processes of magmas. The knowledge of the CO_2 speciation in silicate liquids is crucial for understanding the CO_2 dissolution mechanisms, the diffusion mechanisms, and the degassing processes. Using IR spectroscopy, we investigated the speciation of CO_2 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_2 species reaction $CO_2 + O^{2-} = CO_3^{2-}$ in silicate glasses/melts shifts towards molecular CO_2 with increasing temperature. The CO_2 species concentrations and an ideal solution model were used to determine equilibrium constants for the homogeneous species reaction. We derived the thermodynamic quantities $\Delta H°$ and $\Delta S°$ for this reaction, assuming that the species concentrations reflect those at experimental temperatures ($\Delta H°$ = -12 ±2 kJ mol^{-1} and $\Delta S°$ = -23 ±3 J $mol^{-1}K^{-1}$ for albitic composition; $\Delta H°$ = -29 ±2 kJ mol^{-1} and $\Delta S°$ = -32 ±3 J $mol^{-1}K^{-1}$ 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 773 K. This is far above the heating duration of 48 h. Nevertheless, we observe a significant change in CO_2 speciation even at 673 K in the albitic glass. We conclude that in contrast to the H_2O species reaction the relaxation of the CO_2 speciation is decoupled from the network structure relaxation of the melt/glass. The CO_2 molecule attached to a bridging oxygen to form carbonate (Kohn et al., 1991) can explain the observed change of CO_2 speciation below T_g. The CO_2 species reaction involving attachment and deattachment of CO_2 molecules from bridging oxygens does not affect the highly polymerised rigid glass network structure.

Kohn SC, Brooker RA & Dopree R, *Geochim. Cosmochim. Acta*, **55**, 3879-3884, (1991).

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^{2-} by replacing O^{2-} on the anion sublattice, as described by the reaction: $S^{2-} + 1/2\ O_2 = O^{2-} + 1/2\ S_2$ suggesting the relationship: $\log C_S = \log [S] + 1/2 \log fO_2/fS_2$ (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: $FeO_{silicate} + 1/2\ S_2 = FeS_{sulfide} + 1/2\ O_2$ For which: $-\Delta G/2.3RT = \log a(FeS) - \log a(FeO) + 1/2 \log fO_2/fS_2$ (2) Subtracting (1) from (2) to eliminate fO_2 and fS_2 gives: $\log [S]_{SCSS} = \Delta G/2.3RT + \log C_S + \log a(FeS) - \log a(FeO)$ (3) where $[S]_{SCSS}$ 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(FeO). The former term has a positive slope versus FeO and dominates at high FeO, whereas the {-log a(FeO)} term has a negative slope versus FeO, and should dominate at low FeO. The net result is that $[S]_{SCSS}$ 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 1400ºC 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.

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: CaO-Gd_2O_3-Al_2O_3-TiO_2-ZrO_2 along compositional line: zirconolite – gadolinium aluminate with perovskite structure ($CaZrTi_2O_7$ – $GdAlO_3$) 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) $CaZrTi_2O_7$ – x $GdAlO_3$ 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 $CaZrTi_2O_7$) 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/loveringite are also present. Prevalence of zirconolite (~70-75%) over perovskite phase (~20-25%) is due to features of elements partitioning among the phases. Zirconolite ($Ca_{0.36}Gd_{0.60}Zr_{1.12}Ti_{1.40}Al_{0.47}O_7$) is capable to incorporate Gd and Al in more extent than perovskite ($Ca_{0.64}Gd_{0.34}Ti_{0.73}Al_{0.26}O_3$). At x = 0.75 only perovskite content becomes approximately equal to zirconolite and XRD pattern for perovskite phase comes nearer to typical of $GdAlO_3$. Average zirconolite and perovskite compositions are $Ca_{0.24}Gd_{1.00}Zr_{0.93}Ti_{1.21}Al_{0.60}O_7$ and $Ca_{0.31}Gd_{0.64}Ti_{0.43}Zr_{0.06}Al_{0.55}O_3$, 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^2·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, Mg_2SiO_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 $Na_2O + CaO + MgO + Al_2O_3 + SiO_2$ (NCMAS) and NCMAS + FeO. Gels and glasses were used as strating 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.

Okamoto K & Maruyama S, *Fluid/Slab/Mantle /UHP-min. workshop at Waseda Univ*, 65-69, (2001).

Gasparik T, *Phys Chem Minerals*, **23**, 476-486, (1996).

Akaogi M, Hamada Y, Suzuki T, Kobayashi M & Okada M, *Phys Earth Planet Inter*, **115**, 67-77, (1999).

Irifune T & Ringwood AE, *Earth Planet Sci Lett*, **117**, 101-110, (1993).

Hirose K, Fek S, Ma Y & Mao HK, *Nature*, **397**, 53-56, (1999).

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 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 (Andrault et al, 2001) should be considered to investigate the densities of high pressure minerals in the multicomponent systems.

Andrault 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 collect 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 2 M_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 $2(OH)^- + 2Fe^{2+} \longrightarrow 2O^{2-} + 2Fe^{3+} + H_2$ 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^{2+} and Fe^{3+} occupy different M-sites, whereas Fe^{2+} was partitioned on two sites before heating (one site shared with Fe^{3+}).

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 2 M_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 2 M_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).