Phase diagram and P-V-T equation of state of Al-bearing seifertite at lowermost mantle conditions


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Abstract

We investigated the properties of Al-bearing SiO$_2$ (with 4 or 6 wt% Al$_2$O$_3$) at pressures and temperatures corresponding to the lowermost mantle, using laser-heated diamond anvil cell coupled with synchrotron-based in-situ X-ray diffraction. The phase transition from CaCl$_2$-structured to α-PbO$_2$-structured (seifertite) polymorphs occurs between 113 and 119 GPa at 2500 K. The range of pressure where the two phases coexist is small. There is a slight decrease of the transition pressure with increasing Al-content. We propose a tentative phase diagram reporting the minerals composition as a function of pressure in the SiO$_2$-Al$_2$O$_3$ system.

We also refine the P-V-T equation of state of Al-bearing seifertite based on volume...
measurements up to more than 160 GPa and 4000 K ($V_0 = 92.73(10) \text{ Å}^3$, $K_0 = 304.2(3.0) \text{ GPa}$, $K'_0 = 4.59$ (fixed), $\Theta_{D0} = 1130 \text{ K}$ (fixed), $\gamma_0 = 1.61$ (3)). At 300 K, the volume decrease at the CaCl$_2$ to $\alpha$-PbO$_2$ transition is 0.5(1) %, a value slightly lower than the 0.6% reported previously for Al-free samples. At high temperature, the Grüneisen parameter of seifertite is found to be similar to that of stishovite. Nevertheless, the $\Delta V/V$ across the CaCl$_2$-form to seifertite transition is found to increase slightly with increasing temperature.

Across the phase transition, volume changes can be translated into density changes only when the Al substitution mechanisms in both CaCl$_2$-form and seifertite are defined. The analysis of all available data sets suggests different substitution mechanisms for the two SiO$_2$ polymorphs. Al-substitution could occur via O-vacancies in the CaCl$_2$-form and via extra interstitial Al in seifertite. This would result in a density increase of 2.2(3) % at 300 K for SiO$_2$ in basaltic lithologies. Alternatively, the same Al-substitution mechanism in both of the SiO$_2$-dominated phases would yield a density increase of 0.5(1) %.

**Keywords:** Seifertite, phase transition in SiO$_2$, P-V-T equation of state, lowermost Earth mantle.

**Introduction**

Seismic tomography suggests that the slab behavior depends primarily on the original plate velocity, the penetration angle of the slab into the mantle and the age of the subducted crust. In several regions the slabs appear to flatten and be delayed near the 660 km discontinuity. In most regions, however, slabs eventually descend through the lower mantle (e.g. (van der Hilst et al., 2007; van der Meer et al., 2010)). The sinking of subducting slabs in the deep mantle is controlled primarily by the density difference between the slab materials and the ambient mantle, while the mantle viscosity governs the speed of the descent. Detailed tomographic mapping of high-velocity regions in the mantle and comparison with surface paleogeography indicate that most slab remnants
sink through the entire mantle in about 250 Ma, i.e. with an average speed of about 1.2 cm/year (van der Meer et al., 2010).

The slab density is partly related to the slab temperature but also to the intrinsic density of the various minerals and their relative proportions. Older and relatively colder slabs are expected to penetrate the deep mantle more easily. Still, a major complication is the layered structure of the subducted slab, including its sedimentary, basaltic and harzburgitic components. The density inversion between peridotite and basaltic material in the uppermost 50-100 km of the lower mantle caused by gradual transformation of majoritic garnet (e.g. (Ringwood, 1991)) led to the suggestion of partial segregation (flotation) of garnetite near the 660 km discontinuity. The low temperature and high viscosity of slab material, however, make such a lithological separation unlikely. Another possible site of basalt-peridotite separation is the core-mantle boundary (CMB) region. Sinking slab material deflected laterally along the CMB thermal boundary layer will be heated considerably, resulting in reduced viscosity (e.g. (Steinberger and Calderwood, 2006)). Even moderate basalt-peridotite density contrasts in the D" zone could therefore lead to such separation.

Difference in chemical composition between basaltic and peridotitic materials yields largely different mineral assemblages and mineral compositions at deep mantle P-T conditions. Peridotites varying from fertile lherzolite to depleted harzburgite are dominated by Mg-perovskite (pv, 70-80%) with minor amounts of ferropericlase (15-25%) and Ca-perovskite (Ca-pv, 0-10%). Basalts have 3-10 times higher concentrations of Al, Ti, Ca and Na and more than 5 times lower concentration of Mg than peridotite. The resulting lower mantle basaltic mineralogy has no ferropericlase and a low proportion of Mg-perovskite (or post-perovskite) with high Fe/Mg-ratio. Over-abundance of silica and alumina produces the separate silica-dominated (Irifune et al., 1994) and Al-rich phases (NAL and Ca-ferrite phases, (Akaogi et al., 1999; Miyajima et al., 1999)). At intermediate lower mantle depths, common basalts crystallize 15-20% CaCl$_2$-structured silica, 15-25% Ca-ferrite, 35-40% Mg-perovskite and 20-30% Ca-perovskite (Hirose et al., 1999). It is generally estimated that the Fe-rich Mg-perovskite makes basaltic material denser than peridotite
throughout the lower mantle below 720 km depth (e.g. (Guignot and Andrault, 2004; Hirose et al., 2005; Ricolleau et al., 2010)). Partly due to its elevated bulk modulus, the CaCl$_2$-structured silica phase becomes the least dense phase of the subducted slabs at 70-120 GPa, with a density difference of more than 3 % relative to the most abundant Mg-rich silicate perovskite.

At ~2500 K, pure SiO$_2$ was reported to undergo a first-order phase transformation from the CaCl$_2$-form to seifertite (adopting the $\alpha$-PbO$_2$-structure (El Goresy et al., 2008)) at ~120 GPa, with a dp/dT-slope of about 10 MPa/K (Murakami et al., 2003). In parallel, (Hirose et al., 2005) showed that the silica-dominated phases in a basaltic composition display considerable Al$_2$O$_3$ solubility.

The presence of Al$_2$O$_3$ produces a considerable pressure reduction of the stishovite to CaCl$_2$-phase transition, from ~50 GPa for pure SiO$_2$ to ~25 GPa for Al-bearing silica (Bolfan-Casanova et al., 2009; Lakshtanov et al., 2007b). On the other hand, the effect of Al$_2$O$_3$ on the CaCl$_2$-form to seifertite transformation and on the density change associated with this transition remains poorly constrained. Our objective here is to further evaluate the phase and density relations in the binary silica-alumina system at the P-T conditions of the lowermost mantle.

**Experimental methods**

Silica glasses with 4 and 6 wt% Al$_2$O$_3$ were prepared in Pt-crucibles at 1650-1670 °C in air, using a vertical furnace at Centre for Material Science, University of Oslo and a Nabertherm furnace at Bayerisches Geoinstitut, Bayreuth, Germany. Tiny air bubbles persisted even after 3-4 repetitions of re-grinding and re-melting. Electron probe microanalyses yield Al-contents of 4.1(4) and 5.8(3) for glasses Al-4% and Al-6%, respectively. Relatively high values of standard deviations denote persistence of some chemical heterogeneity in the glass. Our analytical precision yielded element totals of 99.7(2) and 99.5(2) for more than 20 measurements on glasses Al-4% and Al-6%, respectively. The glasses were finely powdered and mixed with 10-15 wt% Pt-powder which served as a YAG laser absorber and a pressure indicator at high temperatures. Overall, our samples should be homogeneous on a 2-3 micrometer scale, which corresponds to the size of our X-ray probe.
Pressures up to 120 GPa were generated by membrane-type diamond anvil cells (DAC) equipped with beveled diamonds of 150/300 or 100/300 µm diameters. Rhenium gaskets were pre-indented to ~25 µm thickness before laser drilling or spark erosion of 40-60 µm diameters holes. Sample pellets were loaded between two pieces of dry NaCl or KCl, which served as pressure transmitting medium and thermal insulator from the diamonds. Temperatures up to more than 4000 K were generated by two NIR Ytterbium fiber lasers. The size of the hot spot on the sample was kept between 15 and 25 µm by adjusting the distance between the focusing-lenses and the sample. Using the spectral radiometry method, precision in temperature determination is better than 50 K. This value is also a maximum for temperature fluctuations at high temperature. Because phase transformations between dense silica polymorphs are known to be sluggish and depend on the starting material and pressure–temperature history (Prakapenka et al., 2004), we heated for 20-40 min at each temperature point.

Pressures at 300 K were determined based on the equation of state (EoS) of platinum (Holmes et al., 1989). It enables quantitative comparisons with previous reports on the formation of seifertite (mostly (Hirose et al., 2005; Murakami et al., 2003)), in which Pt (Holmes et al., 1989) or Au (Tsuchiya, 2003) EoS were used. Pressures derived from Pt and Au were reported to be fully compatible between each other (Hirose et al., 2005). Alternatively, we used the NaCl-B2 EoS which has been calibrated against Pt (Sata et al., 2002). NaCl provides accurate pressure measurements after annealing at low temperature, when the Pt diffraction peaks remain broad due to poor release of the deviatoric stresses in the silica glass. At high temperature, the Pt that is intimately mixed with the starting material was used as a reliable sample-pressure indicator. We observe that the pressures measured at high temperatures are consistent with a pressure correction $\Delta P = 2.5 \times 10^{-3}$ GPa/K (Andrault et al., 1998) compared to the nominal pressure measured at 300 K. The pressure error is estimated to be about 3%.

Angle dispersive X-ray diffraction was performed in situ at the P02.2 (PETRA III, DESY) and ID27 (ESRF) beamlines. We used a monochromatic X-ray beam tuned at 42.7 keV (P02.2) or 33
keV (ID27) focused to less than 2x2 µm² FWHM by two mirrors in the Kirkpatrick-Baez configuration. Diffraction images were acquired on a Perkin Elmer flat panel (P02.2) or Mar-CCD (ID27) detector with exposure times of 10-30 seconds, with or without sample rotation. Distance between sample and detector of 451 mm (P02.2) or 223 mm (ID27) was calibrated using a CeO₂ (P02.2) or LaB₆ (ID27) standard. Diffraction patterns were integrated and treated using the Fit2D (Hammersley, 1996) and the GSAS (Larson and Von Dreele, 1988) codes (Figures 1 and 2). The orthorhombic lattice (Pbcn) of seifertite contains 4 independent parameters for atomic positions plus thermal factors for Si and O atoms. Due to the limited number of crystallites present in the X-ray spot, we preferred to avoid refinement of all those parameters. We first performed full X-ray profile refinement, using the Rietveld mode and keeping all atomic positions fixed to the values previously reported in the literature (upper frames in Figure 2; (El Goresy et al., 2008)). Although the atomic parameters may evolve slightly with P and T, the changes will be minor because these parameters are closely linked to the atomic arrangement within the lattice. Consequently, the evolution of the diffraction peaks intensity with pressure should also be reduced. This technique allows to model the experimental peaks with $d_{hkl}$ lines of comparable intensities and prevents evolution of the orthorhombic lattice toward solutions that are favorable from a mathematically rather than physical point of view. In a second step, we verified the adequateness between all experimental and theoretical diffraction features, using the Le Bail mode in which the peak intensities are adjustable parameters (lower frames in Figure 2; (Le Bail, 1992)). For the NaCl or KCl pressure medium and platinum, we adjusted each diffraction line intensity independently using the Le Bail method, in order to obtain a best refinement of the diffraction profile. More than 20 diffraction lines were used to identify the CaCl₂-structure and seifertite in two-theta ranges between 5 and 18 (P02.2) and 6 and 22 (ID27) degrees. The reduced chi-squared value are typically 0.15 or 0.07 for seifertite (or the CaCl₂-form) refined in Rietveld or Le Bail modes, respectively. The error in volume determination is less than 0.3%. The XRD data were acquired repeatedly during heating and after quenching to room temperature.
Phase transformation from CaCl$_2$-form to seifertite

We conducted 5 different runs (4 at P02.2 and 1 at ID27) of stepwise compression at 300 K followed by laser heating at successively higher temperatures. When the same sample was used for repeated experiments at increasing pressure, previously unheated sample areas were investigated at each new pressure. Crystallization of the CaCl$_2$-form from the silica glass was obtained after laser heating to 2500 K at 91, 98 and 106 GPa and at 90 and 107 GPa for the samples containing 4 and 6 wt% Al$_2$O$_3$, respectively. After further steps of incremental pressurization, heating led to the formation of seifertite at nominal pressures of 119 and 121 GPa in the samples with 4 and 6 wt% Al$_2$O$_3$, respectively. In the 5$^{th}$ experiment performed on the Al-6% glass at the ID27 beamline, we observed pure CaCl$_2$-phase up to 108 GPa and 2500 K, a mixture of the two silica polymorphs between 108 and 118 GPa, and pure seifertite starting from this pressure. Those results pinpoint at ~2500 K the transition pressures at 108-119 GPa and 108-118 GPa for Al-4% and Al-6% compositions, respectively. Those values are compatible with previous studies: At similar temperatures, the transition pressure was reported at 122 GPa for pure SiO$_2$ (Murakami et al., 2003) and between 100 and 113 GPa for MORB compositions (Hirose et al., 2005). Because our starting material is a glass, we did not observe any metastable formation of seifertite at about 80 GPa as reported previously from cristobalite starting material (Dubrovinsky et al., 2001; Shieh et al., 2005). The glass crystallization is completed above ~3000K (Figures 1-3). In all cases, no further phase transformation was observed upon heating after the glass crystallization. Although additional Al-bearing phases were not detected, we cannot rule out Al$_2$O$_3$ saturation of the CaCl$_2$-structured and seifertite phases. Such saturation would imply that the Al$_2$O$_3$-content in SiO$_2$-dominated phases are lower than the 4 or 6 wt% of our starting materials. However, Al$_2$O$_3$ saturation in our seifertite is unlikely, because seifertite crystallized from a natural basalt was previously reported with 12.8 wt% Al$_2$O$_3$ (Hirose et al., 2005).
Based on the available data, we draw a tentative phase diagram for the Al-bearing SiO$_2$ compositions as a function of pressure (Figure 4). Due to the presence of Al-rich Ca-ferrite (near the MgAl$_2$O$_4$-NaAlSiO$_4$ join), the Al$_2$O$_3$ activity in a MORB composition is expected to be high but lower than unity. Therefore, the Al$_2$O$_3$-contents of 3.4 and 12.6 wt% of the CaCl$_2$-phase and seifertite, respectively, reported by Hirose et al. (2005), provide lower bounds for the Al$_2$O$_3$ solubility limit in silica. These values can hardly be used to calculate an Al partition coefficient between the two phases ($K_{\text{Al}}^{\text{CaCl2/Seifertite}}$), because the changes in mineralogy in their samples, between 60 GPa and 113 GPa, is likely to affect the Al-activity significantly. On the other hand, the pressure of 113 GPa for their run #6 corresponds to a higher bound for the CaCl$_2$-form to seifertite phase transition in case of saturation in Al$_2$O$_3$. The results for our two compositions provide constraints on the position of the phase loop between the two minerals. The binary phase loop tends towards lower pressure with increasing Al-content. We draw straight lines for phase boundaries compatible with all data sets in the phase diagram (Figure 4). By comparing the Al-contents in CaCl$_2$-phase and seifertite at a given pressure, we calculate a $K_{\text{Al}}^{\text{CaCl2/Seifertite}}$ value of $\approx 0.55(5)$. For this value, the phase transformation for e.g. an Al-bearing silica composition with 5 wt% Al$_2$O$_3$ would extend from $\approx 112$ GPa to $\approx 116$ GPa, a pressure gap corresponding to a $\approx 70$ km thick transition interval at a depth of $\approx 2500$ km.

Results for the CaCl$_2$-form of silica

We report our SiO$_2$ volumes measured at 300 K for the CaCl$_2$-form below the transition pressure [Figure 5A]. We also report the data sets available for starting materials made of pure SiO$_2$ (Andrault et al., 2003; Murakami et al., 2003), MORB (Hirose et al., 2005), and an Al-bearing SiO$_2$ glass with 4 wt% Al$_2$O$_3$ (Bolfan-Casanova et al., 2009). In the latest study, stishovite was synthesized with an estimated Al$_2$O$_3$-content of 2.2-3.6 wt%, for a starting material containing 4 wt%. This range of values is comparable to 3.4 wt% Al$_2$O$_3$ measured in the CaCl$_2$-form by Hirose et al. (2005) and slightly less than the 4 and 6 wt% Al$_2$O$_3$ present in our starting materials. At this
point, it is interesting to note significant differences in the CaCl$_2$-form volumes between previous studies. The lowest compression curve, by ~1% of volume or 6 GPa compared to our previous studies, is that of pure SiO$_2$ reported by Murakami et al. (2003). At mid distance between those two curves plot the compression curve of MORB (Hirose et al., 2005). These differences could be due to a difference in pressure determination or in volume measurement of the silicate phase. Because no pressure medium was used in the previous studies, the most likely cause of experimental difference originates from pressure determination. The volume relaxation from high-temperature to 300 K for metallic blobs of Pt or Au pressure markers enclosed in a hard silica matrix can be hampered when shutting down the IR-laser. However, the volume change at the transition from CaCl$_2$-form to seifertite should be precise and significant for all studies, because the same experimental procedure was used throughout.

Our data set plots in perfect agreement with our prior studies performed on Al-free (Andrault et al., 2003) and 4 wt% Al$_2$O$_3$ (Bolfan-Casanova et al., 2009), irrespective of Al-composition. Using the same experimental methods, compression curves of the 4 starting materials (2 in previous studies and 2 in the present one) are found within the experimental error. It shows that Al presents a negligible effect on the volume of CaCl$_2$-structured silica at very high pressures. A study specifically dedicated to the effect of Al on the stishovite bulk modulus, using Brillouin scattering at ambient conditions, showed that addition of 6 wt% Al$_2$O$_3$ induces a ~8% decrease in bulk modulus $K_0$ (Lakshtanov et al., 2007a). However, the well-known tradeoff between $K_0$, its first pressure derivative $K'_0$, and maybe also second derivative $K''_0$, makes the compression curve very similar at high pressures. In our previous studies (dotted black line in Figure 5A), the Birch-Murnaghan formalism was used to refine an isothermal (300 K) compression curve with the following parameters: $V_0 = 46.77 \, \text{Å}^3$, $K_0 = 292 \, \text{GPa}$ and $K'_0 = 4.59$ (see sample PV-20 in Table 1 of (Bolfan-Casanova et al., 2009)), where $V_0$ is the unit cell volume at standard P-T conditions. In this study, we preferred the use of the Vinet EoS formalism for reference isotherms, in order to facilitate the comparison with a recent study on stishovite (Wang et al., 2012). We therefore adjusted the
previous compression curve using the Vinet EoS and obtained $V_0 = 46.77 \, \text{Å}^3$ (fixed), $K_0 = 297(7)$ GPa and $K'_0 = 4.59$ (fixed).

To our knowledge, there is no study reporting the EoS of the CaCl$_2$-form of Al-bearing SiO$_2$ phases at high pressures and temperatures. A previous work performed up to 54 GPa and 1700K reports the following parameters for the high temperature properties of stishovite: $\Theta_{D0} = 1130$ K, $\gamma_0 = 1.67$, $a=1$, $b=3$, where $\Theta_{D0}$ and $\gamma_0$ are the Debye temperature and the Grüneisen parameter at standard P-T conditions, respectively (Wang et al., 2012). The EoS formalism was based on Mie-Grüneisen-Debye to model the high temperature properties. In absence of a more reliable data set, we assume the following parameters to estimate volumes of the CaCl$_2$-form at all P-T conditions:

$V_0 = 46.77 \, \text{Å}^3$, $K_0 = 297$ GPa, $K'_0 = 4.59$, $\Theta_{D0} = 1130$ K, $\gamma_0 = 1.67$, $a=1$, and $b=3$. Based on this PVT EoS, we calculate volumes of the CaCl$_2$-form at 300, 2000 and 4000 K in the pressure range investigated in this study (Figure 5B).

**P-V-T equation of state of seifertite**

We also report our SiO$_2$ volumes measured at 300 K [Figure 5A] and at temperatures up to 4300 K [Figure 5B] for seifertite between the transition pressure and 162 GPa. Because seifertite and the CaCl$_2$-structured phase have 4 and 2 formula units per unit cell, respectively, we divide the seifertite volume by 2 to simplify the comparison. As for the CaCl$_2$-form, we also report data sets for pure SiO$_2$ (Murakami et al., 2003) and MORB (Hirose et al., 2005). We first refine the P-V-300K EoS of seifertite of Al-6 composition to $V_0 = 92.73(10) \, \text{Å}^3$, $K_0 = 304.2(3.0)$ GPa and $K'_0 = 4.59$ (fixed), using the 14 data points recorded at ambient temperature in this study [Table 1]. We fix $K'_0$ because our experimental data set does not allow to adjust precisely the 3 parameters independently, due to the dependency between $K_0$ and $K'_0$ values. The seifertite bulk modulus appears very similar to that of the CaCl$_2$-form, only ~2% higher than the value of 297 GPa recalculated for $K'_0 = 4.59$, based on a study using precisely the same experimental methods (Bolfan-Casanova et al., 2009). If we fix $K'_0 = 5.0$, we obtain $V_0 = 93.75(10) \, \text{Å}^3$ and $K_0 = 270.3(3.0)$ GPa. The bulk modulus is found

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~7% lower than the 292 GPa reported for stishovite in a previous study using a large volume press apparatus (Wang et al., 2012).

At high temperature, we refine $\Theta_{D0}=1130$ K (fixed), $\gamma_0=1.61(3)$, $a=1$ (fixed) and $b=3$ (fixed) [Table 2], using the 16 data points recorded in this study [Table 1]. The choice of fixing $\Theta_{D0}$, $a$, and $b$ is to facilitate the quantitative comparison with a previous study on stishovite (Wang et al., 2012). With these parameters, the maximum difference between the experimental and theoretical pressures is 2.7 GPa, which is within the experimental uncertainties. The refined room pressure Grüneisen parameter of seifertite appears very similar to that proposed recently for stishovite, which was reported as 1.67 (Wang et al., 2012). In the P-T range investigated, we calculate Debye temperature and Grüneisen parameter mean values of $\Theta_D=1488(20)$ K and $\gamma=0.78(4)$, respectively (the $\Theta_{D0}$ and $\gamma_0$ reported above are ambient values). Based on this PVT EoS, we calculate volumes of seifertite at 300, 2000 and 4000 K for the pressure range investigated in this study (Figure 5B).

We finally analyzed the evolution of the seifertite cell parameters with pressure (Figure 6). We treated the fictive volumes $a^3$, $b^3$ and $c^3$ in a similar manner like seifertite unit cell volumes. It results in a set of isothermal and high temperature elastic parameters [Table 2]. The Seifertite unit cell is quite anisotropic at high P and T, with the a parameter being 30% less incompressible than b and c, and with the b parameter showing a Grüneisen parameter about twice of a and c.

**Density change across the phase transition**

A comparison between the 300 K isothermal compression curves of the CaCl$_2$-form and seifertite of Al-6 composition evidences a volume change $\Delta V/V= -0.5(1)\%$ across the phase transition [Figure 5A]. This value is very comparable to the volume changes of -0.6% refined for pure SiO$_2$ (Murakami et al., 2003). For temperatures of 2000 and 4000 K, we refine volume changes of -0.52(10) % and -0.62(10) %, respectively, based on the PVT EoS [Figure 5B]. The fact that $\Delta V/V$ increases slightly with temperature is compatible with a Grüneisen parameter lower in seifertite compared to the CaCl$_2$-form.
The volume reduction of -0.6% observed for pure SiO₂ (Murakami et al., 2003) translates directly in a +0.6% density change at the transition. However, the relationship between volume and density is more complex for Al-bearing SiO₂ compounds. Three different mechanisms are possible for the Al₂O₃ insertion in SiO₂ (Bromiley et al., 2006; Hirose et al., 1999): (a) Formation of one oxygen vacancy per two Si⁴⁺ substituted by Al³⁺; (b) Addition of one extra-interstitial Al³⁺ (i.e. a total of four Al³⁺) when three Si⁴⁺ are replaced; (c) A coupled (Al³⁺,H⁺) substitution in the presence of hydrogen. Also, one should keep in mind that different substitution mechanisms could still coexist in the same silica phase. Deriving density changes from volume changes at the phase transition requires assumptions on the predominant Al substitution mechanism in both the low and high pressure forms of SiO₂. The reason is that the number of atoms per unit cell, and thus the corresponding atomic mass, is not the same for the three different Al-substitution mechanisms.

Based on volume variations available for various Al-bearing compositions, we calculate density changes that should be expected at the transition for all possible types of substitution mechanisms in CaCl₂-form and seifertite (Table 3).

Thermodynamic principles require a density increase (a positive \(\Delta \rho\)) for the pressure-induced phase transformation irrespective of composition. Therefore, some Al-substitution mechanisms can be readily eliminated. First of all, having an identical substitution mechanism (ISM) for both polymorphs would yield a 2.3% density reduction at the transition pressure for Al-bearing silica in the MORB material (Hirose et al., 2005). This situation is not impossible, because this negative \(\Delta \rho\) could be counterbalanced by complementary mineralogical changes and element partitioning in the multi-component material. However, a largely negative \(\Delta \rho\) would be surprising and we therefore search for a more likely situation. The O-vacancy substitution mechanism in seifertite is unlikely, because this would cause negative \(\Delta \rho\) in our samples whatever is the Al₂O₃-substitution mechanisms in the CaCl₂-form (once the ISM case is discarded). In the same way, the Al-interstitial mechanism is unlikely in the CaCl₂-form. In a study at pressures up to 25 GPa, it was shown that the mechanism involving coupled Al³⁺ and H⁺ substitution can only explain 40% of the Al-
substitution in stishovite (Litasov et al., 2007). In our experiments, particular care was taken to
prevent the presence of water. Also, any water present in one polymorph is also likely to be present
in the other, which would yield a similar Al-substitution mechanism in both polymorphs (the ISM
case).

The most likely mechanisms are therefore the O-vacancy substitution in the CaCl₂-form and the
Al³⁺-interstitial substitution in seifertite (the O->Al mechanism in Table 3). This is the only
scenario in which the phase transition obeys the thermodynamic rule of density increase for all the
data sets available. It is compatible with a previous study showing that formation of O-vacancies is
the predominant mechanism for the Al-substitution in stishovite (Bromiley et al., 2006). It remains
unknown how it evolves with the increasing pressure in the rutile-structure, as well as across the
structural distortion that yields the CaCl₂-type structure. For our samples with 4 or 6 wt% Al₂O₃,
the O->Al mechanism would imply a ~2.19% density increase at the phase transition. This density
increase is significantly larger than for the pure SiO₂ system (Δρ/ρ~0.6%), in agreement with a
lowering of the transition pressure with increasing the Al-content. In MORB, the density change is
smaller, with a value of ~0.23%, because of the strong Al-partitioning into seifertite.

Buoyancy of the subducted slabs

Recent studies agree that basaltic materials of subducted slabs have a slight, but significant,
density excess compared to a peridotitic lower mantle, even if the slabs are thermally equilibrated.
Depending on composition and pressure, a density difference of 0.4 to 4.0 wt% was reported
(Guignot and Andrault, 2004; Hirose et al., 2005; Ono et al., 2005; Ricolleau et al., 2010). MORBs
with elevated Fe-content are clearly denser. Despite the density excess, basaltic material under
lower mantle conditions contains free silica phases, which are the lowest density phases at depths
exceeding 1600-1800 km. Altogether, some studies suggest a decrease of the MORB density excess
with increasing mantle depth (Guignot and Andrault, 2004; Ricolleau et al., 2010) and others
suggest a constant Δρ (Hirose et al., 2005; Ono et al., 2005). For sedimentary material, the density
is significantly lower than for MORB, due to low Fe and high Si-contents (Guignot and Andrault, 2004).

Our experimental results on compositions with 4-6 wt% Al₂O₃ suggest a ~2.19% density increase for the transition from the CaCl₂-structured form to seifertite at 113-119 GPa and 300 K. At temperatures above 2000 K, this value should reach ~3%, due to higher volume change found for this transition at high temperature. The strong Al-partitioning from the CaCl₂-structured phase into seifertite will lead to compositional and density adjustments of the other Al-bearing phases in basaltic lithologies, in addition to the density effects caused by the silica-dominated phase transition. In subducted slab material the silica-dominated phases can represent up to about 20 and 40 vol% of MORB and sedimentary components, respectively (Hirose et al., 1999; Irifune et al., 1994). The CaCl₂-structured phase to seifertite transition could have a minor effect on the buoyancy in the peridotitic mantle of the basaltic ocean crust of subducted slabs, because free-SiO₂ is not highly abundant and the MORB density is already significantly higher. For the sedimentary component, however, the CaCl₂ to seifertite transition may have a larger impact and facilitate the descent of the sedimentary material to the lowermost part of the mantle.
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Table 1: Unit cell parameters of seifertite of 6 wt% composition recorded from 100 to 162 GPa and 300 to 4300 K. Pressure is derived from the PVT-EoS of platinum (Holmes et al., 1989) and temperature was determined by radiometric measurements. Uncertainties are 3% for pressures, 50 K for high temperatures, ~0.005 Å for (a, b, c) cell parameters and ~0.1 Å³ for unit cell volumes.

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Table 2: Elastic parameters refined for seifertite, as well as for its 3 fictive $a^3$, $b^3$, $c^3$ volumes. We used the Vinet isothermal compression curves and the Mie-Grüneisen approach for modeling the effect of temperature. $\Theta_{D0}$ and $\gamma_0$ are the Debye temperature and Grüneisen parameter at ambient conditions. Some parameters were fixed following the reports of (Bolfan-Casanova et al., 2009) and (Wang et al., 2012).

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Table 3: Measured volume changes ($\Delta V/V$) and calculated density changes ($\Delta \rho/\rho$) across the CaCl₂-form to seifertite transition (Figure 5A). M-03 and H-05 stand for (Murakami et al., 2003) and (Hirose et al., 2005), respectively. The $\Delta \rho/\rho$ are calculated using the measured $\Delta V/V$ taking into account all possible Al substitution mechanisms in SiO₂ polymorphs. The Al³⁺ substitution can imply formation of an oxygen vacancy (O), insertion of extra-interstitial Al³⁺(Al), or coupled Al³⁺-H⁺ substitution (H). The term "O->Al", for example, means a transition from an oxygen-deficient CaCl₂-form to a seifertite containing interstitial Al³⁺. ISM: Identical substitution mechanism in both polymorphs.

<table>
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<th>$\Delta V/V$ (%)</th>
<th>$\Delta \rho/\rho$ (%)</th>
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**Figure Captions**

**Figure 1:** Selected regions of the 2D diffraction image (upper frames) and its spectral integration (lower frame) recorded *in situ* at 120 GPa and 2500 K. Regions where major seifertite diffraction peaks occur are colored in red. The number of seifertite crystallites is insufficient for a full structural refinement using the Rietveld method. However, the diffraction peak intensities are in good agreement with the structural model of seifertite (see Figure 2).

**Figure 2:** The diffraction spectra are refined in two steps. We first perform a full X-ray profile refinement, using the Rietveld mode and the structural model of seifertite (*upper frames*). Differences between experimental and calculated peak intensities are due to (i) change with pressure and temperature of the seifertite atomic parameters; the structural model that we used corresponds to ambient P-T conditions (El Goresy et al., 2008)), and (ii) an insufficient number of crystallites in the X-ray spot. In a second step, we perform a profile refinement using the Le Bail mode (*lower frames*; see text). In each frame, green, upper red and lower red spectra correspond to the experimental data, fully refined profile, and seifertite contribution, respectively. We also present the major d<sub>hkl</sub> indexation of the seifertite diffraction peaks (we report “several” when more than 2 seifertite diffraction peaks plot at the same 2-theta position). Left and right frames present the same experimental spectrum in 2-theta ranges of 5-10 and 10-20 degrees, respectively.

**Figure 3:** Examples of integrated X-ray diffraction patterns for the CaCl<sub>2</sub>-structured silica phase and seifertite. These patterns were recorded (A) on ID-27 beamline at 3400 K and 121 GPa and (B) on P02.2 beamline after heating at 2500 K at 103 and 114 GPa. Small bumps on the diffraction patterns up to 2500 K are due to still incomplete transformation of the starting material. Platinum and the NaCl or KCl pressure medium are also visible. The reported pressure is based on the equation of state of Pt for the diffraction pattern recorded at high temperature before quenching.
Black crosses, green and red lines are experimental measurements, fitted background and theoretical diffraction spectra, respectively.

**Figure 4:** Approximate phase diagram for the SiO$_2$-Al$_2$O$_3$ system at 2500 K. For pure SiO$_2$, the phase transition is well defined at ~122 GPa (M-03; (Murakami et al., 2003)). For the mid-ocean ridge basalts used in H-05 (Hirose et al., 2005), the CaCl$_2$-form and seifertite phases were observed at 100 GPa, and 123 GPa, respectively. Concerning our samples, the rectangles represent the pressure range between our samples where CaCl$_2$-form or seifertite was synthesized. The pressure uncertainty of 3 GPa is included in the rectangle sizes. The loop diagram represented here is the widest model remaining compatible with the different data sets.

**Figure 5:** (A) Volumes of the two silica polymorphs measured around the transition pressure at 300 K. We also report the data sets reported for pure SiO$_2$ (red: (Murakami et al., 2003); black dotted line: (Andrault et al., 2003)), a MORB-type material (green: (Hirose et al., 2005)), and an Al-bearing SiO$_2$ glass with 4 wt% Al$_2$O$_3$ (black dotted line: (Bolfan-Casanova et al., 2009)). Closed and open symbols represent the CaCl$_2$-phase and seifertite, respectively. (B) High temperature volumes (red circles) recorded for seifertite from 100 to 162 GPa and up to 4300 K. We report the isothermal compression curves calculated at 300 K, 2000 K and 3000 K for the CaCl$_2$-form (blue dotted lines) and seifertite (dashed black lines) based on the PVT EoS refined in this study.

**Figure 6:** Seifertite (a, b, c) unit cell parameters recorded at 300 K (blue diamonds) and up to 4300 K (purple rectangles) for pressures from 100 to 162 GPa.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

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Figure 6

A: Graph showing the relationship between pressure (GPa) and the lattice parameter a (Å) for different temperatures.

B: Graph showing the relationship between pressure (GPa) and the lattice parameter b (Å) for different temperatures.

C: Graph showing the relationship between pressure (GPa) and the lattice parameter c (Å) for different temperatures.