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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.

Andraut D, Bolfan-Casanova N & Guignot N, *Earth Planet. Sci. Lett.*, **193**, 501-508, (2001).

Kesson SE, FitzGerald DJ & Shelley JM, *Nature*, **372**, 767-769, (1994).

Kesson SE, FitzGerald DJ & Shelley JM, *Nature*, **393**, 252-255, (1998).

Ono S, Ito E & Katsura T, *Earth Planet. Sci. Lett.*, **190**, 57-63, (2001).

Ono S, Hirose K, Nishiyama N & Isshiki M, *Am. Mineral.*, **87**, 99-102, (2002).

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; Fe²⁺ and Fe³⁺ occupy different M-sites, whereas Fe²⁺ was partitioned on two sites before heating (one site shared with Fe³⁺).

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).

Comodi P & Zanazzi PF, *Phys. Chem. Miner.*, **27**, 377-385, (2000).

Guggenheim S, Chang YH & Koster Van Gross AF, *Am. Mineral.*, **72**, 537-550, (1987).

Ivaldi G, Ferraris G, Curetti N & Compagnoni R, *Eur. J. Miner.*, **13**, 1025-1034, (2001).

Pavese A, Ferraris G, Pischedda V & Fauth F, *Eur. J. Miner.*, **13**, 1071-1078, (2001).

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Pavese A, Ferraris G, Pischedda V & Radaelli P, *Mineral. Mag.*, **64**, 11-18, (2000).

Pavese A, Ferraris G, Pischedda V & Ibberson R, *Eur. J. Miner.*, **11**, 309-320, (1999).

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 – SbCl_4^- , sulfide – SbS_2^- , $\text{Sb}_2\text{S}_4^{2-}$, HSb_2S_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⁻¹. 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 H₂O or CO₂ 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, H₂, CO₂, H₂O and H₂O-CO₂, H₂O-H₂ 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 CO₂-bearing fluids are used in the experiments.

Using this apparatus, the viscosity of silicate and carbonated melts under high CO₂, Ar and water pressures as well as of the mafic silicate melts - dolomite xenoliths interaction under Ar, CO₂, H₂O and CO₂-H₂O mixtures pressures up to 4 kbars and in the temperature range from 1000° to 1350°C have been recently studied.

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THE HIGH CO₂, Ar AND H₂O PRESSURE EFFECTS ON MELT VISCOSITY IN THE JOIN Ab - Di - Na₂CO₃ IN A WIDE TEMPERATURE RANGE FROM T_m TO T_g 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 - Na₂CO₃ in a wide temperature range from 490°C to 1400°C at atmospheric and under high CO₂, Ar and H₂O 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⁻) and carbon dioxide (CO₃²⁻) which are stabilized into melts structure under high H₂O and CO₂ 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 Ab₃₅Di₃₅NaC₃₀ 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⁻) and carbon dioxide (CO₃²⁻) 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 CO₂ 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 Ab₂₅Di₇₅ 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 Nb⁵⁺ and Ta⁵⁺ 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 ± 0.22 at% Pt, or 0.53 ± 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.

Borisov A & Palme H, *Geochim. Cosmochim. Acta*, **61**, 4349-4357, (1997).

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-

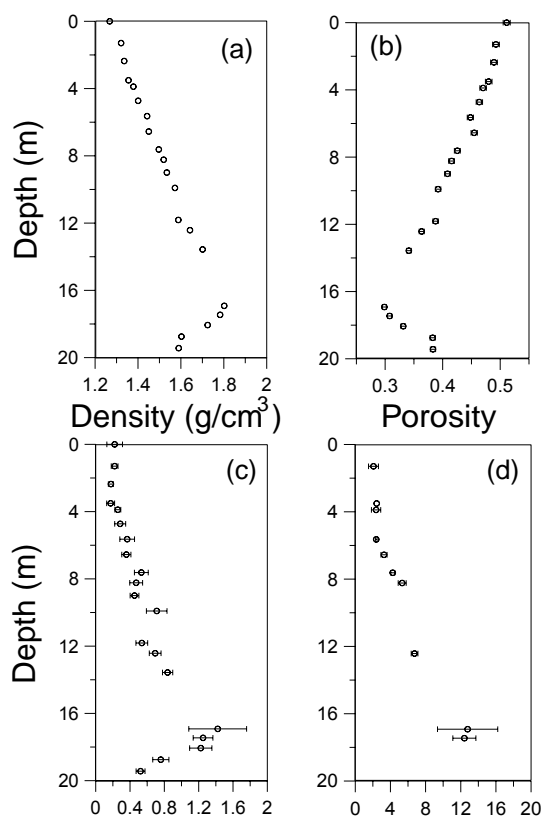


Figure 1: Metrics versus depth in selected drill core. All uncertainties based on replicate measurements: a) uncertainty (2σ) smaller than symbols; b) and c) uncertainty 2σ ; d) uncertainty 1σ .

Broxton, D.E. and Reneau, S.L., *Los Alamos National Lab Report, LA-13013-MS*, (1995).