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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 $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (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_2O -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_2O 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_2O 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_2O_3 was exploited. The K_2O content of the melts in those experiments displaying Fo+Sp+Opx+Cpx+Melt was extrapolated back to 0 K_2O 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.

Presnall et al, 1979, *J. Petrol.* 20, 3-36

Walter & Presnall, 1994, *J. Petrol.* 35, 329-359

THERMODYNAMICS AND CRYSTAL CHEMISTRY OF Al SUBSTITUTED HEMATITE AND GOETHITE

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Synthetic samples of goethite-diaspore (FeOOH-AlOOH) and hematite-corundum ($\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$) 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 $X_{\text{Al}} = 0.2$) 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_3 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_3 -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 $\text{Fe}_{0.95}\text{Al}_{0.05}\text{O}_3$. 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, H₃PO₄), corrosion is weak up to 500°C, but more pronounced above that temperature, and various TiO₂ 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 H₂O up to 45 kbar, crossing the wollastonite I - wollastonite II transition. Similarly, we have investigated the solubility rate of SiO₂ 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, H₂O-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 H₂O 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 PbO AND Cr_2O_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 PbO and Cr_2O_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 H_2O , 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 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 NaCl solutions, the water clusters are considered to be de-polymerized by the insertion of Na^+ and Cl^- . On the other hand, for the carbonate solutions, the water clusters are considered to be polymerized by the insertion of carbonate anion. 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, Na_2CO_3 1 M solution conserves above polymeric "hard" nature up to 100°C. On the other hand, less polymeric "soft" nature of 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 NaCl-rich and 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). Subsidiary assembly is represented by clinopyroxene, grossular - pyrope garnet and carbonates. K_2O 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, K_2O content in clinopyroxene is more than 4,5 wt.% (Matveev et al., 1998). Diamonds were synthesized with the use of $(\text{Di}_{25}\text{Py}_{25}\text{KCC}_{50})_{60}$ - graphite₄₀ mixture at 7 - 8 GPa. It can be seen that the natural diamond - bearing carbonate - silicate assembly is reproducible in high - pressure experiment. This provides 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/Al₂O₃ ratios (up to 1.7) of these melts cannot be explained by lherzolite melting under anhydrous or hydrous conditions. Lherzolite melting involving CO₂-rich fluids (Schmidt et al., 2001) produces high-CaO/Al₂O₃ liquids, however, requires significant amounts of CO₂ 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 H₂O 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 H₂O+2.5% CO₂+2.5% O₂ 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 CO₂ 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 Al₂SiO₅ 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 Al₂SiO₅, however they could influence the thermodynamics of the aluminum silicates which connect with Al₂SiO₅ 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% SiO₂ and between 5 and 10 wt% MgO and MnO. Al₂O₃, TiO₂ and P₂O₅ are present in amounts < 5 wt%. Most abundant mineral phases found in solid slag are magnesio-wuestite ([Fe,Mg]O), lime (CaO), srebrodolskite (Ca₂Fe₂O₅), larnite (Ca₂SiO₄), hatrurite (Ca₃SiO₅) 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 to thermodynamic calculations it partially dissolved in the slag during the experiment. Nevertheless, the DTA analysis shows exothermic 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 corresponds to crystallisation of a Mo-Fe alloy.

FILLING CHRYSOTILE NANOTUBES WITH METALS

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Chrysotile is a sheet silicate (Mg₃Si₂O₅(OH)₄) 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)¹ 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 dehydroxylation 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 dehydroxylation leads to the development of an amorphous state, but TEM imaging shows that the tubular structure is still present at that temperature. Between 700°C and 850°C transformation to forsterite (Mg₂SiO₄) of the amorphous tube-walls takes place and the nanotube collapses to a polycrystalline fiber. This phase transformation is coherent with the maximum of the exothermic 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, Mg₂Al₃(AlSi₅O₁₂), has been subject to numerous experimental studies, in particular focussing on the Al,Si ordering and the storage of volatiles such as CO₂ and H₂O. 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. C₁₁^aC₂₂^a > C₃₃^a. 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 ± 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 CO₂ 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 qtz-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 qtz-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 SiO₂ 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 (FeTiO₃) and rutile (TiO₂) 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 Fe²⁺ vs. Ti⁴⁺ on O⁼ coupled with oxygen site geometry plus symmetry. As the electronic transitions are governed by the dipole rule, L_{2,3}-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 H₂O-CO₂ 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 H₂O, CO₂, and S between silicate melt and coexisting fluid, and the composition of the fluid phase in terms of H₂O, CO₂, SO₂, and H₂S, 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⁻¹;

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 CO₂-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_g (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 H₂O-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 H₂O 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 H₂O 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]. H₂O content was varied by mixing variable proportions of a dry and H₂O-bearing powder of the same composition, which resulted in an initial H₂O content between 4 and 8 wt%. To minimize Fe-loss, iron pre-saturated Au₉₀Pd₁₀ 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 H₂ 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

H₂O 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 H₂O contents examined. In addition to clinopyroxene, amphibole±magnetite are the liquidus phases at high H₂O contents, while garnet was the liquidus phase at relatively low H₂O content. The main compositional effects of increasing the H₂O 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 H₂O 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_{n/2}-Al₂O₃-SiO₂, where M = Na, K, Mg, Fe²⁺, 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 (Si⁴⁺ and charge-balanced Al³⁺). These units are linked via their nonbridging oxygens between the metal cation(s).

The equilibria among these units 2Qⁿ⇌Qⁿ⁻¹+Qⁿ⁺¹ 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/r² 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_i (activity coefficient) and log X_{Q_i} (mol fraction of species, i). By combining structural data with available information of configurational heat capacity, C_p^{config}, values of C_p^{config} for individual Q-species, C_p^{config}(Qⁱ), can be extracted. The C_p^{config}(Qⁱ)-values do not depend on metal cation properties. That information, in turn, can be used to calculate C_p^{config} from the structure of silicate melts and also aid in estimating the viscosity of silicate melts at magmatic temperatures.

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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 CaSi_4O_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% Al_2O_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 Al_2O_3 content.

The aluminosilicate solubility along the join CaSi_4O_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 H_2O in both Na- Ca-silicate-saturated aqueous fluids, $V_{\text{H}_2\text{O}}^{\text{fluid}}$, ranges between ~17 and ~27 cm^3/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 H_2O is the dominant component.

The isochors of both Na- and Ca-aluminosilicate-saturated aqueous fluids differ from those of pure H_2O 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.

¹H 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 ¹H 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 ¹H 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 H₂O) 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), LaCrO₃ heater, mixed Fe-FeO powdered specimen, and Al₂O₃ 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.