100\mu\text{m}$  in diameter) and homogeneous garnet, but zircon grain size was always smaller than  $5\mu\text{m}$ . A combination of electron microprobe, laser ablation-ICPMS and ion microprobe (SHRIMP-RG) analysis have been used to obtain the trace elements composition of the phases.

Y and HREE strongly partition into garnet with respect to melt ( $D = 20\text{-}80$ ); the distribution coefficients for MREE, Zr and Hf are close to unity; whereas Ba, LREE, Th and U preferentially enter the melt. With respect to garnet, zircon incorporates higher amounts of most MREE, HREE and in particular Zr, Hf, U and Th. Results are consistent with mass balance calculation and data from natural samples.

Zircon-garnet partitioning has been applied to natural samples to determine the coexistence of zircon and garnet zones. This allows correlating the age of selected zircon domains to metamorphic conditions obtained from garnet.

# EMPG IX

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### A RAMAN SPECTROSCOPIC STUDY OF THE INTERMOLECULAR INTERACTIONS IN WATER AND THEIR DEPENDENCE ON ELECTROLYTE CONCENTRATION

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The knowledge of structural properties of aqueous solutions is of capital importance in the understanding of the transport properties, crystal growth and mineral formation in the earth crust. These properties are, in their turn closely related to the molecular and ionic interactions between solvent molecules and solvent-solute molecules. It is well known that vibrational spectroscopy and particularly Raman spectroscopy is a powerful tool in the quantitative analysis of these interactions. In the context of a long study of the dynamical properties of water and inorganic aqueous solutions undertaken in our laboratory at Valladolid and Nancy (Rull and Saja 1986, Rull et al. 1995, Rull and Ohtaki 1997, Dubessy 1999) we present here recent results related with the influence of the salt concentration on the dynamics of water molecules and polyatomic anions when dissolved in H<sub>2</sub>O, D<sub>2</sub>O and H<sub>2</sub>O/ D<sub>2</sub>O mixtures at room temperature. The systems studied were salts of type X<sub>n</sub>Y<sub>m</sub> (where X=Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup> and Y= Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). Raman spectra were taken in the conventional 90° configuration using polarised light and in retro mode using a micro-Raman and depolarised light. In the present work interest has been focussed in the study of internal vibrations of water and hydration bands of cations. The ν(OH) band undergoes strong modifications in intensity and band profile on the concentration of different salts. These modifications, depends mainly on the nature of anions while cations have a weak influence. The quantitative analysis of these changes is subjected to several difficulties due to the intrinsic overlapping of the components bands to the whole envelope. To introduce new insight in this analysis a combined methodology joining the capabilities of the self-resolution and new band-fitting methods is used. Of particular importance is the study of aqueous solutions using as solvent H<sub>2</sub>O/ D<sub>2</sub>O mixtures in which the vibrational decoupling induced by isotopic substitution simplify the band profile analysis. From these results a precise model of vibrational water bands is suggested and discussed.

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### EXPERIMENTAL AND THERMODYNAMIC MODELING OF POTASSIUM-BEARING CLINOPYROXENE EQUILIBRIA IN THE SYSTEM CaMgSi<sub>2</sub>O<sub>6</sub>-KAlSi<sub>2</sub>O<sub>6</sub>

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Potassium-bearing clinopyroxene (KCpx) is characteristic for high-pressure magmatic and metamorphic environments, and it is considered as a potential reservoir for potassium in the deep mantle (e.g., Harlow & Veblen, 1991; Sobolev & Shatsky, 1990). The KCpx is the diopside (Di)- "K-jadeite" (CaMgSi<sub>2</sub>O<sub>6</sub>-KAlSi<sub>2</sub>O<sub>6</sub>) solid solution whose thermodynamic properties are unknown so far. We experimentally studied the join CaMgSi<sub>2</sub>O<sub>6</sub>-KAlSi<sub>2</sub>O<sub>6</sub> (e.g., Luth, 1992) at 7 GPa and 980-1650°C using the "anvil-with-hole" assembly (Litvin, 1990). The KCpx solid solution is the liquidus phase (Perchuk & Yapaskurt, 1998) in the diopside-rich portion of this pseudo-binary system, while grossular-rich garnet presents at the liquidus on the K-rich portion of the diagram. The K<sub>2</sub>O content in the KCpx increases from the melting point of pure diopside up to 5.5 wt.% K<sub>2</sub>O at ~1300°C. The crystal structure of KCpx with 5.0 and 1.57 wt.% of K<sub>2</sub>O was refined by the x-ray method. This substitution K for Ca causes strong modifications of the average structure, reflecting mainly in the enlargement of the M2 polyhedron. No evidence for Mg in the M2 site as a structural stabilizer for K in the K-Cpx structure (i.e. Harlow, 1996) was found. The thermodynamic treatment of existing experimental data on KCpx-melt equilibria within 1100-1900°C and 1.5-11 GPa for wide range of silicate systems allowed to describe the KAlSi<sub>2</sub>O<sub>6</sub> content in KCpx on the basis of the equilibrium  $KAlSi_2O_6 = 1/4K_4Si_2O_6 + 3/4Al_{4/3}Si_2O_6$  (in melt) with the accuracy ±0.91 GPa and ±1.2 mol.% of KAlSi<sub>2</sub>O<sub>6</sub> in KCpx. The study is supported by the Russian Foundation for Basic Research (projects 01-05-64775 to OGS), the Program "Leading Scientific Schools" (project 00-15-98519 to LLP) and the Integration Program of Russian Academy of Science (project A0113 to YAL).

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# EMPG IX

## Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

### MINERALOGY AND FORMATION CONDITIONS OF THE MANTLE XENOLITHS FROM THE ALKALINE BASALTS OF TARIAT AND DARIGANGA PLATEAUS, MONGOLIA

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The mantle xenoliths permit us to study the composition, the structure and thermal state of mantle. In the present work the spinel(Sp)- and garnet-spinel(Sp-Gar)-bearing peridotites and pyroxenites from the Cenozoic alkaline basalts from the Central (Tariat plateau) and South-East (Dariganga plateau) Mongolia are studied. The main minerals are the Cr-rich diopside, orthopyroxene (Opx)(>En<sub>85-90</sub>) and olivine (Ol) (>Fo<sub>90</sub>). The accessory minerals are Sp (MgAl<sub>2</sub>O<sub>4</sub> - FeAl<sub>2</sub>O<sub>4</sub> - MgCr<sub>2</sub>O<sub>4</sub> - FeCr<sub>2</sub>O<sub>4</sub>) and pyrope. The secondary minerals (phlogopite, magnetite, alkaline pyroxenes, pyrotite) are found also. These minerals were formed by mantle metasomatism. The composition of main minerals slightly varies. The primary zoning is absent. The signs of light deformation of rocks are established. The valency state of iron in the Opx, Cpx, Ol, Sp and Gar is determined by Moessbauer spectroscopy. High disorder degree of Fe<sup>2+</sup> in the structure is revealed. The rocks composition shows their different depleting degree. By the ratio Ca/Si the rocks are divided into low (>0.09), middle (0.09-0.06) and high depleted (<0.06). The T and P for Sp-Gar rocks are determined by Gar-Opx geothermobarometer. T for Sp rocks is evaluated by Cpx-Opx and Ol-Cpx geothermometers. P is determined by geotherm for the Mongolia region. The Sp rocks were formed at 1000-1300°C and 25-40 kb, the Sp-Gar rocks at 1300-1550°C and 35-50 kb. The disorder degree of Fe<sup>2+</sup> and Fe<sup>3+</sup>/Fe<sup>2+</sup> are caused by high temperature crystallization and quenching during eruption.

### IN SITU MEASUREMENT OF THE SOLUBILITY OF STRONTIANITE AT HP-HT CONDITIONS

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Subducted oceanic crust carries large quantities of volatile species, mostly as hydrous minerals (e.g. serpentines, amphibole, chlorite, micas, lawsonite,...) and as carbonates. In the course of subduction, these minerals break down and the

volatile species, H<sub>2</sub>O and CO<sub>2</sub>, are liberated into the mantle through dehydration/decarbonation reactions. The fluid phases thus produced, i.e. aqueous solutions enriched in various ionic species (trace elements such as Rb, Sr, Ba, Pb, U,...), react with the mantle, inducing melting, eventually leading to arc magmatism. It is therefore of great importance to constrain the chemical composition of these fluids and to study their reactivity toward silicates and carbonates. However, the composition of these deep fluids has remained highly uncertain, due to the lack of *in situ* studies.

X-ray fluorescence spectroscopy, thanks to its high sensitivity, is a powerful technique capable of determining quantitatively trace-element distribution and concentrations with micrometric resolution and ppm sensitivity.

We report here the first *in situ* experiments on the dissolution of carbonate minerals at pressures (up to 4 GPa) and at temperatures (up to 250°C) characteristic of subducted slabs. Using X-ray fluorescence, the dissolution of strontianite (SrCO<sub>3</sub>), in rubidium-bearing aqueous solution, has been followed in a membrane-type diamond anvil-cell (MDAC) equipped with an external resistive furnace. Experiments were carried out at ESRF (ID22 micro-fluorescence beamline). Given the geometry of the MDAC, the fluorescence of Rb and Sr has been detected in transmission mode, at the rear side of the anvil. In order to use Sr/Rb ratio as a tracer of the dissolution process, fluorescence peaks of these elements (K $\alpha$  at 14.2 and 13.4 keV, respectively) have been calibrated first, using solutions of known Rb and Sr concentrations. These preliminary calibrations demonstrate that concentrations as low as 10<sup>-4</sup>M of Sr and Rb can be measured in a DAC.

Afterwards, we have measured the solubility of strontianite as a function of pressure at different temperatures. The results show that, at a given temperature, the dissolution rate increases as pressure increases, following the paradoxical behavior of carbonate minerals. This will allow further thermodynamic modelling of carbonate dissolution.

### EXPERIMENTAL SEQUENCES OF SULPHIDES AND CARBONATE REACTIONS: AN ANALOGY OF THE MARINE SEDIMENTATION IN ANOXIC ENVIRONMENTS

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With the aim of establishing the relations that exist between certain types of minerals, sulphides and carbonates, in anoxic marine environments as well as to understand the factors and mechanisms that control the reactions that are necessary for their formation or dissolution, a number of laboratory experiments are carried out to simulate the sulphate reduction reactions in shallow water sediments of siliciclastic shelves in which the content and the reactivity of Fe is not a limiting factor. In the experiments a series of coupled reactions take place that cause the formation of amorphous iron sulphides and the formation of siderite. In addition the diagenetic environ-

ments for the formation of these components, sulphides and carbonates, in the sediments of the Bay of Cadiz are explained. The experiments which were carried out in an aqueous solution were designed taking into consideration that the bacterially-catalyzed sulfate reduction (Coleman, 1993) may be schematically expressed by means of the following reaction:  $\text{CH}_3\text{COOH} + \text{SO}_4^{2-} \rightarrow \text{HS}^- + 2\text{HCO}_3^- + \text{H}^+$  (1). Thus aqueous solutions of 60 ml of distilled water were prepared to which 0.16 grms of sodium sulphide were successively added as a source for the formation of  $\text{HS}^-$  ions, and 0.10 grms of sodium bicarbonate as a source for the production of  $\text{HCO}_3^-$  ions. These concentrations allow for the ratio 1: 2 M between  $\text{HS}^-$  and  $\text{HCO}_3^-$  as can be observed in (1). Likewise 0.20 grms of aragonite were added which was extracted as a biogenic component of *Sepia Officinalis* and 0.5 grms of ferrous chloride as a source of  $\text{Fe}^{2+}$  ions. Under these conditions the pH of the solution was 6.88 and the experiments were carried out in inert  $\text{N}_2$  atmosphere and the evolution of the experiments was monitored by checking pH. Immediately after adding the  $\text{Fe}^{2+}$  ions a decrease in the pH value as well as the presence of a black fine grain precipitation can be observed. Once the lower pH value has been reached a relative stabilization of the pH value (7.01) takes place. After a few days the precipitation is analysed by means of X-ray diffraction. The precipitation of siderite as well as the presence of an amorphous component can be concluded from the observation of the profiles. The last one is identified as FeS by EDS. These results can be interpreted on the basis of the decreasing variation of the pH whose values are balanced by the  $\text{H}^+$  liberated in the formation of the FeS, which at first causes a quick decrease in the pH values until a certain value is reached. In a later stage and from this value onwards the decrease slows down due to the dissolution of the aragonite and the liberation of  $\text{HCO}_3^-$  until the value 6.88 and its relative stabilization at 7.01 is reached. During experiments carried out under absence of aragonite the pH reaches a value of 6.1. Thus the formation of siderite is possible once the necessary degree of supersaturation has been achieved which is the sum of the  $\text{HCO}_3^-$  content in the solution and that which is liberated through the dissolution of the aragonite. The formation of siderite is due to the presence of an excess of iron in the solution after the formation of FeS. Never was siderite detected when the molar proportion of Fe and S was the same, in that case calcite precipitates, or with lower proportions of Fe with respect to S.

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### THE ELASTIC PROPERTIES OF MODEL BASALTIC MELT-COMPOSITIONS AT HIGH TEMPERATURES

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To constrain the effect of composition and temperature on the elasticity of glasses and super-cooled liquids, acoustic velocities of samples in the pseudo-ternary system anorthite-diopside-forsterite (An-Di-Fo) were measured by Brillouin

spectroscopy. Both the longitudinal and shear wave velocities where measured in the glassy state and into the region of super-cooled liquids. The glass transformation temperatures  $T_g$  inferred from the Brillouin measurements compared to previous studies are equal within the limits of experimental uncertainties. The variation of the elastic properties with temperature is approximately linear, both for the glassy state (below  $T_g$ ) and in the super-cooled liquid state (above  $T_g$ ). The temperature derivative of vibrational contributions to Young's (E), bulk (Ks), and shear (G) modulus is approx. 6-12x greater for super cooled liquids than for glasses. In the glassy state the elastic moduli and their temperature derivatives are described by ideal mixing of molar properties of oxides. The pronounced variations with composition in the elastic and anelastic properties above the glass transformation can be related to changes in configurational contributions. The configurational contribution for chemically complex glasses (mixtures of the An-Di-Fo end members) does not affect the overall compressibility at lower temperatures, whereas at higher temperatures they dominate the temperature derivatives of the moduli. The configurational contribution to compressibility is higher for complex compositions than expected from end-member compositions. Therefore, the density of complex melts in the basaltic anorthite-diopside-forsterite-system cannot be easily approximated from the behavior of pure anorthite or diopside samples. Our results indicate that with increasing temperature, configurations with a higher bonding strength were preferentially occupied. Isothermal relaxation times, varying between 0.01 and 1s at 950°C, show a minimum for intermediate anorthite-diopside-compositions and are related to the maximum in configurational entropy.

### THERMODYNAMIC PROPERTIES OF Mg-Al-PHOSPHATES: POLYMORPHISM AND STABILITY OF $\text{MgAlPO}_4\text{O}$ , A KEY PHASE IN THE $\text{MgO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ LAZULITE SYSTEM

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Ca-Mg-Al-phosphates (e.g. P-ellenbergerite, bearthite, lazulite, farringtonite...) have attracted increasing interest in experimental mineralogy during the last years because of their stability properties which make them potential index minerals and the formation of solid solutions with silicates (Brunet et al., 1998, Brunet & Chopin, 1995; Cemic & Schmid-Beurmann, 1995). However, for a successful application of calculated  $f$  to geobar- and/or geothermometry an internally consistent database for phosphate minerals is required.

This contribution focuses onto the sub-system  $\text{Al}_2\text{O}_3\text{-MgO-P}_2\text{O}_5\text{-H}_2\text{O}$  of lazulite,  $\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$ . Experimentally lazulite was found to share phase relations with berlinite, farringtonite, corundum,  $\text{HD}_2\text{O}$  and the phase  $\text{MgAlPO}_4\text{O}$ . Therefore knowledge of the thermochemical properties of  $\text{MgAlPO}_4\text{O}$  is a requisite to the extraction of those of lazulite from available experimental phase relation data (Cemic and Schmid-Beurmann, 1995). In contrast to previous results of Holland & Segnit (1980) DSC measurements in the range 25 to 700°C show a single transition:  $\beta \Rightarrow 485^\circ\text{C} \Rightarrow \alpha$  with  $\Delta H(\text{tr})$

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= 0.65 kJ/mole instead of three (Holland & Segnit, 1980). HT X-Ray powder diffraction revealed a reduction of the molar volume by 1.5% at the transition temperature. Thermodynamic data for  $\text{MgAlPO}_4\text{O}$  were extracted from the reaction  $\text{MgAlPO}_4\text{O} \rightleftharpoons \text{cor} + \text{farringtonite} + \text{berlinite}$  which was bracketed using an internally heated pressure vessel in the P-T range 0.4 to 0.8 GPa and 800 to 1100°C. In agreement with the calculated slope of the univariant curve of the phase transition HP-HT X-ray diffraction showed that under these conditions  $\alpha$ - $\text{MgAlPO}_4\text{O}$  is the stable modification. The following formation enthalpy and third-law entropy were retrieved for  $\text{MgAlPO}_4\text{O}$  taking heat capacities and thermal expansions of all reactants into account:  $\Delta H(f)^\circ = -2387$  (kJ/mole) and  $S^\circ = 111.5$  J/mole K.

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### COMPOSITIONAL DEPENDENCY OF FERRIC IRON INCORPORATION IN SOLID SOLUTIONS OF THE LAZULITE-TYPE

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Iron bearing minerals with a variable  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio can be used as petrogenetic indicators for the oxygen fugacity. However, it was found experimentally that besides oxygen fugacity and to a lesser amount temperature this ratio can be strongly dependent on composition, e.g. in the case of synthetic (Mg,Fe)-foitites (Velickov & Abs-Wurmbach, 2000). Another interesting (Mg,Fe) dominated solid solution is the lazulite - scorzalite system the composition of which is ideally given as  $(\text{Mg,Fe})\text{Al}_2(\text{PO}_4)_2(\text{OH})_2$ . Natural lazulites are present as accessory phases in a variety of metamorphic environments (Pecora & Fahey, 1950). Under hydrothermal conditions the system forms a complete solid solution series which is mainly characterised by the exchange of Mg and  $\text{Fe}^{2+}$  on the octahedral  $\text{Me}^{2+}$  position of the Al-Me<sup>2+</sup>-Al trimers (Schmid-Beurmann et al., 1999).  $\text{Fe}^{3+}$  incorporation in synthetic lazulite - scorzalite solid solutions was investigated at 486°C and 0.3 GPa under the control of different solid state oxygen buffers like QFI-, Ni/NiO- and Hem/Mgt. With increasing oxygen fugacity the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio raises from 0.03 up to 0.06 in pure iron end member scorzalite. At constant oxygen fugacity this value was found to be significantly dependent on composition. Under the fugacity of the Ni/NiO buffer the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio increases from 0.04 in pure scorzalite up to 0.15 in the magnesium rich member  $\text{Laz}_{0.875}\text{Sco}_{0.125}$ . For the incorporation of  $\text{Fe}^{3+}$  into stoichiometric ferrous iron compounds a charge compensation mechanism is necessary. For an explanation a defect mechanism is formulated on the basis of the interpretation of the Mössbauer spectra of natural samples (Amthauer & Rossman, 1984). In their structure  $\text{Fe}^{3+}$  occupies the  $\text{Me}^{2+}$  as well as the  $\text{Al}^{3+}$  position. Such a mechanism is able to explain generally the hyperbolic increase of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio with decreasing Fe content.

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### STRUCTURAL INFLUENCE OF WATER DISSOLUTION IN MELTS AND GLASSES ALONG THE JOIN REEDMERGNERITE-ALBITE

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In the present study we combined complementary spectroscopic techniques such as NMR, Raman and infrared spectroscopy in order to investigate the structural variations associated with B/Al substitution in a series of glasses along the join reedmergnerite-albite ( $\text{NaBSi}_3\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$ ). Since natural B-rich melts are commonly associated with hydrous granitic magmas or an aqueous fluid phase, we focused in particular on the structural effects of water dissolution.

Glasses with five different compositions along the join reedmergnerite-albite (Rd-Ab) were investigated ( $\text{Rd}_{100}$ ,  $\text{Rd}_{75}\text{Ab}_{25}$ ,  $\text{Rd}_{50}\text{Ab}_{50}$ ,  $\text{Rd}_{25}\text{Ab}_{75}$  and  $\text{Ab}_{100}$ , in mol%). Hydrous glasses containing about 4 wt% water were synthesised at 2 kbar and 1000° C in TZM rapid quench autoclaves. Dry glasses were prepared at similar conditions (2 kbar, 1100° C, rapid quench) in order to minimize possible effects of different synthesis conditions on the glass structure. All glasses were analysed with IR, Raman and NMR spectroscopy.

The results show that B incorporates in the glasses as both, tetrahedral  $\text{BO}_4$  and trigonal  $\text{BO}_3$  groups. The B-speciation strongly depends on the anhydrous melt/glass composition and on the water content. Since <sup>27</sup>Al NMR data demonstrate that Al is only present in tetrahedral coordination, the presence of  $\text{BO}_3$  groups indicates the presence of non-bridging oxygens. Only if all B-atoms were in tetrahedral coordination, the glasses would be fully polymerised. Near-infrared spectroscopy indicates important changes in the water speciation upon B-incorporation. The variations in the spectra indicate that for a constant total water content the concentration of structurally bonded hydroxyl groups increases while the concentration of molecular  $\text{H}_2\text{O}$  decreases with increasing B-content. Furthermore the spectral details may suggest the presence of B-OH complexes. However, the exact nature of such complexes cannot be deduced from the present data and needs further investigation.

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### EXPERIMENTAL OBSERVATION OF TRANSFORMATION PLASTICITY IN QUARTZ USING A HYDROTHERMAL DIAMOND-ANVIL CELL

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Transformation plasticity has long been proposed to be a significant mechanism for the localization of deformation in both Earth's crust and mantle. However, unequivocal experimental evidence of transformation plasticity in geologically relevant materials is still lacking. In this study, we used a hydrothermal diamond-anvil for in-situ deformation experiments of quartz containing synthetic water inclusions. During heating, a hydrostatic confining pressure was exerted on the quartz sample, which caused stress on the inclusion walls. The sample was monitored optically to determine the temperature of the  $\alpha$ - $\beta$  transition and PT conditions at which permanent deformation of the quartz around the fluid inclusions occurred. Plastic deformation of the quartz was recognized from permanent changes in inclusion shape and liquid-vapor homogenization temperature reflecting the change in inclusion density. Run durations were a few seconds to minutes at the maximum temperature and confining pressure. TEM images showed that deformation of the quartz around inclusions involved the motion of dislocations. Very high differences between confining and inclusion pressure above 400 MPa were required within the  $\alpha$ -quartz stability field for the onset of plastic deformation. At the transition temperature, plastic deformation occurred at lower pressure differences (165 - 280 MPa). A pressure difference of 210 MPa was not large enough to cause plastic deformation in the  $\beta$ -quartz stability field at 760°C. However, the same inclusions deformed visibly at the transition temperature (710°C) at a pressure difference of 200 MPa after cooling of the sample along an isochore. These results indicate that there is a pronounced minimum of the creep strength of quartz at the  $\alpha$ - $\beta$  transition. Our experimental results imply that deformation in quartz-bearing shear zones can occur at much lower stresses than anticipated from existing flow laws and that fluid and melt inclusions in quartz can re-equilibrate at much shorter timescales than previously thought

### IN-SITU DETERMINATION OF MINERAL SOLUBILITIES AT HIGH PRESSURES AND TEMPERATURES USING SYNCHROTRON RADIATION XRF

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Data for the solubility of minerals in aqueous fluids at the P-T conditions of the Earth's crust are fundamental in geochemistry because mineral-fluid equilibria control the behavior of elements during geological processes. One of the major difficulties associated with most available techniques for such studies is sampling of the fluid present at high temperatures and pressures. Here we present an experimental technique, which circumvents the sampling problem. This was achieved by determining the concentration of dissolved elements in a fluid

in-situ at high pressures and temperatures through the windows of a modified hydrothermal diamond-anvil cell using synchrotron radiation X-ray fluorescence. The cell was tested successfully to 800°C and 1.1 GPa, without reaching the upper P-T limits. The current experimental conditions permit analysis of elements with  $Z > 18$  and concentrations above 10 ppm. The solubility of AgCl in water was determined as a function of pressure along two isotherms (300 and 455°C) to test internal consistency, accuracy, and reproducibility of the analyses. For standardless quantification, concentrations were calculated from the ratios of normalized peak areas of measured and Monte Carlo simulated spectra. These calculated concentrations show the expected increase in solubility with temperature, but are lower than literature data for the solubility of AgCl in water. This is probably not caused by sluggish dissolution of AgCl because the Ag concentration at 350 MPa and 300°C increased only insignificantly when the run duration was extended by 3000 s. Calibration against known solubility data along the liquid-vapor curve improved the accuracy. The reproducibility obtained from measurements at almost identical conditions was within 7%. Our preliminary data indicate that this in-situ technique has great potential for high P-T solubility studies because it can be applied to sparingly or incongruently soluble compounds and for studies of dissolution kinetics.

### A 'ROCKING' MULTI-ANVIL APPARATUS: ELIMINATION OF COMPOSITIONAL SEGREGATION IN FLUID-RICH HIGH PRESSURE EXPERIMENTS

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Static experiments at high and ultra-high pressure conditions on equilibria involving hydrous phases and fluids suffer from an intrinsic problem: solubilities of solid components in high-pressure fluids are extreme and the gravitationally driven migration of the fluid to the top-end of the capsule causes chemical segregation. As a consequence, a strong compositional gradient results in the solid phase assemblages, zones with different mineral assemblages are frequently observed (e.g. Stalder & Ulmer, 2001). In addition, fluid migration and the dissolution processes are time- and fluid/rock ratio - dependent. Experimental determinations of high-pressure dehydration reactions from different groups are generally inconsistent (at least in the MgO-SiO<sub>2</sub>-H<sub>2</sub>O and in K-rich systems), part of this inconsistency might be attributed to chemical time-dependent segregation.

In order to overcome these problems we installed a rocking multi-anvil. A combined multi-anvil / piston-cylinder apparatus (total working range 1-20 GPa) has been mounted in such a way that it can be turned by 180 degrees while pressure and temperature are applied to the sample. We thus invert the gravitational field in our sample and the fluid is forced to migrate from one end of the capsule to the other. Preliminary experiments in the MSH system show that repeated turning results in a compositionally homogeneous environment thus avoiding the segregation problem. Continuous fluid migration also enhances reaction rates, which in future will allow the use of minimal fluid/rock ratios in the experimental charge.

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### DISCONTINUOUS P-V-T BEHAVIOUR OF CORDIERITE BETWEEN 25 AND 800°C AND 0.0001- 1 GPa AND 0.0001- 1. GPa

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A reinvestigation of the thermal expansion up to 800°C at room temperature on Mg-cordierite from White Well/Australia and of the compression at room temperature up to 1 GPa on a MgFe-cordierite from Madagascar by X-ray diffractometry has been conducted.

The thermal expansion results confirm in a general way previous results (in Mirwald 1981a) exhibiting small positive thermal expansion for the basis parameters and a negative expansivity for the c-parameter. Detailed analysis, however, reveals clear discontinuities of anisotropic thermal expansion at 300°C and less pronounced at 550°C, leading to three temperature regions characterised by distinctly different trends of the thermal expansion coefficients what confirms earlier work (Mirwald, 1981a). The discontinuities are also manifested by intensity changes. The small volume changes which are mainly to be related with distortions within the vicinity of the Mg(Fe)-octahedron and the T1-tetrahedron, but not with changes in crystal symmetry, suggests isostructural transitions of displacive character within this framework silicate.

Discontinuous volume behaviour at 0.22±0.03 GPa had been suggested in a compression study by Mirwald et al. (1984). The present high-pressure X-ray study reveals closer details, a small change in the pressure-dependent evolution of both the lattice parameters and the unit-cell volume at 0.21 GPa. The apparent transition is very weak and shows the characteristics of a second-order transitions. Both polymorphs are of orthorhombic symmetry and compression behaviour is similar above and below the critical transition pressure with the a- and b-axis being approximately twice as compressible than the c-axis. These findings suggest very similar structural relationship between the two polymorphs with a displacive character for the structural transition.

The three transitions observed seem to fit in a system of discontinuous volume behaviour of cordierite lined out in a previous compression study at elevated P-T-conditions (Mirwald, 1981b).

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### TETRAHEDRAL BORON IN OLENITE FROM THE TYPE LOCALITY: A CHEMICAL AND STRUCTURAL INVESTIGATION

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The recent discovery of tetrahedral boron with >1 <sup>14</sup>B *apfu* in natural and synthetic olenite samples led to a reexamination of olenite from the type locality, Oleny, Kola, Russia. Contrary to the original publication from Sokolov et al. (1986) a single crystal structure analysis (*R* = 0.014) shows *ca.* 0.4 <sup>14</sup>B *apfu* by site-refinement and chemical analysis. The optimized formula, calculated using chemical (EMPA and SIMS) and structural data is: (Na<sub>0.54</sub>Ca<sub>0.02</sub>)<sub>Sum 0.56</sub> (Al<sub>2.07</sub>Li<sub>0.63</sub>Mn<sub>0.09</sub>Fe<sub>0.04</sub>)<sub>Sum 2.83</sub> Al<sub>6</sub> (Si<sub>5.45</sub>B<sub>0.40</sub>Al<sub>0.14</sub>) O<sub>18</sub> (BO<sub>3</sub>)<sub>3</sub> (OH<sub>3.83</sub>F<sub>0.16</sub>O<sub>0.01</sub>). The ideal formula was given by Sokolov et al. (1986) as Na<sub>1-x</sub>Al<sub>3</sub>Al<sub>6</sub>B<sub>3</sub>Si<sub>6</sub>O<sub>27</sub>(O,OH)<sub>4</sub>. In contrast, the new investigation shows the *V* and *W* sites to be nearly fully occupied by (OH) with only small amounts of F and essentially no O. There is also a substantial amount of Li in the crystal investigated. The lattice constants of the studied material (*a* = 15.792(2), *c* = 7.0878(6) Å) are very similar to the parameters given by Gorskaya et al. (1982).

The chemical and structural detection of <sup>14</sup>B in an olenite crystal from the type locality has important implications for future studies of the crystal chemistry of tourmaline group minerals. Substantial amounts of tetrahedral boron may be common in tourmalines with relatively high Al contents.

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### HALIDE ION HYDRATION IN HYDROTHERMAL SOLUTIONS TO 350°C

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The interaction of dissolved species with solvent molecules is a fundamental feature defining the physical chemistry of aqueous electrolyte solutions. With increasing temperature to the critical point, the dielectric and transport properties of water change quite dramatically as changes in the hydrogen

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bonding occur. The associated changes in ion hydration play an important role in determination the nature of oxygen and hydrogen isotope fractionations in high-temperature high-pressure aqueous systems. We have studied the interaction of iodide ion with solvent molecules using ultraviolet spectroscopy, X-ray absorption spectroscopy (EXAFS) and ab-initio/molecular dynamics techniques up to 350°C at equilibrium vapour pressures. The iodide-oxygen (water) distance was found to change from 3.55 to 3.63 Å from EXAFS measurement with increasing temperature from 25 to 350°C. This expansion of the hydration shell is consistent with the red-shifted ultraviolet charge-transfer-to-solvent spectra and the molecular dynamics simulation results.

#### PERMEABILITY OF THE CONTINENTAL CRUST: IMPLICATIONS OF EXPERIMENTAL DATA

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Permeability is an important geochemical and geophysical property controlling the migration of fluids which, in turn, play a fundamental role in mass and heat transfer within the crust as well as crust rheology. Field permeability measurements were conducted on sand, sandy loam, loam and humus strata (Orlovka ecologic testing area, Eastern Transbaikalia) at ambient pressure and temperature. Laboratory permeability measurements were conducted on granitoid, gneiss and amphibolite samples from Kazakhstan and Kola super-deep borehole at T = 20-600°C and P<sub>eff</sub> up to 200 MPa. The analytical expression for the permeability (k, m<sup>2</sup>) – depth (H, km) trend (15 samples, 229 experimental points) is given by  $\log k = -12.55 - 3.374 H^{0.2093}$ . At the 90% prediction interval the permeability decreases from  $2.82 \times 10^{-13 \pm 1.8}$  m<sup>2</sup> at the surface to  $1.67 \times 10^{-20 \pm 1.5}$  m<sup>2</sup> at the base of the crust. These permeability values refer to the crust under isotropic stress conditions ( $\sigma_x = \sigma_y = \sigma_z$ ) in the state of mechanical ( $d\epsilon_x = d\epsilon_y = d\epsilon_z = 0$ ) and chemical ( $\Delta G = \min$ ) equilibrium. The experimental results are compared to the permeability estimates from the oxygen isotope front propagation [Dipple & Ferry, 1992] and the hydrothermal flow rate in metamorphic systems [Manning & Ingebritsen, 1999]. This work was financially supported by the RFFR grant 01-05-64531.

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#### STUDY OF THE HAWAITE MELTING DIAGRAM AT PH<sub>2</sub>O=600 bar WHILE USING SEED TECHNIQUE

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Seed technique is an experimental method used in some instances for the equilibrium diagram determination. Observation of the reaction zone on the border of the large plagioclase crystals was used in the study of granite melting diagram [1], in the simple systems mineral solubility relates to its liquidus. In the current study we use diopside, forsterite and plagioclase seeds to define liquidus or metastable liquidus extension (metastable equilibrium of the single given phase with the melt) temperature of the correspondent phases. Experiments have been carried out on IHGV at the parameter values close to the levels assumed for the intermediate storage magma chamber at the Mt. Etna volcano PH<sub>2</sub>O=600 bar, fO<sub>2</sub> about Ni-NiO. Water solubility for these conditions is about 2.5 wt.%. We observe switch from the seed dissolution to the seed overgrowth in the experiments with duration 10-30 min. Liquidus temperature of the clinopyroxene is found to be 1100±5°C and olivine 1120±5°C. These values fit with experimental uncertainty to the estimates found with program MELTS [2] for the given melt composition (Ol- 1120±8, Cpx- 1105±2, estimates range connects with possible melt composition and fO<sub>2</sub> variations). Experimentally determined metastable liquidus extension for the plagioclase is 1060±5 (liquidus at 1045±5°C) exceeding on 20°C estimate made with MELTS. Clinopyroxen growth rate at DT=25-30°C for the elongated crystals consists 2-3 10<sup>-5</sup> cm/s while for the smooth overgrowth it is order of magnitude lower 2-3 10<sup>-6</sup> cm/s. Registered Al<sub>2</sub>O<sub>3</sub> content in clinopyroxen at small undercoolings is 4-6.5 wt.% very close to the level predicted with MELTS. Experimental estimates of the clinopyroxen growth rate are in accordance with the scenario of the crystallization due to degassing at the magma uplift from the shallow (depth about 2 km) reservoir to the surface. Clinopyroxen can reach maximum size 0.8-0.9 mm just around maximum size found by CSD measurements in Mt. Etna lavas. This study was supported with RFFR grant #00-05-65371.

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### CARBORN NANOTUBES AND FULLERENE-LIKE PHASE FORMATION AT THE METAMORPHIC PARAMETERS

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At low temperatures and pressures (700-750°C and 5 kbar) from the methane and hydrocarbon gases graphite, fullerite structures and carborn nanotubes were synthesised. Fullerite formations have overall forms and multyplies structure. Nanotubes has length up to 1 µm, diameter nearly 600 Å and diameter of the channel nearly 40 Å. Microdiffraction were provided for these structures. As a result we can conclude that rare phases of the carborn - fullerene-like structutes and nanotubes which are known for very high temperatures processes could be formed at the metamorphic P-T parameters.

### SYNTHESIS OF MORDENITE SINGLE CRYSTALS FOR DYE INCORPORATION

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Natural antenna systems in plants where the sunlight is transformed into chemical energy are well known. This principle of energy transfer can also be reproduced by artificial antenna systems using zeolites used as hosts for supramolecular organization of dyes. Dye molecules loaded into zeolite channels mimic the natural function of chlorophyll in plants. The incorporation of the organic dye molecules is dependent on the aperture of the zeolite channels. The orientation of the molecule in the channel is determined by the shape and size of the dye and the zeolite channels. Very little is known about geometrical arrangement of the dyes in these channels. The exact position of the chromophores in the zeolite structure may provide better understanding how the antenna systems work and how the energy transfer can be improved. A suitable method to analyze the modified zeolite structure is single-crystal diffractometry applying synchrotron radiation.

Mordenite ( $\text{Na}_8(\text{Si}_{40}\text{Al}_8\text{O}_{96})(\text{H}_2\text{O})_{24}$ , space group Cmc<sub>2</sub>m, was chosen as an ideal candidate for dye incorporation. The large ellipsoidal 12-membered ring channels along [001] with an aperture of  $7.0 \cdot 6.5$  Å are tailor-made for incorporation of small organic dyes. The anisotropic shape of the channel cross-section limits disorder of the enclosed molecules.

Different hydrothermal-synthesis methods were applied to obtain suitable single crystals. The most important aspects during the synthesis were control of size, morphology, and quality of the single-crystals. Mordenite single crystals up to 180 µm in length with different morphology (platy, prismatic) were synthesized. Some of these crystals were loaded in gas phase with the organic dye fluorenone ( $\text{C}_{13}\text{H}_8\text{O}$ ). IR spectra were collected to confirm dye incorporation into the mordenite structure. However, only small amounts of the dye could be loaded during the first trials. For successful single-crystal diffractometry, the filling procedure has to be improved.

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### EFFECTS OF HYDRATION ON THE CRYSTAL STRUCTURE OF OLIVINE

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The effects of hydration on the crystal structure of olivine have been investigated by means of X-ray single crystal structure refinements on a series of samples synthesized at elevated temperatures and pressures. The samples were synthesized in the multianvil press laboratory at BGI from powdered mixtures of olivine, brucite, orthopyroxene, and magnetite. Under hydrous conditions, the olivine to wadsleyite transformation occurs at about 1 GPa lower pressure than in the dry system. Preliminary IR spectroscopic data indicate that the samples synthesized at contain up to about 1500 ppm by weight  $\text{H}_2\text{O}$  as hydroxyl. High precision X-ray single crystal structure determinations were conducted on four of the synthetic hydrous samples together with two natural and one synthetic anhydrous samples for comparison. The hydrous olivines indicate that the unit cell expands by approximately 0.17% relative to the anhydrous equivalent. This is sufficient to reduce the bulk modulus and seismic velocities significantly. Crystal structure refinements indicate that the principal hydration mechanism is by M2 vacancy based on observed scattering deficiency coupled with volume expansion of the M2 coordination polyhedron.

### PYROGENIC TRANSFORMATION OF PELITES

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High-temperature transformation of pelitic rocks during prolonged combustion metamorphic events was studied on the example of the matter from burned coal dumps (the Urals, Russia). The parent rocks are mainly mudstones containing muscovite-illite, quartz with small amounts of montmorillonite, kaolinite, chlorite, and diaspore. At the initial stage of

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heating ( $T=600-700^{\circ}\text{C}$ ) decomposition of layer silicates involving their dehydroxylation ( $\text{H}_2\text{O}$  and Na loss) and amorphization is the principal process. Amorphous phase dominates in the annealing products, whereas crystalline phases are represented only by quartz, mullite and thermally altered muscovite. With increasing temperature up to  $900^{\circ}\text{C}$  and prolonging the heating processes of sintering and crystal growth occurred in amorphous matrix. Crystalline phases are quartz, mullite, hercynite, and cordierite. The amount of cordierite is inversely related to hercynite ones. This result allows to predict cordierite generation by solid-state reaction: Herc +  $\text{SiO}_2$  (amorph.) = Cord. Hercynite is intermediate short-lived phase petering during the prolonged heat treatment.

The melting of dehydrated and amorphized substrate starts below  $900^{\circ}\text{C}$ . The first partial melts have a near constant composition which is controlled by the eutectic of mudstones. High-temperature clinkers ( $T=900 - 1250^{\circ}\text{C}$ ) are largely composed of Al-K high-silica glasses, corresponding in their composition to S-granites. Minerals are represented by K-bearing cordierite, tridymite, mullite, and magnetite, which crystallized during cooling. Thus during the dimensioned coal conflagrations in dumps primary mineral assemblages were transformed into anhydrous silicates, oxides and glasses.

Principal feature of combustion metamorphic reconstruction of sedimentary matter is the amorphization phenomenon. Within several years mudstones are baked at the temperature  $500 - 700^{\circ}\text{C}$ , which is sufficient for dehydroxylation and amorphization of layer silicates. As temperature rose, not crystalline phases, but a fine-grained admixture of amorphous products were melted. This feature is a key to understanding the similarity between the processes of pyrogenic transformations of pelites and industrial ceramics production.

### EXPERIMENTAL CONSTRAINTS ON MAGMA FRAGMENTATION DURING THE SUMMER 2001 FLANK ERUPTION OF MT. ETNA (ITALY)

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The experimental fragmentation of magma provides insights into mechanisms inaccessible to field-geology, such as the brittle fragmentation of magma due to rapid decompression. This mechanism plays a role in a variety of explosive eruptions, and is believed to be responsible for the pulsated ash explosions that occurred in the last explosive phase (1-5 Aug.) of the 2001 flank eruption of Mt. Etna (Italy). We are using a shock-tube-like fragmentation bomb to define the overpressure range responsible for the magma fragmentation. The fragmentation threshold is measured on samples (60 mm long, 24 mm diameter) drilled from porphyritic, micro- to crypto-crystalline, trachybasaltic bombs from the last explosive phase. These are believed to represent the pre-fragmented magma.

During the experiments the samples are loaded into an autoclave that is taken to high temperature (up to  $900^{\circ}\text{C}$ ) and high pressure (up to 50 MPa). The autoclave is separated from a tank at ambient temperature and pressure by a set of diaphragms. The pressure in the autoclave is increased and rapid decom-

pression is triggered by the bursting of the diaphragms. Starting the experiments far below the expected threshold, the experimental pressure is raised stepwise up to the fragmentation threshold.

Pressure drops of 7.5-20 MPa caused fragmentation of samples with total porosities ranging from 4-21% and a variety of pore-textures. There is an inverse correlation between porosity and fragmentation threshold. Temperature changes on the order of  $100^{\circ}\text{C}$  do not have a major effect on the threshold. Future work will include comparison of the grain size, morphology and petrology of the experimental and natural pyroclasts. This will further define the physical constraints of the eruption mechanism.

### DIAMOND CRYSTALLIZATION IN CARBONATE-SILICATE MELTS OF DIAMOND-BEARING ROCKS OF THE KOKCHETAV MASSIF (EXPERIMENT AT 5.5 - 7.5 GPa)

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Experimental modeling of diamonds genesis of metamorphic complexes (Kokchetav, Kazakhstan; Dabie Shan, China) was executed. Carbonate-silicate dolomite-garnet-clinopyroxene rock from the Kumdy-Kol, Kokchetav deposit was used in experiments at high pressures. This type of the rocks differs by the extreme contents of diamonds (2000 carat/ton). Both tectonic and mineralogical data testify genesis of diamond-bearing rocks of the metamorphic complexes at the mantle conditions under high pressure (Perchuk et al, 1995).

Diamond synthesis at pressures 5.5 - 7.5 GPa was realized in dolomite-garnet-clinopyroxene melts of the rock from Kumdy-Kol. The melts were supersaturated with carbon of graphite from a starting mixture. Experimental PT - diagram of diamond formation is constructed. Diamond crystallization occurs both at spontaneous nucleation in first 1 - 2 minutes of exposition and at seeded growth. The diamonds crystallize as octahedron single crystals with smooth facets, spinel twins, aggregates by the sizes up to 100  $\mu\text{m}$ . High pressure generation of garnets and clinopyroxenes is formed in the same melts as diamonds crystallize. These results support the carbonatite model of diamond genesis in the mantle, justified by experiments on diamond synthesis in the substances of primary fluid - carbonatite inclusions in diamonds from kimberlites (Litvin & Zharikov, 2000)

Experimental evidence of high efficiency of the carbonate-silicate melts as a parental medium for natural diamond genesis is found. In addition to the mineralogical studies (Perchuk et al, 1995), experimental data indicate that carbonate-silicate melts could be both primary medium of diamond formation in the mantle and diamond carrier to the Earth's crust. Support: grant 01-05-64775 of FRBR.

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### HYDROGEN INCORPORATION IN ENSTATITE

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Orthopyroxene is the second most abundant mineral in the Earth's upper mantle. Although nominally anhydrous, it is able to dissolve traces of OH as point defects and might be a major host for water in the Earth's mantle. The aim of this study is to investigate the incorporation mechanism of hydrogen in enstatite and to reveal potential lattice sites for hydrogen in the crystal.

A series of enstatite crystals containing between 0 and 1000 ppm Al has been synthesized at 25 kbar under hydrous conditions. Crystals with different Al-content were oriented in a thermoplastic resin according to their crystallographic axes, and ground and polished on both sides. IR-spectra of each sample were recorded in the wavelength range of 1000 and 4000  $\text{cm}^{-1}$ , and the water contents were determined.

All spectra show several absorption bands in the region between 3000 and 3600  $\text{cm}^{-1}$ , which are assigned to O-H stretching modes; the strongest absorption occurs when  $\gamma$  is parallel to the electric field vector of the incident light. Pure enstatite only exhibits two major O-H absorption bands at 3070 and 3360  $\text{cm}^{-1}$ , whereas in Al-bearing samples additional peaks above 3400  $\text{cm}^{-1}$  are present. Furthermore the absorption band at 3360  $\text{cm}^{-1}$  is split into three peaks, the main peak shrinking on the costs of two sidebands at approximately 3330 and 3380  $\text{cm}^{-1}$  with increasing Al-content. The observations are consistent with a model, where hydrogen in pure, Al-free enstatite is linked to the oxygen atoms O(3A) and O(3B), which are located at  $\text{SiO}_4$ -tetrahedron faces pointing towards the cavity between two M2-positions along the crystallographic b-axis. In Al-bearing samples additional water is mainly incorporated between the oxygen atoms O(2A) - O(1A) and O(2B)-O(1B), i.e. at the M1 and M2 polyhedra.

### AN EXPERIMENTAL STUDY OF SILVER TRANSPORT IN HYDROTHERMAL SOLUTIONS

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A knowledge of the stability of aqueous silver(I) complexes in hydrothermal solutions is essential for quantitative interpretation of the transport and deposition mechanisms of silver by hydrothermal fluids in the earth's crust. High temperature experimentally obtained data exist for many aqueous silver(I) complexes including chloride, hydroxy, hydroxychloro, carbonate and hydroxycarbonate complexes. Less is known about the stability and stoichiometry of silver(I) sulphide complexes in aqueous solutions at high temperatures and pressures. The solubility of well characterised silver sulphide (argentite/acanthite) was measured in dilute sulphide solution to 400°C at vapour saturation pressure and 500 bar. The experiments were carried out in a flow-through autoclave, connected to an HPLC pump, titanium-sampling loop and a back-pressure regulator on line. Samples for silver determination were collected via the titanium-sampling loop at experimental

temperatures and pressures. The solubilities, measured as total dissolved silver, were in the range  $1.0\text{E-}7$  to  $1.30\text{E-}4$  mol  $\text{kg}^{-1}$ , in solutions of total reduced sulphur between 0.007 and 0.176 mol  $\text{kg}^{-1}$  and pH(T,P) of 3.7 to 12.7. A non-linear least squares treatment of the data demonstrate that silver sulphide dissolves in aqueous sulphide solutions to form  $\text{AgHS}(\text{aq})$ ,  $\text{Ag}(\text{HS})_2^-$  and  $\text{Ag}_2\text{S}(\text{HS})_2^{2-}$  complexes dominating in acidic, neutral and alkaline solutions, respectively. The solubility constants and the cumulative and stepwise formation constants for the respective species have been calculated to 400°C. The complex formation at 25°C is characterised by exothermic enthalpy and a small entropy indicating the chemical bonds formed between  $\text{Ag}^+$  and  $\text{HS}^-$  are predominantly covalent. At higher temperatures the formations reactions become more endothermic with large positive entropies, indicating of greater electrostatic interaction. Sulphide complexes will play an important role in the transport and deposition of silver by hydrothermal fluids in the crust.

### EXPERIMENTAL MODELLING OF THE SILICATE-CARBONATE LIQUID IMMISCIBILITY

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Silicate-carbonate liquid immiscibility was experimentally studied in a high gas pressure vessel at  $T=1100$  and  $1250^\circ\text{C}$  and  $P=2$  kbar to modelling the separation of carbonatite melt from silicate magma. The splitting of initial melts into two liquids (silicate and carbonate) was determined. The distribution of REE (La, Ce, Y), Nb, Ta, Ba, Sr between immiscible phases was investigated.

At  $T=1100^\circ\text{C}$  the dependence of the coefficient of distribution of REE on the initial composition of the system is determined: in alkaline silicate-carbonate systems REE are accumulated in carbonate phases, but in lime ones they are redistributed in favour of silicate liquid. These data make it possible to conclude about the formation of REE-deposits exclusively with respect to alkaline (agpaitic) magmatism. The dependence of this coefficient on the temperature is also determined: the increase of temperature from 1100 to  $1250^\circ\text{C}$  results in redistribution of REE in favour of silicate phase. Nb and Ta are mostly concentrated in silicate melt, but Ba and Sr are accumulated in carbonate phase.

Inhomogeneity of the obtained carbonate liquids, manifesting itself in the division of carbonate phase into alkaline (mostly sodium) and alkaline-lime (mostly calcium) facies is pointed out. This type of splitting probably played a certain part in the formation of carbonatite intrusions of various types and their ore-bearing.

The effect of salt additions (phosphate, fluoride, chloride, sulphate) on silicate-carbonate layering of melts and distribution of ore elements between immiscible phases has been investigated. Experimental results illustrate positive role of phosphorus and fluorine and negative role of chlorine on the extraction of REE by salt melts. This fact can explain usual presence of apatite mineralization at the REE-deposits of carbonatite type.

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### AN EXPERIMENTAL STUDY OF VANADIUM PARTITIONING IN FERROBASALTIC SYSTEMS WITH IMPLICATIONS FOR VANADIUM CONCENTRATION IN LAYERED INTRUSIONS

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Mineral-melt partition coefficients of vanadium have been experimentally determined for ferrobaltic bulk compositions at constant temperature (1068°C) and pressure (one atmosphere) over a range of oxygen fugacity from 0.7 log units below to 2.6 log units above the NNO buffer (NNO-0.7 to NNO+2.6). All experiments were saturated in clinopyroxene and titanomagnetite. Vanadium partitioning is found to be strongly dependent on oxygen fugacity, decreasing by approximately one order of magnitude upon oxidation from NNO-0.7 to NNO+2.6 for both clinopyroxene and magnetite. Based upon thermodynamic modelling of the relative proportions of V<sup>3+</sup>, V<sup>4+</sup> and V<sup>5+</sup> in our liquids, this behaviour is inferred to be dominated by partitioning of V<sup>3+</sup>, despite the fact that this valence state is predicted to occur in low relative abundance. Derived values of the partition coefficient of V<sup>3+</sup> show no systematic dependence on melt polymerisation, but do show a systematic dependence on mineral composition. In particular, our data and those of the literature are combined to show that the partition coefficient of V<sup>3+</sup> between liquid and clinopyroxene increases significantly as clinopyroxenes become more iron-rich. The partition coefficients for vanadium determined in this study have been used to model the V concentration of liquid and magnetite as a function of differentiation at different oxygen fugacities. These results show that extreme enrichments of V<sub>2</sub>O<sub>5</sub> in magnetite will only occur for a relatively small range of oxygen fugacity between NNO and NNO-1.5. The results of our modelling are shown to be consistent with observations made on the V-rich magnetite layers of the Bushveld intrusion.

### THE BREAKDOWN OF GLAUCOPHANE AT HIGH PRESSURES AND TEMPERATURES

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Glaucophane is an important index mineral in high pressure/low temperature metamorphic rocks. The findings of glaucophane-rich amphibole solid solutions in ultra-high pressure rocks from China and northern Italy indicates that glaucophane-rich amphiboles may be stable up to very high pressures (>2.5 - 3.0 GPa) and temperatures (>700°C). Since these amphiboles show considerable deviations from stoichiometric glaucophane, this suggests that the breakdown of glaucophane-rich amphiboles is not a simple univariant reaction such as (1) Glaucophane = 2Jadeite + Talc as shown by Carman and

Gilbert (1983) but instead involves continuous reactions involving additional components such as nyböite, cummingtonite etc. To characterize the compositional adjustments of glaucophane at UHP conditions near its upper stability limits, we performed the first experiments on the upper stability limit of natural glaucophane in the temperature range of 750 - 800°C and pressures ranging from 3.6 - 4.0 GPa in a piston-cylinder. Our experiments with the starting assemblage glaucophane + jadeite + talc show that the breakdown reaction taking place is 2 Glaucophane = 4Jadeite + 3Enstatite + 2Coesite + 2H<sub>2</sub>O. At 3.7 GPa at 800°C, sodic amphiboles, rich in glaucophane component, overgrew glaucophane from the starting mixture. Compositions of the newly formed amphiboles show Al<sup>IV</sup> substitution for tetrahedral Si (0.1 - 0.26 apfu.), Mg excess on the M(123)-sites (2.93 - 3.72 apfu.), Mg on the M(4) site (0 - 0.27 apfu.) and Na on the A-site (0 - 0.25 apfu.). These compositions are similar to the compositions of sodic amphiboles from UHP terranes. At 3.8 GPa at 800°C, the assemblage jadeite(Jd<sub>75-95</sub>En<sub>5-25</sub>) + enstatite(En<sub>77-97</sub>Jd<sub>3-23</sub>) + coesite + H<sub>2</sub>O is stable. Similar pyroxene compositions have not been observed in UHP rocks yet. The inability to form talc in the experiments according to reaction (1) reflects either the reduction of enstatite activity due to the Fe-rich composition of the natural glaucophane, or the reduction of a(H<sub>2</sub>O) in the experiments, which stabilized enstatite-bearing pyroxenes relative to talc.

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### EXPERIMENTAL CONSTRAINTS ON P-X<sub>Al</sub> AND T-X<sub>Al</sub> PHASE RELATIONS IN THE SYSTEM CaTiSiO<sub>4</sub>O - CaAlSiO<sub>4</sub>F

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Experimental studies were carried out to evaluate phase relations involving titanite - F-Al titanite solid solution in the system CaSiO<sub>3</sub>- Al<sub>2</sub>SiO<sub>5</sub> - TiO<sub>2</sub> - CaF<sub>2</sub>. Piston-cylinder experiments at 900 - 1000°C and 1.1 - 4.0 GPa characterized the effect of excess fluorite on titanite composition for the equilibrium titanite + kyanite = anorthite + rutile (TARK). The average F/Al ratio in titanite solid solution in experimental run products is 1.01 ±0.06, and X<sub>Al</sub> ranges from 0.33 ±0.02 to 0.91 ±0.05, consistent with the substitution [Ti + O]<sub>1</sub> [Al + F]<sub>1</sub>. The reduction in titanite activity resulted in shifts from the stoichiometric equilibrium of 1.60 GPa to 1.15 ±0.05 GPa at 900°C, 1.79 GPa to 1.375 ±0.025 GPa at 1000°C and from 1.98 GPa to 1.575 ±0.025 GPa at 1100°C. The activity of CaTiSiO<sub>4</sub>O is closely approximated by an ideal molecular activity model (X<sub>Ti</sub>) at 1100°C, but shows a negative deviation at 1000°C and 900°C from ideality. The phase relations implied by our experiments may be interpreted in terms of isothermal P-X<sub>Al</sub> and isobaric T-X<sub>Al</sub> diagrams. In these diagrams, the reactions anorthite + fluorite = 2F-Al-titanite (AFT), titanite + kyanite + fluorite = 2F-Al-titanite + rutile (TAFT) and (TARK) intersect in an isothermal or isobaric invariant point. The different assemblages and F-Al-titanite compositions at 1.1 - 1.2 GPa and X<sub>Al</sub> ~0.40 - 0.50 at 900°C, 1.30 - 1.35 GPa and X<sub>Al</sub> ~0.45 - 0.50 at 1000°C and 1.55 - 1.60 GPa and X<sub>Al</sub> ~0.50 at

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1100°C tightly constrain the invariant point in T- $X_{Al}$  or P- $X_{Al}$  space. Analysis of the phase relations indicates that titanite solid solutions coexisting with rutile are always low in  $X_{Al}$ , whereas the maximum  $X_{Al}$  of titanite solid solution occurs with fluorite and either anorthite or  $Al_2SiO_5$ . These results demonstrate the influence of the coexisting mineral assemblage rather than the P-T conditions on the composition of titanite solid solutions.

### ASSESSMENT OF TEMPERATURE GRADIENTS IN MULTI-ANVIL ASSEMBLIES USING SPINEL GROWTH KINETICS

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Accurate measurements of axial and radial temperature distributions in high-pressure cells are a requirement for optimising assembly designs and constraining maximum sample volumes. Recently, Watson et al. (2002) presented an empirical equation linking the thickness of a  $MgAl_2O_4$  spinel layer growing at the interface between widely used  $MgO$  and  $Al_2O_3$  assembly pieces to pressure ( $P$ ), temperature ( $T$ ), and experimental duration ( $t$ ). Their equation, based on around 45 piston cylinder experiments at  $P$  up to 4 GPa and  $T$  up to 2250 K, can be inverted to calculate the temperature in different parts of high-pressure assemblies if  $P$ ,  $t$  and layer thickness are known.

We extended the  $PT$  range of this parametrisation to 16 GPa and 2250 K, using a multi-anvil press with 18/11 and 8/3 pressure cells, and high-resolution X-ray maps to determine spinel layer thicknesses. Our model, which deviates slightly from the Watson et al. (2002) lower-pressure parametrisation, can be used to assess thermal gradients in these common assemblies. At 6 GPa and 2123 K, axial  $T$  in the 18/11 assembly remains constant over a length of 4 mm when untapered graphite heaters are used.  $T$  decreases parabolically with axial distance from the edges of this 'hot spot'. The radial gradient is small (on the order of 30 K/mm distance from the center of the assembly). At 13-16 GPa in the 8/3 assembly with a rhenium foil heater, the hot spot is around 1 mm in length.  $T$  gradients outside this hot spot are large: 1 mm from the assembly center  $T$  has decreased by around 150 K.

Watson EB, Wark DA, Price JD & Van Orman JA, *Contrib. Mineral. Petrol.* (2002).

### MAGMATIC HYDROSALINE MELTS: EXAMPLES OF GRANITIC PEGMATITES AND NATROCARBONATITIC LAVAS

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Topology of some silicate-salt-water systems, such as Albite -  $NaCl - H_2O$ , or Albite -  $Na_2CO_3 - H_2O$  (Koster van Groos and Wyllie, 1968, 1969) shows that three immiscible fluids: aluminosilicate melt, hydrosaline melt and low-salinity aqueous fluid can stably coexist over a broad range of pressures and temperatures. The existence of three-fluid immiscibility in natural

magmatic systems is supported by numerous studies of melt and fluid inclusions (Roedder, 1992). Recent years have seen a growing interest in magmatic hydrosaline melts and their ore-forming capacity (e.g., Heinrich et al., 1999). However, despite the success of melt inclusion studies there was little progress in experimental characterisation of hydrosaline melts and almost no constraints on three-fluid element partitioning.

Hydrosaline melts may hold clues to understanding the most unusual and enigmatic igneous rocks: granitic pegmatites and natrocarbonatitic lavas. Our recent experimental study of B-, F- and P-rich peraluminous pegmatitic composition confirmed the formation of immiscible boro-alumino-fluoride melt in equilibrium with aluminosilicate melt and low-density aqueous fluid. Three-fluid immiscibility has been observed directly in hydrothermal diamond-anvil cells and in products of rapid-quench experiments in cold-seal pressure vessels at 0.1-0.4 GPa and 500-900°C. Immiscibility occurs at moderate concentrations of  $B_2O_3$ ,  $P_2O_5$  and F (each at about 3-5 weight percent) achievable in some types of pegmatites. Al, F, B and Na partition strongly to hydrosaline liquid, while P and K stay in aluminosilicate melt.

Dry silicate-carbonate liquid immiscibility is a broadly accepted mechanism explaining the origin of the unique natrocarbonatitic eruptions at the Oldoinyo Lengai (Tanzania). Detailed analysis reveals, however, significant discrepancies between experimental constraints on the two-liquid major and trace element partitioning and geochemical characteristics of natural natrocarbonatites (Nielsen and Veksler, in press). We believe that natrocarbonatitic lavas are likely to represent dried residues of originally water-bearing hydrosaline carbonatitic fluids.

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Nielsen TFD & Veksler IV, *Contrib. Mineral. Petrol.*, in press

### KINETICS OF MULLITE CRISTALLIZATION FROM NEUTRON THERMODIFFRACTOMETRY

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#### 1. Introduction.

The sequence of phases development leading the mullite formation during thermal treatment of its amorphous powder precursors, was followed by neutron powder thermodiffractometry. In this experiments, the role played by the Al-Si amorphous in the crystallization of the spinel precursor phase and its effects in the kinetics and mechanisms of the mullite formation, has been analysed as a function of the temperature (Villar et al, 2000).

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### 2. Experimental.

Amorphous precursor powders with stoichiometric mullite composition were heated up to 1700 °C by using the HTF in vacuum conditions at the E2 powder diffractometer. To test the possibility of reaction between the sample and the container, two different sample holders made from V and Pt were used.

The kinetics of phase transformation vs. temperature was obtained from the sequential refinement of the profiles by using the FullProf program [1] with a three-phase model. Estimation of the wt% fraction between the amorphous and crystalline phase was made from the integrated intensity of the whole background. Further treatment of the structural evolution of the amorphous phase was made by using reverse Montecarlo and Percus-Yevick models (Gago-Duport et al. 1995).

### 3. Results and discussion.

Starting from the amorphous precursor, a first crystallization of an Al-Si spinel-like phase takes place around 900°C (S.G. Fd3 m.  $a=7.79$  Å).

The mullite crystallization starts at 900°C. as is marked by the appearance of the (120) reflection. Both phases coexist until the temperature of 1275°C, from which the intensities corresponding to the reflections of the cubic spinel phase start to decrease. Finally, at 1400°C the only crystalline remaining phase in the sample is mullite.

One fact of interest is that the crystallization of mullite did not induce modifications in the intensities of the previously formed spinel phase at the first stages. Furthermore, every crystallization process is preceded of noticeable inflexions of the general shape and intensity of the background profile which can be connected with structural transformations in the amorphous Al-Si precursor during the nucleation of the crystalline phases.

This indicates that the crystallization of mullite and its precursor, spinel, results from independent nucleation events, both taken place directly by structural rearrangement of the amorphous phase.

Finally, a second relevant aspect concerns with the way of disappearance of the spinel phase at high temperatures. The kinetic analysis performed by the profile refinements shows that the intensity decrease of the spinel reflections is also related with the background modifications (Villar, 2000). This fact suggests that an amorphous-mediated transformation occurs by solid-state diffusion of the Al-Si in the spinel to the amorphous phase, with further recrystallization in the stable form of mullite (Gerardin et al, 1994)

These results indicate that, instead a polymorphic transformation from their precursor phases, the crystallization of mullite is a consequence of a direct nucleation followed of a solid-state diffusion and recrystallization processes where the amorphous phase plays a significative role.

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### EXPERIMENTAL DETERMINATION OF THE LIQUID LINE OF DESCENT OF ANHYDROUS THOLEIITIC MAGMAS AT 1.0 GPa

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Tholeiitic magmas are the most common eruptive products, which differentiate in deep-seated magma chambers ponding at the crust-mantle-boundary. The goal of this study is to quantify the liquid line of descent of dry mantle-derived tholeiitic magmas at pressures of 1.0 GPa.

As starting material we chose a mixture of synthetic oxides, fayalite, K-feldspar and NaSiO<sub>3</sub>, which corresponds to an experimentally produced liquid that was in equilibrium with a lherzolite mantle at 1.5 GPa and 1350°C (Hirose and Kushiro, 1993). The finely ground starting material was filled into a 2.6 mm OD graphite container, which was placed into a 3.0 mm OD platinum-capsule welded shut to prevent iron loss to the capsule and to fix the fO<sub>2</sub> at the C-CO<sub>2</sub> equilibrium. For the experiments a piston-cylinder-apparatus (Boyd-England-type), NaCl-Pyrex-MgO-Assemblies and Pt-Pt<sub>90</sub>Rh<sub>10</sub>-thermocouples were used. All experiments simulated equilibrium crystallization at 1.0 GPa.

In a first series of experiments olivine (ol) and Cr-spinel (spi) crystallized at 1270°C followed by clinopyroxene (cpx) at 1240°C. At 1210°C ol disappeared and orthopyroxene (opx) crystallized with cpx and Cr-spi. At 1180°C two pyroxenes but no spinel were present. Between 1150 and 1060°C cpx, opx and Al-spi represented the solid phases. No plagioclase (plg) occurred in this series.

In a second series of experiments 0.5 wt% of pure anorthite seeds were added to the starting material in order to test an eventual feldspar nucleation problem. In this series ol disappeared at 1180°C where opx, cpx but no spi crystallized. At 1150°C the solid products were cpx, opx and Al-spi. Cpx, opx, plg and Al-spi are the solid phases at 1120°C and 1090°C. These solid products represent ultramafic to mafic cumulates like dunites, wherlites, websterites and gabbronorites, which are common in plutonic rocks of the lower crust (e.g. layered series of the Ivrea-Zone, Rivalenti et al., 1981).

To understand the role of differentiation mechanisms of tholeiitic magmas at high pressure fractional crystallization experiments have been initiated.

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### NANOTEXTURES OF LASER-HEATED BIOTITES

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Chloritized biotites have been laser-heated according to four heating steps (laser power of 0.3, 0.7, 1.2, 2.2 W, corresponding to approximately 600, 810, 940, 1080°C, respectively; 2 min/step followed by 3 min of pumping out). Samples heated up to 600, 810, 940 and 1080°C have been investigated by high resolution TEM, in order to understand the structural and chemical transformation of biotite and interlayered chlorite. Most important results are: a) 600°C: biotite crystallinity is lower than in the untreated sample, reasonably due to dehydration processes. Chlorite breakdown is almost completed. b) 810°C: occurrence of diffuse delamination, 10-100 nm thick. Chlorite breakdown products start to crystallize. Main phases are spinels with variable composition, olivines and amorphous silica, occurring as irregular domains 10-20 nm in size, within the poorly crystalline biotite. c) 940°C: delamination is still present but it is reduced. Biotite is more crystalline than in previous sample. The chlorite breakdown products (olivines and spinels) form larger crystalline grains, typically elongated parallel to biotite (001). d) 1080°C: biotite (reasonably, oxybiotite) is characterized by higher crystallinity with respect to both treated and untreated samples, due to advanced structural annealing. EDS analyses performed on pure biotite domains are completely similar to those of the untreated biotite, thus indicating that biotite thermal transformation (i.e., dehydration followed by annealing at high temperature) was essentially isochemical. Olivine and spinels are hosted within perfectly euhedral negative crystals and show topotactic relation with the host biotite (thus, with the original chlorite): in particular [111]Spl parallel to [001]Bt(chl) and [100]Ol parallel to [001]Bt(chl). This evidence suggests that the crystallization of new phases is strongly influenced by the close packing of oxygens in the layer silicates; in particular the oxygen network of chlorite is inherited by its breakdown products.

### STRUCTURE AND RHEOLOGY OF PERALUMINOUS MELTS: THE EFFECT OF Fe<sub>2</sub>O<sub>3</sub>

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The Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is used to model a large number of petrological processes. But even in this simple system there are anomalous changes in rheology as a function of composition. It has been previously shown for sodium-aluminosilicate melts that, at a constant temperature and constant SiO<sub>2</sub> content, there is a shallow maximum in viscosity in the vicinity of the subaluminous join. This maximum occurs within the peraluminous field, suggesting the presence of triclusters consisting of one aluminate and two silicate tetrahedra.

The viscosity of a range of Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> compositions with 67 mol% SiO<sub>2</sub> and 0.60 > Na/(Na+Al) > 0.35, has been determined using the micro-penetration technique in the 8 < (log<sub>10</sub> Pa s) < 14 range. For these melts, at a temperature of 1050K, viscosity abruptly increases by 6.5 log<sub>10</sub> Pa s from an almost composition independent low viscosity for peralkaline compositions, to a composition independent viscosity as the melt composition becomes increasingly peraluminous. Thus, the shallow maximum in viscosity previously observed appears to be a plateau in viscosity for peraluminous composition Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts. The activation energy for viscous flow also changes dramatically as a function of melt composition; increasing from ~480 kJ mol<sup>-1</sup> for the peralkaline compositions, to ~630 kJ mol<sup>-1</sup> for the peraluminous compositions. This suggests that the change in melt structure due to the change in Na:Al has a dramatic effect on the flow mechanism of the melt.

The substitution of Fe<sub>2</sub>O<sub>3</sub> for up to 5% of the Al<sub>2</sub>O<sub>3</sub> in this system results in a decrease in viscosity. The activation energy for viscous flow for the peraluminous composition melts is decreased by ~20% upon the substitution of Fe<sub>2</sub>O<sub>3</sub> for Al<sub>2</sub>O<sub>3</sub>; but no change in activation energy is observed for the peralkaline compositions.

### TEXTURAL DEVELOPMENT OF DEHYDRATION-MELTING IN AMPHIBOLITE AT 2.0 GPa AND 950°: EFFECT OF TIME

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We have carried out the dehydration-melting of a natural amphibolite (56vol.% hornblende, 44vol.% plagioclase), in multi-anvil apparatus, experiments at 2.0 GPa and 950° for 1-170 hours. The samples are put into graphite capsules, which are sealed in gold capsules. As the annealing time less than 4 hours, Liquid and garnet appeared in the boundary of plagioclase and hornblende, which indicates this reaction: Hb + Pl — Liquid + Gt. In the mean time, two other reactions took place: Hb — Cpx + H<sub>2</sub>O and Pl — Ky + Na-Cpx + SiO<sub>2</sub>. Melting dominated by the growth of clinopyroxene and garnet. Liquid interconnectivity is attained, as the annealing time is 7 hours, with only about 5% liquid. As the annealing time increasing (from 10 hours to 72hours), liquids increased rapidly along with the loss of plagioclase (Ky + Na-Cpx + SiO<sub>2</sub>). As annealing time in range of 72-170 hours, only garnet and clinopyroxene is the solidus mineral. Most garnets are around the clinopyroxene. Garnet is enriched in pyrope. Liquids enrich first in An and then in Ab. And liquids are always silica rich (60-70 wt.% SiO<sub>2</sub>), strongly peraluminous (2-5 wt.% normative corundum), very felsic (Mg + FeO\* + TiO<sub>2</sub> less than 4wt.%). It is likely that segregation of initial liquids could not only effectively remove incompatible trace elements but although left the Gt + Cpx + Na-Cpx + Ky + SiO<sub>2</sub> assemblage during the transition from amphibolites-faces to eclogite-faces.

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### COORDINATION CHEMISTRY OF Fe IN HYDROUS SYNTHETIC GLASSES

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We present a combined, Mössbauer and high-resolution XANES spectroscopies at the Fe K-edge in synthetic glasses of the haplotonalitic ternary  $\text{SiO}_2$  (Qz)- $\text{NaAlSi}_3\text{O}_8$  (Ab)- $\text{CaAl}_2\text{Si}_2\text{O}_8$  (An), containing 0.4-1.0 wt.% Fe. Similarly, a series of other Fe-bearing glasses was studied such as albite, orthoclase, anorthite, sodium trisilicate glass. High pressure, hydrated glass samples were quenched in an IHPV device from 200-500 MPa and 850-1000°C. The  $\text{Fe}^{3+}/\text{Fe}$  ratio of these glasses (between 0 and 0.6) was measured using  $^{57}\text{Fe}$  - Mössbauer spectroscopy. Fe K-edge XANES spectra were collected at the ID26 beamline, using double-crystal Si(220) monochromator, ensuring a 1.1 eV core-hole lifetime convoluted by a 0.6 eV experimental resolution. A set of 25 model compounds containing Fe(II) and Fe(III) in 4 ( $T_d$  or  $D_{4h}$ ), 5 ( $C_{3v}$ ), 6 or 8-coordinated environments were collected in parallel to derive a coherent picture of the effect of redox state and coordination environment in the pre-edge and XANES spectra. To be independent from resolution effects, the pre-edge information was reduced to centroid position and integrated intensity. Glasses systematically show a doublet in the pre-edge spectra, their respective intensity increasing with increasing  $\text{Fe}^{3+}/\text{Fe}$  ratio. In parallel, the energy of the centroid increases with the  $\text{Fe}^{3+}/\text{Fe}$  in a non-linear fashion, suggesting that ferric and ferrous iron do not have the same coordination environments. The  $\text{Fe}^{3+}/\text{Fe}$  derived from pre-edge information is consistent with Mössbauer spectroscopy despite the pre-edge derived values are systematically shifted towards higher values as compared to those from Mössbauer spectroscopy. The pre-edge parameters obtained from the spectra of the glasses suggest mixture between 5-6-coordinated Fe(II) and mostly 4-coordinated Fe(III). There is a considerable effect of the network modifiers (Na, K, Ca) on the speciation of Fe(II) and Fe(III). The introduction of water in these glasses does not significantly affect the structure of the pre-edge spectra suggesting only negligible changes in the first coordination shell. However, major differences compared to the dry counterparts are observed in the XANES spectra at the main crest of the edge, which show dramatic signs of structural reorganizations around Fe as a function of quench rate. These changes are more significant for the tonalite and orthoclase glass than for the albitic one. Transmission Electron Microscopy (TEM) has evidenced a variety of nano-crystals which may be assigned to Fe-oxides in a tonalitic sample quenched at very low speed. Samples quenched more rapidly ( $> 150$  K/min) do not show such nano-crystals. Our studies show that the extraction of redox information about Fe in glasses is not straightforward from pre-edge analysis if variations in speciation are not taken into account. Co-relation of the spectroscopic data with TEM imaging is done to elucidate the nature of the structural rearrangements responsible for the characteristics observed in spectra of the hydrous glass samples.

### SIMULTANEOUS GROWTH AND DISSOLUTION PHENOMENA OBSERVED BY SPM ON HYDROTHERMALLY GROWN SPESSARTINE

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Spessartine ( $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) has been grown from hydrothermal solutions at temperatures ranging from 550°C (0.1 GPa) to 650°C (0.3 GPa). At the highest pressure and temperature {110} is dominant, while at intermediate temperatures and pressures corroded {100} determines the growth habit with {110}, {211} and {111} as minor forms.

Scanning Force Microscopy (SFM) shows the presence of growth spirals on {110}, {211} and {100} that are according to the Hartman-Perdok theory morphologically important F forms (Boutz and Woensdregt, 1993). On {110} the growth spirals have a rhombic shape due to the presence of two equivalent strong PBCs parallel to  $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle$ . The form {211} is commonly striated and demonstrates macroscopically the typical features of an S (tepped) form. However, it is an F form, because of the presence of very elongated growth spirals.

Scanning Electron Microscopical (SEM) observations showed that the {100} are always dome shaped and often strongly corroded. These rough {100} interfaces are the dominant interfaces at the first stage of the crystallization at all temperatures and pressures. SEM observations demonstrate that, when the supersaturation decreases after 24 hours during the growth process at intermediate temperatures and pressures, flat {110} and {211} are becoming more stable and {100} is very strongly corroded. SFM observations show that an additional hopper-like layer spreads over the surface of {110} parallel to the edges between {110} and {100}. These hopper rims have steps with step height and a step width, which are much smaller than those of the original steps on {110}. They are formed due to the local supersaturation at the edge of the stable {110} caused by the dissolution of the unstable {100} interface.

Instead of the classical idea that habit changes are due to relative growth rate changes, we can now demonstrate habit change can also occur by simultaneous growth and dissolution.

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### DIRECT EXPERIMENTAL INVESTIGATIONS OF INITIAL MELT TEXTURES IN NATURAL, INTACT PELITIC AND GRANITIC ROCKS

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Migmatites occur at the western corner of the Little Cottonwood (LC) stock within the sill-kfsp zone. We have started a series of experiments to simulate the partial melting of these pelites. 25 Experiments were performed in cold seal vessels under H<sub>2</sub>O-undersaturated and (near) H<sub>2</sub>O-saturated conditions at 2 kb, at 700°, 750° and 800°C (167-508hrs run duration). Cores of 1 cm length and 0.3 cm diameter were drilled from andalusite-cordierite-biotite-muscovite-zone rocks of the LC contact aureole. The cores were loaded into 4 mm diameter gold capsules (with 60-125 ml of H<sub>2</sub>O for water-saturated runs). Grain size of samples varied between 10 and 100 µm. After quench, melt and mineral compositions, as well as textures were analysed by SEM and electron microprobe.

Melt formed continuous seams along all grain boundaries. The initial texture, including grain shapes, are preserved. New minerals grew on specific textural sites, e.g. hercynite grew around the iron-titanium-oxides, and sillimanite and biotite nucleated in melt pools, which replaced muscovite. The amount of melt along grain boundaries depended on the run duration and amount of water added to the samples. Melt fraction is 48% for a sample run for 240 hrs at 800°C (water added), while a fraction of 53% was estimated for a run of 507 hrs at 800°C without additional water. A sample with the initial composition of qtz-ms-bt-crd-magnetite has a melt fraction of 24% after 186 hrs at 700°C and 58% after 330 hrs at 750°C. Melt on grain boundaries is compositionally zoned, with gradients of 1-2% in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O over a distance of 10 µm. Normative melt composition for a run at 800°C (with additional water) results is 88.5% quartz, 7.8% k-fsp and 3.7% albite. The water absent experiments yielded less normative quartz (82.7%), and more normative albite (7.4%).

### STEPWISE ARGON EXTRACTION EXPERIMENTS AND CONVENTIONAL K-Ar DATA ON ILLITE-SMECTITE

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Stepwise argon extraction experiments and conventional K-Ar dating on 0.5-1.0 µm, 1-2 µm and 2-4 µm size fractions separated from hydrothermally altered late Miocene dacite provide information on argon releasing pattern and reliability of K-Ar dating of Illite-smectite (I/S). Up to 300 °C argon release patterns of I/S dominated by non-radiogenic argon, subsequently radiogenic argon quantity continuously increase and peak at about 500 to 700 °C. For 0.5-1.0 µm and 1-2 µm size fractions the radiogenic argon release reaches its maximum at

about 550-600 °C and insignificant amount argon was released at 1500 °C, whereas for 2-4 µm grain size fraction the radiogenic argon release reach its maximum at about 650-700 °C and significant amount of radiogenic argon released at 1500 °C. K-Ar ages of finer, 0.5-1.0 µm, fraction show tendency to be younger than coarse fractions from the same sample, also most of these age differences are within the error limits. All clay minerals in those rocks are hydrothermal minerals and primary minerals are plagioclase, K-feldspar, quartz, pyroxene and hornblende. Similar radiogenic argon releasing pattern for 0.5-1.0 and 1-2 µm fractions verify that little or no detrital K-feldspar phase present, whereas minor differences in argon release pattern for 2-4 µm grain size fraction suggest presence of small detrital K-feldspar. K-Ar ages of 0.5-1.0 m size fractions from seven samples range from 6.2 to 6.7 Ma. The K-Ar ages of 1-2 µm and 2-4 µm grain size fractions range from 6.7 to 7.0 Ma and 6.6 to 7.0 Ma respectively. These values are consistence with estimated age of the hydrothermal alteration, which is within 1 Ma of the age of host dacite (c 7.2 Ma).

### INTERLAYER VACANCY CHARACTERIZATION OF SYNTHETIC DI- AND TRIOCTAHEDRAL (K,Rb,Cs,Ba)-MICAS BY IR-SPECTROSCOPY

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Phlogopitic micas of the solid-solution binaries KMg<sub>3</sub>[AlSi<sub>3</sub>O<sub>10</sub>](OH)<sub>2</sub> (phlogopite) - Rb-phlogopite, phlogopite - Cs-phlogopite, and phlogopite - BaMg<sub>3</sub>[Al<sub>2</sub>Si<sub>2</sub>O<sub>10</sub>](OH)<sub>2</sub> (kinoshitalite) were synthesized at temperatures of 700 and 800°C and pressures of 0.2 and 2.0 GPa. The run products were investigated by optical microscopy, X-ray powder diffraction, electron microprobe (EMP), and infrared (IR) spectroscopy. All runs yielded between 81 to 100 wt.% of phlogopitic micas, beside traces of quartz, sanidine, and in one run talc. Celsian and cymrite formed as additional phases in the runs of the (K-Ba)-series. Based on EMP-analyses, interlayer vacancy concentrations of up to 0.29 (p.f.u.) were determined, indicating a significant talc component within the synthesized phlogopitic micas. In addition to the known characteristic phlogopite OH-stretching vibrational bands, the IR-spectra of the synthetic trioctahedral micas with incompletely filled interlayer sites exhibit a further OH-band, centered in the spectral-range 3674 - 3678 cm<sup>-1</sup>. The intensity of this band is correlated with the amount of vacancies. The vacancy concentration of phlogopitic micas was determined quantitatively from the intensity of this IR-band by using the intensity of the principal OH-band of synthetic talc as a standard. The vacancy concentration of the interlayer site determined by IR-spectroscopy agrees with the vacancy-values derived by EMP-analyses. Additionally, (K, Rb, Cs)-phengites were synthesized in the same PT-range. For these dioctahedral micas we determined interlayer vacancies concentrations of up to 0.27 by EMP-analyses. Such interlayer vacancies of phengitic micas can be chemically characterized by a pyrophyllite-component. However, no pyrophyllite-band was detected by IR-spectroscopy for the synthetic phengites. Therefore, our preliminary assumption is that the phengitic micas synthesized within this study do not exhibit any interlayer vacancies and that, in contradiction to the synthetic phlogopitic micas, the apparent EMP-determined vacancies only result from alkali-loss during the EMP-measurements.

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### THERMAL DIFFUSIVITY MEASUREMENTS OF UPPER MANTLE PHASES OLIVINE, WADSLLEYITE, AND RINGWOODITE TO 20 GPa

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Because heat-transport properties are essential for understanding and modeling thermal regimes in Earth's mantle, we have measured thermal diffusivity of the upper mantle phases olivine, wadsleyite, and ringwoodite at temperatures and pressures equivalent to mantle conditions. Direct measurements of these properties, previously obtained for olivine at ambient and high pressures and temperatures, have been lacking for the high-pressure polymorphs. We performed thermal diffusivity measurements at the Bayerisches Geoinstitut in a 5000 tonne, 6-8 type multi-anvil apparatus up to 20 GPa and 1400 K using the periodic temperature wave method. The sample volume in this apparatus is larger by at least a factor of 10 compared with sample volumes in conventional multianvil systems. Measurements were performed on 2.5 mm diameter cylindrical samples of San Carlos olivine (Fo<sub>90</sub>) and wadsleyite and ringwoodite that were previously synthesized from San Carlos olivine of the same composition. The samples were all polycrystalline and single phase, and their purity and microstructures were characterized by X-ray diffraction and TEM. Our measurements of the thermal diffusivity of olivine are consistent with those measured at 1 atm (e.g. Tommasi et al., 2001) when the effect of high pressure is taken into account. The thermal diffusivity of wadsleyite measured at 14 GPa is significantly higher than that of olivine as extrapolated to conditions at the 410 km discontinuity (13.5 GPa, 1700 K). At these conditions, thermal diffusivity increases by about 27% when olivine transforms to wadsleyite. The thermal diffusivity of ringwoodite, measured at 20 GPa, is slightly higher than that of wadsleyite at 14 GPa. However, their thermal diffusivities might be similar at the same pressure. Thermal conductivities of olivine calculated from densities and heat capacities and the magnitude of the jump at the olivine-wadsleyite transition agree with or are slightly lower than estimates of Hofmeister (1999) for Mg end member compositions. The discrepancies can be explained by a compositional effect because increasing Fe content of silicates results in a decrease in thermal diffusivity.

Tommasi A, Gibert B & Seipold U, *Nature*, **411**, 783-786, (2001). Hofmeister AM, *Science*, **283**, 1699-1706, (1999).

### WATER SPECIATION IN BASALT MELTS DETERMINED BY HIGH-TEMPERATURE INFRARED SPECTROSCOPY

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Knowledge of the water speciation in silicate melts is of importance for understanding the physicochemical properties of magmas. Recent experimental studies (e.g. Novak & Behrens, 2001) tightly constrain the water speciation, but they focus on feldspathic or rhyolitic compositions and can not be extended to mafic compositions. Here I present results from high-temperature infrared spectroscopy of water-bearing basalt glasses to reconnoiter the effect of composition on the water speciation in silicate melts.

Near-infrared absorption peaks due to OH groups and H<sub>2</sub>O molecules were measured in two basalt glasses (one containing 1.3 wt% H<sub>2</sub>O<sub>tot</sub>, one containing 3.0 wt% H<sub>2</sub>O<sub>tot</sub>; the anhydrous composition remains unchanged) as a function of temperature between 298 and 850 K, using a microscope heating stage. The concentrations of OH groups and H<sub>2</sub>O molecules were determined using the Yamashita et al. (1997)'s room-temperature calibrations of the molar absorption coefficients. The results show that both OH groups and H<sub>2</sub>O molecules are equilibrium species in the melts, which is consistent with the idea that water is incorporated in a silicate melt through homogeneous reaction H<sub>2</sub>O + O = 2OH (Stolper, 1982). The product is favored by increase of temperature above the glass transition (~740 K for the 1.3 wt% H<sub>2</sub>O<sub>tot</sub> melt and ~700 K for the 3.0 wt% H<sub>2</sub>O<sub>tot</sub> melt), and the homogeneous equilibria in these two melts show a good agreement with each other; an equation  $\ln k = -3590/T + 3.01$  reproduces both. The  $\ln k$  values obtained in the melts are approximately 0.5 order magnitude greater than those obtained by Novak & Behrens (2001) in rhyolitic melts over the temperature range investigated.

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Yamashita S, Kitamura T & Kusakabe M, *Geochem. J.*, **31**, 169-174, (1997).

### GOLD COMPOSITION AND PHYSICO-CHEMICAL CONDITIONS OF FORMATION OF Au-Cu DEPOSITS

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The presence of Hg-gold is specific feature of gold deposits of Au-Cu geochemical type. Fineness trend of gold composition (from 850-900‰ down to 600-480‰) and increase of Ag content (from 15 to 45%) and Hg content (from 0.1 to 26%) are determined using microprobe analysis from early stages to last low-temperature (Fig.1). Mercurous gold occurs in mineral assemblages of late gold-copper-quartz stage and the Hg-content is defined by two factors: 1) the temperature of forming and 2) host rocks composition. The role of the first factor can

be shown on example of following deposits: Sinyuhinskoe - first form. - 350-280°C, Hg concentration in gold - 0,8%; Fedorovskoe - first form. - 300-280°C, Hg concentration in gold - 1,5%; Tardanskoe - first form. - 300-250°C, Hg concentration in gold - 5,4%; Lysogorskoe - first form. - 280-180°C, Hg concentration in gold - 24,6%; Novolusnikovskoe - first form. - 250-170°C, concentration<sub>Hg</sub> - 26%. Cinnabar, Hg-sphalerite, coloradoit, Hg-tetrahedrit, as well as barite and other low-temperature minerals occur in association with low-temperature gold. Hg content in gold is less than 1-2% for deposits localized in limestone host rocks, in spite of the gold, deposited at low temperatures and associated with cinnabar and other minerals. The thermodynamic analysis (Chiller program) of Au and Hg behavior in hydrothermal solutions has shown that temperature, Eh, C<sub>H<sub>2</sub>S</sub> of the solutions are the determining factors of Hg-gold deposition. This work is supported by RFBR #01-05-65096.

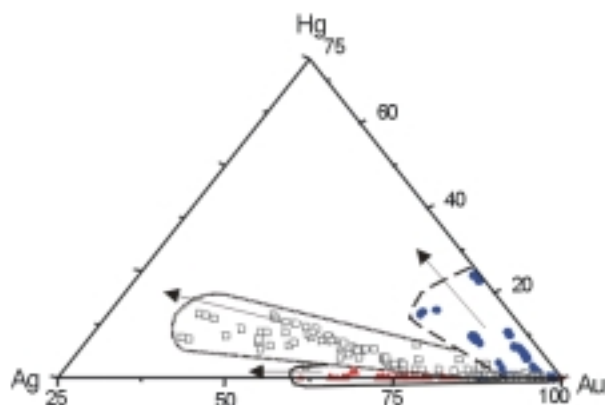


Figure 1: Trends of gold composition in time are shown by arrows.

### EXPERIMENTAL DETERMINATION OF OXYGEN ISOTOPE FRACTIONATION BETWEEN ZIRCON AND WATER

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Oxygen isotope fractionation between zircon and water has been experimentally quantified at 700, 800, 900 and 1000°C. Zircons were synthesised at 2000 MPa pressure from reagent-grade ZrO<sub>2</sub> and SiO<sub>2</sub> using conventional hydrothermal techniques. The charges consisted of approximately 80 mg mixture of solid reagents and 200 mg of doubly distilled water, sealed in 5x30±6 mm platinum capsules. Run duration varied from 105 to 290 hours. After the completion of the experiment, ampoules were cooled to room temperature over about 30 minutes, weighed again to check for leakage and centrifuged before opening. Water and solid products were separated and the solid phase was dried at 120°C. X-ray diffraction and scanning electron microscope examinations showed no evidence of impurities in zircon. Oxygen was extracted from zircon by reaction with ClF<sub>3</sub> at 550°C (Borthwick & Harmon, 1982). Water was converted to CO<sub>2</sub> for the isotopic analyses using guanidine hydrochloride (NH<sub>2</sub>)<sub>2</sub>CNH\*HCl (reagent quality) (Boyer et al., 1961). A least

square fitting to the results (Table) using the two-term polynomial  $1000\ln\alpha \sim a + bx^2$ , where  $x = 10^3/T$  (K), (Bottinga & Javoy, 1973) yields:  $1000\ln\alpha_{zrn-w} = -3.74 \pm 0.18 + 2.77 \pm 0.23x^2$ . The value obtained for "a" is fairly close to the expected value of -3.7 for high-temperature fractionations between anhydrous silicates and water (Bottinga & Javoy, 1973). Constraining the term "a" to a value of -3.7 for the experimental results leads to the following interpolation:  $1000\ln\alpha_{zrn-w} = -3.70 + 2.72 \pm 0.04x^2$

Acknowledgements. This work was supported by INTAS grant No 97-0172.

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### SPECTROPHOTOMETRIC STUDY OF As(III) AND Sb(III) CHEMISTRY IN HYDROTHERMAL SOLUTIONS TO 300°C

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The hydrothermal chemistry of arsenic and antimony is poorly known despite their importance in ore forming systems and their role in the hydrothermal biogeochemistry of certain thermophilic bacteria. As(III) and Sb(III) hydroxide and sulphide species occur in hydrothermal solutions and therefore the aim of this study has been to obtain data on ionization constants for the both arsenous and antimonous acid from 25 to 300°C at saturated vapour pressures. These equilibrium constants were obtained by means of high temperature ultraviolet spectrophotometry. Absorbance measurements were carried out in a flow-through Ti-Pd alloy cell with windows of uv-quality fused silica.

Solution preparation and handling as well as pH determination were carried out in such a way as to exclude any contact with air. All spectra were corrected at each temperature for the background absorption of the silica windows and water solvent. The pK<sub>1</sub> for H<sub>3</sub>AsO<sub>3</sub> was found to decrease from 9.25 to 7.11 over the temperature range, indicating that the H<sub>2</sub>AsO<sub>3</sub><sup>-</sup> becomes a more important arsenic-containing species in near neutral, geothermal fluids at 300°C. The pK<sub>1</sub> for H<sub>3</sub>SbO<sub>3</sub> ionization was found to change from 11.88 to 9.87 as temperature increases from 25 to 300°C.

Experiments in As(III)- and Sb(III)-containing sulphide solutions are underway to determine the stabilities and stoichiometry of thioarsenite and thioantimonites.

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#### THERMAL EXPANSION OF COLUMBITE: AN IN SITU X-RAY SINGLE CRYSTAL DIFFRACTION STUDY

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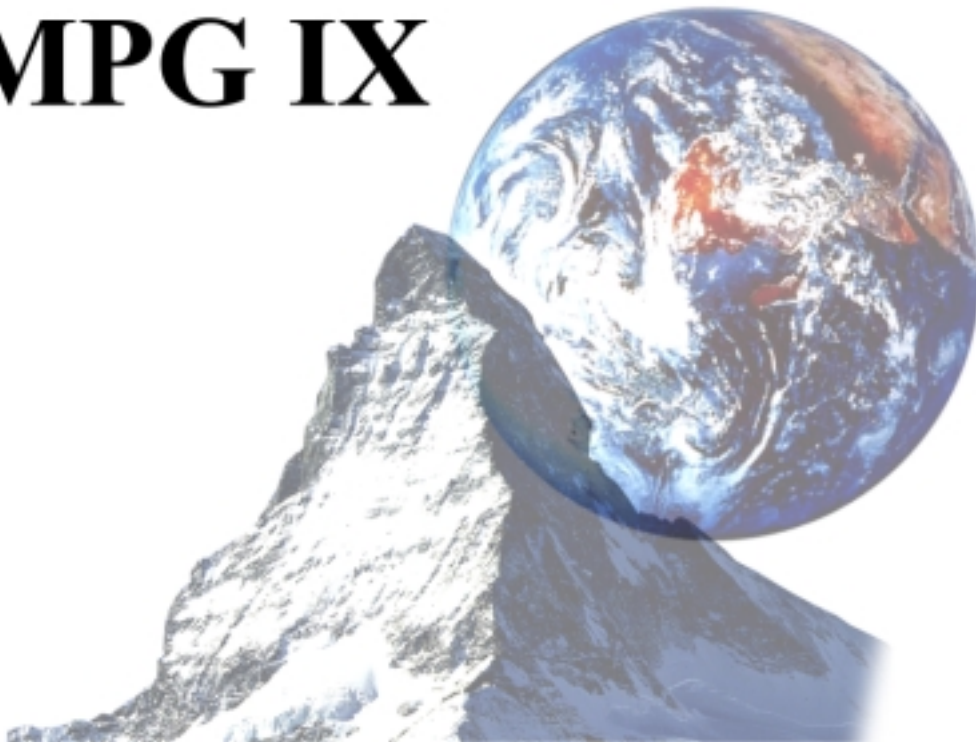
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Structural thermal expansion of an ordered natural columbite from Ambatofotsikely (Madagascar), having formula  $\text{Mn}_{0.39}\text{Fe}_{0.50}\text{Ti}_{0.19}\text{Sc}_{0.04}\text{Ta}_{0.09}\text{Nb}_{1.79}\text{O}_6$ , was measured by in-situ X-ray single crystal diffraction in the temperature range 25 - 900°C. The selected crystal, 0.28 x 0.33 x 0.41 mm in size, was put in a silica tube and fastened using quartz wool in order to avoid any mechanical stress. A small piece of graphite was used to prevent oxidation of the sample. A temperature-controlled microfurnace, specifically designed for the Philips PW1100 diffractometer, was used for the annealing experiments. The lattice parameters after each annealing run were derived from a least-squares procedure based on the Philips LAT routine which allows to take into account up to 60  $d^*$ -spacings, each measured considering all the reflections in the range  $3^\circ < \theta < 25^\circ$ . In order to avoid the superimposition of the effects of cation ordering on unit-cell parameters, the crystal was previously ordered by heating at 900°C. In fact, preliminary annealing experiments performed on several columbite crystals showed that the complete ordered cation distribution is stable over the T,P conditions of this study. In-situ high temperature data showed positive expansion of  $a$ ,  $b$ ,  $c$  lattice constants and cell volume. All the expansion curves could be fitted using linear correlation in the temperature range 100 - 900°C and very good  $R^2$  statistical tests were obtained for all the regressions. Thermal expansion coefficients indicated a very low degree of anisotropy; slightly higher expansions occur along  $a$  and  $c$  directions. High temperature diffraction studies under heating up and cooling down conditions yielded reversible expansion effects. The degree of order of the crystal under investigation remained constant for the duration of the experiment.

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