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Equation of state and CaCl_2 transformation of

Al-bearing silica up to 100 GPa and 3000 K

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Abstract

Structure and density of the Al-bearing silica phases were investigated at high pressure and temperature by means of powder X-ray diffraction in laser heated diamond anvil cell at the ID30 beamline of the ESRF. The transition from rutile (TiO_2) to calcium chloride (CaCl_2) phase occurs at lower pressure, down to 23 GPa at 300 Kelvin, compared to 50 GPa in the pure SiO_2 system. The distortion increases with pressure and decreases with temperature. We determined experimentally the clapeyron slope of the transition: dP/dT of 0.02 GPa/K. According to the phase diagram determined by *in-situ* X-ray diffraction, Al-bearing silica should be in the CaCl_2 form in most of the transition zone and lower mantle. Also, aluminous silica, whether in the rutile or calcium chloride form, is softer than pure silica. Our results show that the incorporation of ~2.3 weight % of alumina in silica decreases its bulk modulus of around 7-10% in case of the rutile form and of 3.5 % in case of the CaCl_2 form.

Keywords: stishovite, CaCl_2 , aluminum, phase transition, Clapeyron slope

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25

26 **Introduction**

27 Since seismic tomography images have shown slabs entering the lower mantle,
 28 comprised between 670 and 2900 km depth (van der Hilst et al., 1997), the recycling of
 29 oceanic crust into the deep Earth offers a way of enriching the mantle in silica. Indeed,
 30 experimental petrology studies indicate that in subduction zones stishovite (tetragonal rutile
 31 structure $P4_2/mnm$) crystallises above 9 GPa in the basaltic and sedimentary portions of the
 32 subducted oceanic crust. Stishovite becomes more and more abundant as a result of the
 33 dissolution of clinopyroxene into garnet structure (Irifune and Ringwood, 1987). Also,
 34 stishovite has been shown to be an ubiquitous product of dehydration reactions occurring in
 35 sedimentary and basaltic wet compositions (Ono, 1998). In such a subduction context
 36 stishovite could contain up to 9 weight percent Al_2O_3 (Ono, 1999)(Ono, 1998). The
 37 incorporation of even small amounts of this element and its possible coupling with oxygen
 38 vacancies, following the reaction $Si^{4+} = Al^{3+} + \frac{1}{2} \square_O^{2+}$, can influence the stability, density and
 39 the compressibility of mantle phases. Such parameters are important in the assessment of the
 40 density, composition and thermal structure of the deep mantle.

41 In addition, pure stishovite undergoes a displacive phase transition to orthorhombic
 42 $CaCl_2$ structure ($Pnmm$ space group) at pressure around 50 GPa, as demonstrated by several
 43 experiments using either X-ray diffraction (Andrault et al., 1998a; Hemley et al., 2000;
 44 Kingma et al., 1996; Tsuchida and Yagi, 1989) or Raman spectroscopy (Hemley et al., 2000;
 45 Kingma et al., 1995). The onset of the phase transformation was reported between ~45 and
 46 ~60 GPa by the different authors. Here, we present the first structural evidence on the effect
 47 of aluminium on the transition of rutile to $CaCl_2$ structure of silica *in-situ* at high-pressure and
 48 high-temperature using the laser-heated diamond anvil cell technique up to ~100 GPa and
 49 more than 3000 K.

50

51 **Experimental procedure**

52 Two different types of aluminous silica containing around 4 wt% Al_2O_3 were used as starting
53 material. One of them is a glass, loaded without any grinding. Due to its treatment at very
54 high temperature and small surface/volume ratio of the sample, it should contain a negligible
55 amount of water. This sample is ideal for heating using CO_2 laser. However, in order to heat
56 with a YAG laser and to be able to measure pressure at high-temperature we had to mix the
57 sample with a laser absorber such as platinum. Thus, a gel of the same composition was
58 prepared in order to be mechanically mixed with Pt powder.

59 We performed experiments at different pressure and temperature conditions (see
60 **Table 1**). To generate high pressures, we used a membrane-type diamond anvil cell equipped
61 with 300- μm diamond culets. Re-gaskets were pre-indented to 40-50 μm thickness before
62 drilling a 80- μm hole using electro-erosion. Samples were loaded together with a small ruby
63 chip and the pressure medium. Ar pressure medium (loaded cryogenically) was used in CO_2 -
64 laser heating experiments whereas NaCl pressure medium was preferred for YAG-laser
65 heating experiments, still Ar was sometimes used. Laser-heating was used to synthesize
66 stishovite or post-stishovite *in-situ* in the DAC, and to release the deviatoric stresses after
67 each pressure increase. The setup is composed of two 40 W single-mode continuous YAG
68 lasers with excellent power stability focused on each side of the sample. The X-ray beam
69 intensity on ID30 was sufficient to obtain high quality angle-dispersive diffraction patterns in
70 60 s, which further minimizes any potential temperature deviation to a few tens of K. We
71 measured temperature on one side of the sample by the spectroradiometric method using
72 reflective collecting optics. Temperature were measured three times during collection of X-
73 ray diffractograms and the temperature variation was within 50 degrees in average, except

74 above 2200K where it reached 100 degrees due to melting of the pressure medium Ar or
75 NaCl.

76 For decompression measurements in Argon, no annealing was performed in order to
77 avoid to revert into the low-pressure phase. As a consequence of such decompression
78 measurements the pressure derivative of the bulk modulus cannot be derived with a good
79 degree of accuracy.

80 The X-ray diffraction patterns were collected *in-situ* at high pressure at the ID30
81 beamline of the European Synchrotron Radiation Facility (ESRF) using angle dispersive
82 radiation (Andrault and Fiquet, 2001; Mezouar et al., 2005; Schultz et al., 2005). A channel-
83 cut, water-cooled monochromator was used to produce a bright monochromatic X-ray beam
84 at 0.3738 Å wavelength. Vertical and horizontal focusing was achieved by bent-silicon
85 mirrors, the curvatures of which were adapted to obtain an optimal X-ray flux on a full width
86 at half maximum of less than 10x10 µm spot on the sample. Two-dimensional images were
87 recorded on an image plate and integrated using the Fit2d code (Hammersley, 1996). All X-
88 ray spectra were treated using the Rietveld method with the GSAS package (Larson and Von
89 Dreele, 1988).

90 Both Ar, ruby, and/or Pt pressure standards were available in our pressure chamber.
91 Ruby was mainly used to reach the target pressure for first synthesis. We preferred the
92 pressure provided by the Ar or Pt equation of state (EoS) (Holmes et al., 1989; Jamieson et
93 al., 1982; Jephcoat, 1998), because it can be recorded at the same position as the sample, and
94 therefore the potential artefacts related to pressure gradient in the sample chamber are
95 discarded. At high temperature, we used the Pt EoS (Jamieson et al., 1982) to derive the
96 pressure in the hot sample that can be affected by the effect of thermal pressure (Andrault et
97 al., 1998b). The error of volume measurement at the ID30 beamline was of about $2 \cdot 10^{-4}$. At

30 GPa pressure, it translates to pressure errors of ~ 0.3 or ~ 1 GPa, when using Ar or Pt pressure standards, respectively.

Experimental results

a) Lattice distortion at room temperature

At high pressures, X-ray diffraction patterns display the presence of the pressure medium, Ar or NaCl, Pt black if added, SiO_2 , and sometimes corundum (**Fig. 1**). The latter being due to an excess of alumina in the starting composition compared to the Al solubility in silica under some conditions of pressure and temperature. Looking closely at the diffraction patterns recorded at lower pressure, it appears that the CaCl_2 -form appears at a pressure as low as about 23 GPa at 300 K, as shown in **Figure 2a** by the splitting of the c/a and c/b parameter ratios recorded at room temperature after laser annealing.

Figure 3a also shows the increase of the splitting of diffraction peaks with pressure at 298 K. Indeed, the rutile model of stishovite fails to explain spectral regions located at ~ 12 , 14 , and 17 degrees of the 2θ diffraction angle, where splitting of the $[120,210]$, $[121,211]$, and $[130,310]$ lines is observed (see insets in **Fig. 1**). This clearly evidences the occurrence of the orthorhombic ($Pnnm$) lattice of the CaCl_2 -form of SiO_2 at such low pressure. In **Figure 2a**, we also report previous results for Al-free stishovite (Andrault et al., 1998a) showing that at 300 K the transition occurs at ~ 50 GPa. The comparison between Al-bearing and Al-free samples raises three important points: first, the distortion appears at much lower pressure in the Al-bearing SiO_2 system. Second, the distortion increases quite rapidly above the transition pressure for the Al-free phase, while it is very progressive for the Al-bearing samples. Finally, the distortion appears similar for both Al-free and Al-bearing compounds above 70 GPa. Therefore, the most apparent effect of Al on the structure of stishovite is to facilitate the CaCl_2 -distortion in the 23-70 GPa pressure range.

Figure 2b displays the distortion of aluminous silica samples synthesized at different pressures and decompressed in Ar without annealing. In the case where the sample is synthesized in the stability field of the rutile-form, e.g. stishovite, the decompression curves display a normal, i.e. linear, behavior. Whereas, in the case where the sample is synthesized in the stability field of the CaCl_2 form we observe a peculiar behavior during decompression. In one case, the CaCl_2 structure of silica is conserved down to 10 GPa and then the sample reverts to the rutile form. In the other case the CaCl_2 form was quenched to room pressure.

However, in the laser-annealed experiments we did not detect any systematic difference in cell parameters due to a change in starting material from glass to gel nor from a change in laser from CO_2 to YAG.

b) Lattice distortion at high temperature

For nominal pressures (at 300K) of 23, 26, and 36 GPa, we clearly observe a decrease of the CaCl_2 cell distortion as a function of increasing temperature (**Fig. 3b** and **Fig. 4**). Because of thermal pressure, the pressure increases with increasing temperature (Andrault et al., 1998b), and the thermal pressures measured in this study thanks to the Pt scale (Jamieson et al., 1982) agree with those calculated from an average bulk modulus of 290 GPa for aluminous silica and an expansion coefficient of $1.6 \times 10^{-5} \text{ K}^{-1}$ as measured for pure stishovite (Nishihara et al., 2005). Thus, we find that the rutile structure appears around 2230 K at 20.3 GPa, 2934 K at 35.0 GPa and potentially ~ 3500 K at 49 GPa, if we extrapolate the c/a and c/b ratios of **Figure 4** using the pressure-temperature relationship measured in this study using Pt. This clearly evidences a positive Clapeyron slope for the transition from rutile to CaCl_2 polymorphs of Al-bearing silica (see discussion).

Discussion

a) Al incorporation in rutile and CaCl_2 phases of silica

The volumes of the aluminous silica phases (rutile or CaCl_2 structure) measured at room pressure are significantly higher than that of pure stishovite (see **Figure 5**). In our study all samples were quenched to room pressure under the form of stishovite except for one sample, Alsti-06, that was quenched in the form of post-stishovite. In **Figure 5** the correlation between the volume of Al-bearing stishovite and its Al content is $V_0(\text{\AA}^3) = 46.517 + 12.461 \times X_{\text{Al}}$ (Al p.f.u.) as retrieved by Lakshtanov et al. (2005; 2007) based on multi-anvil samples. We used this relationship to interpolate the Al content of the silica phases synthesized in this study knowing their ambient pressure volume. One limitation of this method for determining the Al content could be that our silica phases were synthesized under dry conditions whereas the correlation is built from the volume of stishovite synthesized under wet conditions (except for pure stishovite). Still, (Litasov et al., 2007) have shown that only one seventh of Al incorporated into stishovite is associated with H. It is thus expected that hydration has a small effect on the correlation of cell volume and Al content. Using this correlation, we calculate that our samples (only those quenched under the rutile form) contain between 2.2 and 3.6 wt% Al_2O_3 , or an average Al content of 2.9 ± 0.6 wt% Al_2O_3 . This variation is explained by the fact that solubility of Al in silica is not that high. It is thus difficult to avoid changes in concentration due to overstepping the solubility limit when different pressure conditions are used together with laser annealing. The sample quenched under the form of CaCl_2 displays a very large volume of $47.773 \text{ \AA}^3$ (see **Table 1**), which leads to an Al content in the phase (0.1 Al per formula unit) that is anomalously large given that the starting material only contains 0.047 Al p.f.u (4 wt% Al_2O_3). The fact that this sample falls off the trend can be explained by its structural difference with stishovite.

Still, a systematic study of the effect of pressure and temperature on the solubility of Al_2O_3 in both the rutile and CaCl_2 stability field of silica is lacking. Ono (1999) reports that in the Al_2O_3 - SiO_2 - H_2O system the Al content in stishovite increases with temperature up to 9 wt% at 20 GPa and 1700°C. However, in the dry system incorporation of aluminum into silica seems to be much more limited. In the Al_2O_3 - SiO_2 , kyanite, composition (Liu et al., 2006) find that solubility increases with temperature up to 2.5 wt% Al_2O_3 at 2000°C then decreases, at least up to pressures of 22 GPa. This maximum Al content is consistent with the values for two samples synthesized here at 16.7 and 23.7 GPa for which the correlation between cell volume and Al content yields 2.2 and 2.4 wt% Al_2O_3 , respectively. They also report that solubility of Al_2O_3 decreases with increasing pressure which is contradictory to our observation. But note that the observation of (Liu et al., 2006) that Al solubility decreases with increasing temperature is valid only until 22 GPa. Thus the information is lacking for the solubility of Al in the silica phase within the stability field of the CaCl_2 phase of silica, *i.e.* above 23 GPa, which represents the case of our most aluminous samples. In addition, (Ono et al., 2001b) report that at 30 GPa in the MORB composition, Al content in stishovite (as recovered at room pressure) reaches 4.2 wt% Al_2O_3 , thus indicating a different behavior from the results of (Liu et al., 2006) at high pressures within the stability field of the CaCl_2 phase. The difference could be due either to the presence of water or to intrinsically different solubility of Al in rutile or CaCl_2 structure.

b) Lattice strain

(Kingma et al., 1995) evidenced the softening of the B_{1g} rutile mode in pure SiO_2 using Raman spectroscopy with neon pressure medium up to 60 GPa. They observed the transition from tetragonal to orthorhombic structure at 50 GPa and that it is reversible. They concluded to a second order phase transition. (Andrault et al., 1998a) observed the transition at 54 GPa

using powder X-ray diffraction, without any pressure medium but with laser-annealing, and did not observe any substantial discontinuity in volume, suggesting that the transition has mainly a second order character. Still, they noted a sudden increase of distortion of the tetragonal lattice just above the transition pressure, which could indicate a certain degree of first-order character of the transition. (Hemley et al., 2000) performed reversal compression experiments using X-ray single crystal diffraction and Raman spectroscopy in hydrogen pressure medium. They observed the transition to CaCl_2 structure at 58 GPa but also observed an hysteresis on decompression and CaCl_2 remaining down to 40 GPa. This provides another argument for a weak first-order character of the transition.

In this study, we observe that the incorporation of Al in silica promotes the transition from rutile to CaCl_2 at very low pressures, down to 23 GPa. If one compares the transition pressure found in the different studies on pure SiO_2 , the effect of the pressure media (only 8 GPa, see references above) is clearly not enough to explain the lowering of the transition to 23 GPa. Thus, the lowering of the transition pressure is due to the presence of aluminum and not to stress. Indeed, because Al^{3+} is larger than Si^{4+} , incorporation of aluminum induces a chemical pressure that destabilizes the low-pressure polymorph, thus shifting the transition to lower pressure. Very recently, (Lakshtanov et al., 2007b) have observed the CaCl_2 phase of silica containing 5 wt% Al_2O_3 at 24.3 GPa at room temperature. Our results are identical to theirs within experimental uncertainty, especially Al content. We find that the transition occurs at pressures between 19 and 23 GPa for a maximum Al content of 4 wt% Al_2O_3 .

The interesting point is that a second order character provides the formalism to calculate thermodynamic parameters, especially the entropy change associated with such progressive transition. In such case, we can define an order parameter that represents the degree of lattice strain. For small strains, the order parameter is $Q=(a-b)/a$ (Andrault et al., 1998a; Carpenter et al., 2000). The order parameter shows lattice strain above ~23 GPa at 300

K in annealed samples (**Figure 6**). In this figure (a) it is confirmed that the distortion appears above ~23 GPa for the Al-bearing stishovite, (b) the change with pressure of order parameter $[d(Q^2)/dP]$ is found similar for Al-free and Al-bearing stishovite and (c) the abrupt change of order parameter $[\Delta S]$ appears negligible for Al-bearing stishovite while it is clearly visible for the Al-free phase.

c) Equation of state at 300 K

Figure 7 displays the volumes at 300 K for the different samples measured during compression+annealing or during decompression to room pressure. All aluminous silica phases display higher volumes due to the fact that Al incorporation expands the unit-cell of silica. On the other hand, the volume of aluminous silica tends to converge at high pressure, with lower V/V_0 for Al-bearing stishovite compared to pure silica (except PV20). Firstly, if we consider the range of pressure where the stishovite structure is stable, for example for decompression curves of aluminous stishovite (Alsti-01 and Alsti-07), we observe that the Al-bearing stishovite is clearly more compressible than pure stishovite with bulk modulus of 278 ± 4 GPa and 287 ± 5 GPa (for $K'=4.59$) or 284 ± 4 GPa and 291 ± 4 GPa (for $K'=4$), depending on the pressure of synthesis or Al content (16.7 and 23.7 GPa, or 2.2 and 2.4 wt% Al_2O_3 respectively), instead of $K_0=310 \pm 1$ GPa (for $K'=4.59$) or 324 GPa (for $K'=4$) for pure stishovite (Andrault et al., 2003). These two Al-bearing stishovite samples have very similar volumes and elastic behavior in agreement with their similar aluminum content.

Concerning the $CaCl_2$ -form, we report three P-V curves: one compression+annealing up to 99.9 GPa (PV20) and two decompressions without annealing from 47.6 and 50.5 GPa down to room pressure. Among these last two experiments one sample reverted to the rutile structure without heating at ~10 GPa (PV21) whereas the other one retained its $CaCl_2$ structure down to ambient conditions (Alsti-06). The room pressure volume V_0 is thus

determined directly from the X-ray diffraction measurement or from extrapolation to 1 bar of a second order Birch-Murnaghan EoS (**Table 1**). Compared to pure silica, aluminous silica with CaCl_2 structure also displays higher volumes and lower V/V_0 than pure silica (Andrault et al., 2003) (see **Figure 7**). The compression + annealing of aluminous silica up to 99.9 GPa yields a K_0 of 322 ± 7 GPa (for $K'=4$) or K_0 of 292 ± 7 GPa (for $K'_0=4.59$). Compared to pure CaCl_2 silica (K_0 of 334 ± 7 GPa for $K'=4$, from (Andrault et al., 2003)) it appears that aluminous silica with the CaCl_2 structure is slightly more compressible. The two decompression experiments yield K_0 of 300 ± 4 GPa (for $K'=4$) and K_0 of 259 ± 3 GPa (for $K'=4$) for PV21 and Alsti-06, respectively. The value for PV21 should be regarded with caution because the sample changed structure in the course of the P-V measurement.

Thus, in this study we show that aluminium softens both the rutile and CaCl_2 phases of silica. This softening is in agreement with expectations because K_0V_0 can be regarded as almost constant. Concerning the rutile phase in comparison with pure silica, and using the same K_0' of 4.59 determined by Andrault et al. (2003), the incorporation of an average of ~2.3 weight % of alumina in stishovite decreases its bulk modulus of around 7-10%. Concerning the CaCl_2 phase we also observe a decrease of bulk modulus of 3.5%.

Previous compressibility studies of aluminous silica have used P-V data sets that cross the transition between the rutile to the CaCl_2 transition (Lakshtanov et al., 2005; Ono et al., 2002). Thus the bulk moduli reported include compression behaviour of both the low and high-pressure phases. (Ono et al., 2002) determined a K_0 of 282 GPa from 10 to 40 GPa whereas (Lakshtanov et al., 2005) determined a K_0 of 304 GPa from 2 to 58 GPa, both using second order Birch-Murnaghan Eos ($K'=4$), for samples containing 2.1 and 1.8 wt% Al_2O_3 , respectively. Our results indicate that the relationship K_0V_0 is a function of the structure of aluminous silica (see **Figure 8**). The two data points from (Lakshtanov et al., 2007a) display much higher volume for the rutile phase containing both aluminum and hydrogen whereas the

bulk moduli are similar to stishovite measured in this study. There appears to be an additional effect that may be related to the fact that these samples contain about 2400-2900 ppm by weight of water (Lakshtanov et al., 2007a). It is clear that more data is needed to refine the effect of Al content, water content and structure on the elasticity of aluminous silica at high-pressure and temperature.

d) Phase diagram

As shown on **Figure 4** from the evolution of the cell parameter ratios we can see that the orthorhombic distortion increases with pressure and decreases with temperature. **Figure 9** shows all the experimental points from this study. The resulting clapeyron slope of the transition is: dP/dT of 0.02 GPa/K. Such positive clapeyron slope of the transition is expected for a pressure-induced order-disorder phase transformation (Andrault et al., 1998a; Ono et al., 2001a). The rutile structure is stable at high temperature and low pressure while the calcium chloride structure is stable at low temperature and high pressure. Comparing the transition boundary with that of pure silica determined experimentally by (Ono et al., 2001a) clearly shows that aluminum has a very large effect on the stability of the CaCl_2 form in the Earth's mantle. In the presence of aluminum this phase can be found in most of the transition zone and lower mantle. Of course, it is expected that the clapeyron slope of the transition depends on Al content, but given that the $\text{SiO}_2 + 4 \text{ wt\% Al}_2\text{O}_3$ system is close to saturation, the transition boundary determined here should correspond to the lowest pressure one. As shown in **Figure 5**, the Al content of the silica phases recovered under the rutile form at ambient pressure varies between 2.2 and 3.6 wt% Al_2O_3 , due to synthesis of the samples at different pressures. Since the system contained initially 4 wt% Al_2O_3 some corundum must have been present in excess in the samples, but which was rarely detectable because of its low amount. (Lakshtanov et al., 2007b) report the transition from rutile to CaCl_2 phase to take place

between 20.0 and 24.8 GPa at 300 K for an Al content of 6 wt% Al_2O_3 . Such pressure is extremely similar to that found in this study between 20 and 23 GPa but for an estimated Al content of 3.1 wt% Al_2O_3 .

Experimental petrology studies have shown that stishovite can incorporate substantial Al contents, which are controlled by exchange with neighbouring phases such as clinopyroxene or garnet. In sediment composition (Ono, 1998) has shown that Al content increases with temperature at 15 GPa from 0.43 at 1100°C to 1.92 wt% Al_2O_3 at 1400°C. In MORB composition, Al content ranges from 0.15 wt% Al_2O_3 at 18 GPa and 1000°C up to 4.2 % at 30 GPa and 1800°C (Litasov and Ohtani, 2005; Ono et al., 2001b). In our study the ambient volumes of the different silica phases quenched from different pressures suggest a variation in Al content from 2.2 to 3.6 wt% Al_2O_3 . Thus values that are within the range of those found in experiments on natural compositions.

Conclusions

In subducted slabs, a free SiO_2 -phase is expected because the composition is much enriched in incompatible elements. Since such elements comprise aluminum, the transition from stishovite to the CaCl_2 phase will occur at lower pressures than in the Al-free system. According to the phase diagram determined by *in-situ* X-ray diffraction, silica should be in the CaCl_2 form in most of transition zone and lower mantle. Although we did not observe any change in volume across the transition, the transformations show a high degree of hysteresis. Thus, it is likely that the transition should not be connected with any density change, but it can affect the seismic properties of descending slabs, because shear properties can be strongly affected by such type of phase transformation (Carpenter et al., 2000; Lakshtanov et al., 2007b).

322 **Acknowledgments**

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Figure captions:

Figure 1: X-ray diffractogram recorded at 41 GPa and 300 K after laser heating at ~2500 K using the gel starting composition. Diffraction peaks of Ar, Pt and the CaCl_2 -form are clearly visible. Small diffraction peaks (not indexed) correspond to minor amounts of corundum. A, B, and C insets show selected two-theta regions where splitting of diffraction peaks evidence the CaCl_2 -distortion.

Figure 2: Evolution of the c/a and c/b cell parameter ratio of the silica structure as recorded at 300 K (a) on compression+annealing steps and (b) on decompression without annealing in Ar pressure medium. Empty symbols represent the CaCl_2 structure, and full symbols the rutile structure. Distortion is evidenced above ~23 GPa in Al-bearing system whereas for Al-free silica the transition occurs around 50 GPa as reported previously (Andrault et al., 1998a). In b) we can observe that the CaCl_2 can be quenched down to 10 GPa or even room pressure.

Figure 3: Evolution of the CaCl_2 -distortion (a) with pressure at room temperature in Ar pressure medium (experiment AlSti2 up to 49 GPa) and (b) with temperature at 23 GPa of nominal pressure in NaCl pressure medium (experiment StiAl-01), for selected two-theta zones.

Figure 4: Evolution with temperature of the c/a and c/b cell parameters ratio of aluminous silica for three different nominal pressures (as measured at 300 K) for samples StiAl-01, StiAl-02, StiAl-03 (see **Table 1**). Of course, the pressure is not constant at high-temperature

due to thermal pressure. The rutile structure appears around 2230 K at 20.3 GPa, 2934 K at 35.0 GPa and potentially ~3500 K at 49 GPa, if we extrapolate the c/a and c/b ratios.

Figure 5: Correlation between the room pressure volume of aluminous wet stishovite synthesized in the multi-anvil press and its Al content. Previous data for pure stishovite are from (Andrault et al., 2003), and for aluminous stishovite from (Smyth et al., 1995), (Ono et al., 2002) and (Lakshtanov et al., 2005). Plotting the ambient cell volumes of the aluminous silica phases synthesized in this study using DAC (circles) into this diagram allows to retrieve their Al content. Empty symbols indicate samples that have been decompressed after one single annealing, full symbols those which have experienced multiple pressures and annealings. This figure suggests that the silica samples synthesized in this study (recovered under the rutile form) contain between 2.2 and 3.6 wt% Al_2O_3 .

Figure 6: Evolution with pressure of the square of the order parameter $Q=(a-b)/a$ used to quantify the lattice strain associated with the CaCl_2 distortion. Circles represent the decompression in Ar pressure medium from 50.5 GPa, and squares the compression + annealing in NaCl pressure medium up to 99 GPa. Also shown is the order parameter for pure silica from Andrault et al. (2003) (diamonds). Although the cell parameters ratios of aluminous silica show an hysteresis on decompression that would indicate a first order character, there is no discontinuity on the order parameter across the transition. Also, the gap observed for pure silica may be due to insufficient pressure resolution of the data coverage rather than to a small degree of first order character.

Figure 7: P-V curves measured at 300 K for Al-bearing silica compounds shown as a function of volume during compression+annealing and during decompression without annealing. Open symbols represent the CaCl_2 structure and full symbols the rutile structure. Also shown is the compression curve for pure silica from (Andrault et al., 2003).

Figure 8: Correlation between bulk modulus (for $K'=4$) and room pressure volume of aluminous silica from this study and comparison with previous studies. The structure of the phase is specified because in some cases the compression curve crossed the transition between rutile to CaCl_2 phase. See text.

Figure 9: Phase diagram drawn for Al-bearing silica. Pressures at high temperature are derived from volume measurements of the Pt pressure standard that is mixed with the sample. The mantle geotherm is from (Katsura et al., 2004). Also shown as the dotted black curve is the Clapeyron slope of the stishovite to post-stishovite phase transition in pure SiO_2 from (Ono et al., 2001a). The phase boundary for aluminous stishovite can be expressed as dP/dT of 0.02 GPa/K (green curve).

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Table 1. Experimental run conditions and elastic parameters results

Run number	Pressure range* (GPa)	Laser used	Pressure medium and standard	Starting material	Vo measured ($\text{\AA}^3$)	Vo fitted using Eos ($\text{\AA}^3$)	Ko (GPa)	Method	Al content (p.f.u.) ³
Alsti-01	21.7 -> 10^{-4}	CO ₂	Ar	glass	46.861	46.866 (025) ¹ 46.875 (028) ²	284 ± 4^1 278 ± 4^2	Decompression	2.4
Alsti-07	15.2 -> 10^{-4}	CO ₂	Ar	glass	46.845	46.871 (020) ¹ 46.874 (022) ²	291 ± 5^1 287 ± 5^2		2.2
Alsti-06	43.5 -> 10^{-4}	CO ₂	Ar	glass	47.773	47.881 (049) ¹ 47.932 (060) ²	259 ± 3^1 248 ± 4^2		3.5
PV20	26.2 -> 99	YAG	NaCl + Pt	gel	-	46.513 (126) ¹ 46.770 (135) ²	322 ± 7^1 292 ± 7^2	Compression + annealing	
PV21	51.8 -> 10^{-4}	YAG	Ar + Pt	gel	47.043	47.076 (049) ¹ 47.121 (046) ²	300 ± 4^1 287 ± 4^2	Decompression	3.6
AlSti2	21 -> 49	YAG	Ar + Pt	gel	-			In-situ high temperature experiments	
AlSti5	19 -> 31	YAG	NaCl + Pt	gel	46.911				2.5
StiAl-01	23 GPa	YAG	NaCl + Pt	gel	46.983			In-situ high temperature experiments	3.1
StiAl-02	26 GPa	YAG	NaCl + Pt	gel	-				
StiAl-03	36 GPa	YAG	NaCl + Pt	gel	47.055				3.7

* pressure measured by the Pt or Ar scale (Jamieson et al., 1982; Jephcoat, 1998).

¹ elastic parameters fitted using a second order Birch-Murnaghan eos using a K' of 4, and

² K' of 4.59 as in the case of pure SiO₂ (Andrault et al., 2003). Pressure for determining the Eos is measured thanks to Pt or Ar Eos (Holmes et al., 1989; Jamieson et al., 1982; Jephcoat, 1998).

³ as determined from **Figure 5**.

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Figure 1

Figure 2a

Figure 2b

Figure 3

Figure 4
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Figure 5

Figure 6

Figure 7

Figure 8

Figure 9