High Pressure-Temperature Study on the Thermal Equations of State of Seifertite and CaCl$_2$-Type SiO$_2$

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Abstract

In this study, we have determined the thermal equations of state (EoS) of CaCl$_2$-type SiO$_2$ and seifertite ($\alpha$-PbO$_2$-type SiO$_2$) from 55 to 147 GPa up to 3500 K using X-ray diffraction in laser-heated diamond anvil cells. The phase transition from stishovite to CaCl$_2$-type SiO$_2$ is in good agreement with previous experimental results, whereas the transition from CaCl$_2$-type SiO$_2$ to seifertite was observed to strongly rely on the starting material. For CaCl$_2$-type SiO$_2$, we obtained a bulk modulus, $K_T = 245(7)$ GPa with a fixed $K_T' = 4$, $V_0 = 48.1(2)$ Å$^3$, $\gamma_0 = 1.3(3)$, $q = 1$ (fixed), and $T_{10} = 1100(400)$ K. Seifertite has a greater $K_T = 290(10)$ GPa ($K_T' = 4$ fixed) than CaCl$_2$-type SiO$_2$. Other thermoelastic parameters of seifertite are $V_0 = 92.3(5)$ Å$^3$, $\gamma_0 = 1.6(2)$, $q = 1$ (fixed), and $\theta_{10} = 1600(200)$ K. Using the obtained results and phase boundary in previous studies, we have found that the phase transition from stishovite to CaCl$_2$-type SiO$_2$ cannot cause a noticeable change in density but can lower the bulk sound velocity ($V_p$) by ~10%. This phase transition in the subducted oceanic crust with 20 vol.% SiO$_2$ was estimated to generate a ~2% discontinuity in $V_p$, which could be related to the observed seismic velocity anomalies at depths of 1,400–1,800 km. At the bottom of the lower mantle, CaCl$_2$-type SiO$_2$ to seifertite phase transition can lead to a 0.3% jump in $\rho$ and a 0.8% jump in $V_p$ considering 20 vol.% SiO$_2$ in the subducted mid-ocean ridge basalt, which may contribute to the formation of the D$''$ discontinuity above the core-mantle boundary.

1. Introduction

SiO$_2$ is the prototype of various silicates in the Earth’s deep interior. As the low-pressure polymorph of SiO$_2$, quartz is one of the most abundant minerals in the crust (e.g., McLennan & Taylor, 1985; Nesbitt et al., 1997; Wedepohl, 1995). High pressure-temperature experiments reveal that quartz will transform to coesite at ~3 GPa and stishovite (Stv) at ~9 GPa (Coes, 1953; Stishov, 1961). Of particular importance is the decomposition of majorited garnet, which could increase the amount of SiO$_2$ as Stv in the subducted oceanic crust (Hirose et al., 2005; Irfune et al., 1986; Ricolleau et al., 2010; Sekine et al., 1986). In the lower mantle, the volume percentage of free SiO$_2$ in the subducted mid-ocean ridge basalt was estimated to be around 20% (Irfune et al., 1986; Perrillat et al., 2006; Ricolleau et al., 2010). Studies on the physical properties of the high-pressure polymorphs of SiO$_2$, particularly CaCl$_2$-type SiO$_2$ and seifertite ($\alpha$-PbO$_2$-type structure), are critical for understanding the composition of the Earth’s lower mantle (Hirose et al., 2005; Karki et al., 1997; Kingma et al., 1995; Murakami et al., 2003; Oganov et al., 2005; Tsuchiya et al., 2004).

Stv has been known to transform into CaCl$_2$-type structure at the relevant pressure and temperature conditions of the mid-lower mantle (Fischer et al., 2018; Kingma et al., 1995; Nomura et al., 2010; Prakapenka et al., 2004; Shieh et al., 2005; Wang et al., 2012). The phase boundary between Stv and CaCl$_2$-type SiO$_2$, especially at high temperature, has been under debate for years because of the similarity in the X-ray diffraction (XRD) patterns between these two phases (Andrault et al., 1998; Andrault et al., 2003; Fischer et al., 2018; Hemley et al., 2000; Nomura et al., 2010; Singh et al., 2012). In the XRD experiments, the phase transition is characterized by the splitting of the Stv 211 X-ray reflections into the 121 and 211 in CaCl$_2$-type SiO$_2$ which is hard to be detected with relatively low X-ray resolution in the early XRD studies and can be also strongly influenced by the large thermal gradient inside the diamond anvil cells (DAC) during laser heating (Andrault et al., 1998; Andrault et al., 2003; Fischer et al., 2018; Nomura et al., 2010; Ono et al., 2002; Prakapenka et al., 2004; Shieh et al., 2005). The phase transition pressure from Stv to CaCl$_2$-type SiO$_2$ was experimentally determined to be...
50–56 GPa at 300 K with a Clapeyron slope of ~11–16 MPa/K (Fischer et al., 2018; Nomura et al., 2010; Thomson et al., 2019; Yamazaki et al., 2014). Analyzing the variation of the spontaneous strains with pressure yields better constraints on the phase boundary between Stv and CaCl₂-type SiO₂ (Buchen et al., 2018; Carpenter et al., 2000; Singh et al., 2012).

Furthermore, the phase transition between CaCl₂-type SiO₂ and seifertite was reported to strongly rely on the starting material and heating time (Černok et al., 2017; Grocholski et al., 2013; Murakami et al., 2003; Shieh et al., 2005). Seifertite was theoretically predicted to be transformed from CaCl₂-type SiO₂ at ~110 GPa and 2200 K (Driver et al., 2010). It can directly transform from cristobalite-XI by cold compression to 45–48 GPa using α-cristobalite as the starting material (Dubrovinsky et al., 2001; Shieh et al., 2005). Using CaCl₂-type SiO₂ as the starting material, seifertite was observed to be present together with CaCl₂-type SiO₂ at 113–117 GPa and 2100–2300 K (Murakami et al., 2003). Yet elevating the heating time to 2 hr was noted to cause a decrease in the intensity of the seifertite peaks, indicating that seifertite is not a stable phase at 113–117 GPa around 2200 K (Murakami et al., 2003). To investigate the stable phase of SiO₂ at higher pressures, the seifertite and CaCl₂-type SiO₂ mixture was cold compressed to 130 GPa. Laser-heating the seifertite and CaCl₂-type SiO₂ mixture at ~2200 K and 140 GPa showed a decrease in the intensity of the XRD peaks for CaCl₂-type SiO₂, indicating that seifertite has been stable at this pressure (Murakami et al., 2003). In contrast, a single-phase seifertite can be synthesized from the silica glass at 124–128 GPa and ~2400 K which is at a lower pressure than that obtained from heating the seifertite and CaCl₂-type SiO₂ mixture (Murakami et al., 2003). On the other hand, Grocholski et al. (2013) using SiO₂ glass as the starting material reported the presence of seifertite with CaCl₂-type SiO₂ at 136 GPa and 3100 K and synthesized a single-phase seifertite at 138 GPa and 2600 K.

Besides the phase transition, thermal equations of state (EoS) are needed in constraining the density and sound velocity profiles of silica-rich rocks in the Earth’s deep mantle. In contrast to Stv, experimental constraints on the thermal EoS of both CaCl₂-type SiO₂ and seifertite are lacking. Most previous studies for the EoS of CaCl₂-type SiO₂ were limited to measurements at 300 K and high pressures (Andrault et al., 2003; Buchen et al., 2018; Grocholski et al., 2013). Although the thermal EoS of CaCl₂-type SiO₂ were constrained by a recent experimental study, most thermoelastic parameters of CaCl₂-type SiO₂ were assumed to be the same as Stv because of limited experimental data points in a narrow pressure range (Fischer et al., 2018). Up to date, despite of the theoretical results, the thermal EoS of seifertite were only experimentally available for an Al-bearing composition (Andrault et al., 2014; Driver et al., 2010). The influence of temperature on the EoS of pure SiO₂-seifertite is experimentally unknown.

In this study, we have determined the thermal EoS of CaCl₂-type SiO₂ and seifertite between 55 and 147 GPa up to 3500 K using synchrotron XRD in the double-sided laser-heated DACs. Using the obtained thermal EoS together with literature results for Stv, we have modeled the density (ρ) and the bulk sound velocity (V₉) profiles of SiO₂ at high pressure-temperature conditions which are essential for understanding the seismic signature of silica-rich rocks in the lower mantle.

2. Experiment

SiO₂ glass with a purity of 99.9%, purchased from Alfa Aesar Corp., was used as the starting material. 8 wt.% Pt powder used as the laser absorber was mixed with the starting silica. The sample mixture was pressed into foils ~10–15 μm in thickness using a DAC equipped with a pair of 500-μm culet diamonds. The compressed sample foils were broken by a tungsten carbide needle into small pieces in varying diameters. The sample piece was sandwiched by two NaCl layers of ~5–7 μm in thickness and loaded into the symmetric DACs. The NaCl layer, used as the pressure medium and thermal insulator, was dried by at least 4 hr to remove the moisture. Re gaskets were preindented into ~25 μm, and the pressure chamber was typically in diameter of half of the diamond culet. DACs equipped with 200-μm culet diamonds were used for experiments below 90 GPa, while experiments between 90 and 147 GPa were performed using DACs with 150/300- or 75/300-μm beveled diamonds.

High pressure-temperature XRD measurements were conducted at GeoSoilEnviroCARS of the Advanced Photon Source, Argonne National Laboratory, with an X-ray wavelength of 0.3344 Å. Experiments were performed with an X-ray beam of ~3 × 4 μm in size, and a double-sided laser-heating with a flat top size of 10 μm
Figure 1. Phase diagram of SiO$_2$ at high pressures and temperatures. Purple: Stv; red: CaCl$_2$-type SiO$_2$; yellow: CaCl$_2$-type SiO$_2$ and seifertite (Se) mixture; blue: seifertite; gray vertical and horizontal ticks: error bars for pressure and temperature. (a) Experimental pressure and temperature points. Gray solid lines: normal mantle and slab geotherms (Bina & Navrotsky, 2000; Brown & Shankland, 1981; Eberle et al., 2002; Hernlund et al., 2005); gray dashed line: core-mantle boundary. (b) Phase boundary between Stv and CaCl$_2$-type SiO$_2$. Solid gray line: phase boundary in Nomura et al. (2010); dashed gray line: phase boundary in Fischer et al. (2018). (c) Phase boundary between CaCl$_2$-type SiO$_2$ and seifertite. Gray dashed line: core-mantle boundary; circles: this study; lower triangles: Grocholski et al. (2013); open stars: CaCl$_2$-type SiO$_2$ as starting material in Murakami et al. (2003); solid stars: SiO$_2$ glass as starting material in Murakami et al. (2003). All the literature data are recalibrated into a self-consistent pressure scale.

in diameter was used. SiO$_2$ glass was used as the starting material to synthesize both seifertite and CaCl$_2$-type SiO$_2$ at lower-mantle pressure-temperature conditions in four DACs. Another 10 DAC samples were first cold compressed to ~45–50 GPa and heated from both sides (upstream and downstream) using a double-sided flat top laser heating technique to pretransform the starting SiO$_2$ glass to Stv (Prakapenka et al., 2008). Stv obtained at 45–50 GPa was further used to synthesize CaCl$_2$-type SiO$_2$ and seifertite at higher pressures. Temperature was determined by fitting the thermal radiation spectrum with the Planck radiation function under the Graybody approximation (Prakapenka et al., 2008). In each heating cycle, the XRD patterns were collected from 1200 K at an interval of 100–200 K up to 3500 K, and the 2-D patterns are integrated using the program Dioptas (Prescher & Prakapenka, 2015). The difference between the upstream and downstream sides is within ±50 K at 1200–1800 K and within ±100 K between 1800 and 3000 K during heating. Uncertainties in temperature due to the temperature gradient inside the X-ray spot are estimated to be ~10% of the measured value (Kavner & Duffy, 2001). For most heating runs, we controlled the heating time within 20 min to minimize the influence of a spotty pattern on the structure refinement. To test the stability of seifertite above 108 GPa, the heating time in several runs was increased to ~30 min. At a given temperature, we did not note the change in pressure by elevating the heating time, indicating a stable heating.

3. Results

Experimental pressure-temperature points were shown in Figure 1. The starting SiO$_2$ glass in 10 prepared DACs was pretransformed into Stv at ~45–50 GPa and 1500 K before the high pressure-temperature XRD measurements. In the first heating cycle, heating the sample at 63 GPa and 1500 K showed a separation of the peak 121 and 211, indicating the formation of CaCl$_2$-type SiO$_2$. The 121 and 211 peaks in CaCl$_2$-type SiO$_2$ gradually merged into a single peak after elevating temperature to ~1900 K, caused by the phase transition to Stv (Figure 1 and supporting information Figure S1). CaCl$_2$-type SiO$_2$ was noted to be stable up to 108 GPa at 2000 K. Further elevating temperature above 2000 K led to the formation of a seifertite + CaCl$_2$-type SiO$_2$ mixture up to 3500 K. Heating the sample over 2500 K for ~30 min did not influence the intensity of the XRD peaks for both seifertite and CaCl$_2$-type SiO$_2$ (Figures 1 and S2). Seifertite was observed to be present together with CaCl$_2$-type SiO$_2$ between 108 and 130 GPa at 2000 K and between 114 and 137 GPa at 3500 K. For one 75-μm culet DAC, we have synthesized Stv at 50 GPa and 1500 K using the SiO$_2$ glass as the starting material. Compression of the synthesized Stv to 132 GPa at 300 K should transform it into CaCl$_2$-type SiO$_2$. Heating it at ~1400 K led to the formation of a single-phase seifertite which was stable up to 3000 K (Figures 1, 2, and S2). For DACs with the SiO$_2$ glass as the starting material, we were not able to obtain high-quality XRD patterns for CaCl$_2$-type SiO$_2$ between 70 and 110 GPa at 1200–3000 K. Although we also observed the presence of seifertite with CaCl$_2$-type SiO$_2$ using the SiO$_2$ glass as the starting material at ~120–130 GPa upon heating up between 2000 and 3000 K, both seifertite and CaCl$_2$-type SiO$_2$ were shown as weak peaks in the collected XRD patterns which cannot be used to determine the thermal EoS. In contrast, heating one DAC with 75/300-μm culet diamonds and SiO$_2$ glass as the starting material at 135 GPa and 1400 K directly formed single-phase seifertite. We did not
observe the transition from seifertite to a seifertite + CaCl$_2$-type SiO$_2$ mixture by elevating temperature (Figure 1).

Here we excluded unit cell volumes of CaCl$_2$-type SiO$_2$ from the analysis of the EOS when CaCl$_2$-type SiO$_2$ was observed together with seifertite. Due to limited data points at high pressure-temperature conditions, available data including those unit cell volumes at which seifertite was observed to be present together with CaCl$_2$-type SiO$_2$ were also used to constrain the thermal EoS of seifertite (Table S1 and Data Set S2). We have performed the Le Bail refinement to derive the lattice parameters (Toby, 2001). Full profile Rietveld refinement cannot be performed to the spotty pattern shown in Figure 2. Typical residue of the refinement is less than 0.15 (R factor). For the left XRD patterns, at least 7–12 peaks fitted by the Voigt function were used to refine the unit cell parameters using the least squares fit. Since the diffraction peaks of Pt overlapped with the samples or were too weak to be used for pressure calibration, here we used the thermal EoS of NaCl to calculate the pressure (Fei et al., 2007). The pressure-volume-temperature data were fitted using the Mie-Grüneisen equations (Figures 3 and S3) (Jackson & Rigden, 1996).

Pressure, $P$, is a combination of pressure $P_c$ from the Birch-Murnaghan EoS at a reference temperature ($T_0 = 300$ K) and the thermal pressure, $P_{th}$:

$$P = P_c + P_{th}. \quad (1)$$

Following the Birch-Murnaghan EoS, we have $P_c$ as follows (Birch, 1938)
\[ P_c = \frac{3}{2} K_0 T \left[ \left( \frac{V}{V_0} \right)^{-7/3} - \left( \frac{V}{V_0} \right)^{-5/3} \right] \cdot \left[ 1 + \frac{3}{4} (K' - 4) \left( \frac{V}{V_0} \right)^{-2/3} - 1 \right] \]  

(2)

where \( K_0 T \) and \( V_0 \) are the isothermal bulk modulus and molar volume at \( P_0 \) and \( T_0 \), respectively. \( K' = 4 \) (fixed) is the pressure derivative of the bulk modulus. \( P_{th} \) can be written following (Jackson & Rigden, 1996):

\[ P_{th}(V, T) = \frac{\gamma}{V} [E_{th}(V, T) - E_{th}(V, T_0)] \]

(3)

where \( E_{th} \) is the internal thermal energy between temperature \( T \) and \( T_0 \), and \( \gamma \) is the Grüneisen parameter. \( E_{th} \) is associated with the Debye temperature, \( \Theta_D \) (Jackson & Rigden, 1996):

\[ E_{th}(V, T) = 9nRT \left( \frac{\Theta_D}{T} \right)^{-3} \int_0^{\frac{\Theta_D}{T}} \frac{x^3}{e^x - 1} dx \]

(4)

and

\[ \gamma = \gamma_0 \left( \frac{V}{V_0} \right)^q \]

(5)

where \( n \) is 3, representing the number of atoms in the chemical formula of SiO2, \( R \) is the gas constant, \( \gamma_0 \) is the Grüneisen parameter at ambient conditions, and \( q \) is assumed to be independent of volume (Fei et al., 1992). \( \Theta_D \) can be calculated as follows (Jackson & Rigden, 1996):

\[ \Theta_D = \Theta_D^0 \exp \left( -\frac{\gamma - \gamma_0}{q} \right) \]

(6)

The obtained thermoelastic parameters for both CaCl2-type SiO2 and seifertite are listed in Table 1. The fitting residuals are shown in Figure 3 to evaluate the quality of the fitting. We noted that the thermoelastic parameters of CaCl2-type SiO2 are not sensitive to the variation of the Debye temperature, \( \Theta_D^0 \) or the \( q \) value (Table 2). For both CaCl2-type SiO2 and seifertite varying \( q \) from 0.8 to 1.2 can cause a weak increase in \( K_T^{0} \) and has a minor influence on other thermoelastic parameters.

4. Discussion

4.1. High-Pressure Phase SiO2

To compare with literature results for the phase transition of SiO2, we have reanalyzed the pressure data in previous studies using a self-consistent pressure scale of Fei et al. (2007) (Fischer et al., 2018; Grocholski et al., 2013; Murakami et al., 2003; Wang et al., 2012). The phase transition from Stv to CaCl2-type SiO2 has been extensively studied between 45 and 75 GPa up to 2500 K using both large-volume press and laser-heated DACs (Andrault et al., 1998; Buchen et al., 2018; Fischer et al., 2018; Hemley et al., 2000; Nomura et al., 2010; Ono et al., 2002; Prakapenka et al., 2004; Shieh et al., 2005; Wang et al., 2012; Yamazaki et al., 2014). The phase boundary between Stv and CaCl2-type SiO2 was tightly constrained by dense data points in Nomura et al. (2010) with a Clapeyron slope of 11.1 MPa/K. Yet a recent experimental study also using DAC technique argued that, at a given temperature, the phase transition should occur at a higher pressure with a larger Clapeyron slope of 15.6 MPa/K (Fischer et al., 2018). Although we only had limited data points which recorded the presence of Stv, our phase boundary between Stv and CaCl2-type SiO2 is in better agreement with results in Nomura et al. (2010) (Figure 1). The single-phase seifertite was synthesized at 132–136 GPa and 1400 K using either SiO2 glass or CaCl2-type SiO2 as the starting material (Figure 1). After recalculating the experimental pressures in literature using the self-consistent pressure scales (Fei et al., 2007), the stable seifertite observed here is consistent with previous experimental results (Grocholski et al., 2013; Murakami et al., 2003). In addition, we observed a wide pressure range at high temperatures for the presence of seifertite together with CaCl2-type SiO2 (Figure 1). Elevating the temperature above 2000 K between 108 and 130 GPa led to the transition from CaCl2-type SiO2 to a seifertite + CaCl2-type SiO2 mixture. This mixture was observed between 114 and 137 GPa at
3500 K, which is consistent with a previous experimental study using the SiO2 glass as the starting material (Grocholski et al., 2013). Murakami et al. (2003) reported that elevating the heating time up to 2 hr can significantly lower the intensity of the seifertite diffraction peaks at the two-phase region of 113–117 GPa and 2160–2320 K, indicating that seifertite is metastable. Furthermore, heating the seifertite and CaCl2-type SiO2 mixture at over 140 GPa to 2100–2200 K up to 4.5 hr can significantly increase the diffraction intensity of the seifertite peaks, showing that seifertite tends to be stable at this pressure range (Murakami et al., 2003). We did not observe any change in the intensity of the diffraction peaks for both seifertite and CaCl2-type SiO2 in the two-phase region, largely due to our limited heating time and the sluggish kinetics to prohibit the transition of seifertite to CaCl2-type SiO2 at relatively low pressures (Murakami et al., 2003). At a given temperature, the presence of seifertite below the pressure of the phase boundary determined by Murakami et al. (2003) may be caused by the nonhydrostatic condition inside the DACs.

Table 1

| Studies            | $K_{OT}$ (GPa) | $K_{OT}'$ | $V_0$ ($\AA^3$) | $\theta_0$ (K) | $\gamma_0$ | $q$ |
|--------------------|----------------|-----------|-----------------|----------------|------------|-----|
| CaCl2-type phase   |                |           |                 |                |            |     |
| This study         | 245 (7)        | 4 (fixed) | 48.1 (2)        | 1100 (400)     | 1.3 (3)    | 1 (fixed) |
| Fischer et al. (2018) | 341 (4) | 3.20 (16) | 46.57           | 1109           | 2.14 (4)   | 1   |
| Fischer et al. (2018)a | 318 (2) | 4 (fixed) | 46.57 (fixed)   | 1109 (fixed)   | 1.56 (7)   | 1 (fixed) |
| Andrault et al. (2003) | 282 (1) | 4.29      | 46.88 (2)      |                |            |     |
| Buchen et al., (2018) | 241 (18) | 4.72 (4) | 48.22 (44)     |                |            |     |
| Grocholski et al. (2013) | 317 (3) | 4 (fixed) | 46.66 (4)      |                |            |     |
| Oganov et al. (2005)b | 258      | 4.6       | 47.15           |                |            |     |
| seifertite         |                |           |                 |                |            |     |
| This study         | 290 (10)       | 4 (fixed) | 92.3 (5)        | 1600 (200)     | 1.6 (2)    | 1 (fixed) |
| Grocholski et al. (2013) | 322 (4) | 3.5 (2)   | 91.66           |                |            |     |
| Dubrovinsky et al. (2001) | 313 (5) | 3.43 (11) | 93.52 (14)     |                |            |     |
| Driver et al. (2010)b | 329      | 4         | 91.76           |                | 1.27       | 2.05 |

aRefit by fixing $K'$ at 4  bTheoretical results.
with large deviatoric stress (Figure 1). Limited heating time here with strong kinetics barriers for this phase transition makes it difficult to release the large deviatoric stress inside the DAC and leads to the formation of seifertite at a lower pressure than that shown in Murakami et al. (2003) at a given temperature. We thus follow the phase boundary of CaCl$_2$-type SiO$_2$ and seifertite determined by Murakami et al. (2003).

### 4.2. Thermoelastic Parameters, Density, and Velocity Profiles of SiO$_2$

Our high pressure-temperature data provide crucial constraints on the thermal EoS of CaCl$_2$-type SiO$_2$ and seifertite (Table 1). Pressures in previous experimental studies used to derive the EoS of the high-pressure polymorphs of SiO$_2$ were reanalyzed here using a self-consistent pressure scale for comparison (Figure 4) (Fei et al., 2007; Murakami et al., 2003). Our obtained pressure-volume data for CaCl$_2$-type SiO$_2$ at 300 K were in good agreement with literature results (Figure 4) (Grocholski et al., 2013; Murakami et al., 2003). Based on our results and previous studies, transition from Stv to CaCl$_2$-type SiO$_2$ does not cause any discontinuity in the compression curve because of the second-order phase transition but can affect the volume gradient (Andrault et al., 1998; Andrault et al., 2003; Buchen et al., 2018; Fischer et al., 2018; Hemley et al., 2000; Tsuchiya et al., 2004). A recent experimental study reported a greater volume for both Stv and CaCl$_2$-type SiO$_2$ than literature results and our measurements (Buchen et al., 2018). Polycrystalline Stv synthesized from the large-volume press exhibits a less compressible a axis and a larger volume above 10 GPa (Buchen et al., 2018). On the other hand, the phase transition from CaCl$_2$-type SiO$_2$ to

### Table 2

|                | CaCl$_2$-type phase | Seifertite |
|----------------|---------------------|------------|
| **Elastic Parameters** | Model 1 | Model 2 | Model 3 | Model 1 | Model 2 | Model 3 |
| $K_{GT}$ (GPa) | 244 (7) | 245 (8) | 246 (7) | 289 (8) | 290 (10) | 291 (10) |
| $K_{GT}'$ | 4 (fixed) | 4 (fixed) | 4 (fixed) | 4 (fixed) | 4 (fixed) | 4 (fixed) |
| $V_0 (\text{Å}^3)$ | 48.1 (3) | 48.1 (3) | 48.1 (2) | 93.4 (5) | 92.3 (5) | 92.3 (4) |
| $\theta_{D0}$ (K) | 1000 (400) | 1100 (400) | 1100 (500) | 1600 (200) | 1600 (200) | 1500 (200) |
| $\gamma_0$ | 1.2 (3) | 1.3 (3) | 1.3 (3) | 1.5 (1) | 1.6 (2) | 1.7 (2) |
| $q$ | 0.8 (fixed) | 1 (fixed) | 1.2 (fixed) | 0.8 (fixed) | 1 (fixed) | 1.2 (fixed) |

### Figure 4

Pressure-volume (per formula unit) relationship of SiO$_2$ at high pressures and 300 K. Yellow: Stv; red: CaCl$_2$-type SiO$_2$; blue: seifertite; circles: this study; diamonds: Buchen et al. (2018); squares: Andrault et al. (2003); upper triangles: Wang et al. (2012); yellow lower triangles: Nisr et al. (2017); red lower triangles: Grocholski et al. (2013); blue lower triangles: Grocholski et al. (2013); hexagons: Murakami et al. (2003); gray short lines: error bars. Error bars are smaller than symbols when not shown.
seifertite was observed to cause a 2% reduction in the volume with Z normalized to 1 at 300 K (volume per formula unit) (Figure 4). Although our measured volumes of seifertite at 300 K are 1.5% smaller than those reported in Grocholski et al. (2013), they were in good agreement with results in Murakami et al. (2003) considering experimental errors after pressure calibration.

Thermoelastic parameters of CaCl2-type SiO2 are largely unknown. Due to limited experimental data points and narrow pressure range, most thermoelastic parameters for CaCl2-type SiO2, such as \( V_0 \), \( \gamma_0 \), and \( q \), were simply assumed to be the same as Stv’s (Fischer et al., 2018) (Table 1). Due to the second-order phase transition, transition from Stv to CaCl2-type SiO2 does not cause a notable change in density along the slab geotherm based on our result and Wang et al. (2012) (Buchen et al., 2018; Nisr et al., 2017). Yet the phase transition can induce a 10–11% reduction in \( V_\Phi \) because CaCl2-type SiO2 has a lower bulk modulus than Stv but a similar density, which is consistent with previous work (Buchen et al., 2018). Here our calculated \( \rho \) of seifertite using the obtained thermoelastic parameters is ~1.5% greater than the previous theoretical predictions (Driver et al., 2010). CaCl2-type SiO2 to seifertite phase transition will cause a 4% increase in \( \rho \) and a 5% increase in \( V_\Phi \). The change in \( \rho \) across CaCl2-type to seifertite phase transition obtained here is smaller than that estimated using literature results, whereas the magnitude of the jump in \( V_\Phi \) is greater (Driver et al., 2010; Fischer et al., 2018).

Combining the high-pressure phase diagram of SiO2 with the thermal EoS, we have further examined the influence of temperature on the \( \rho \) and \( V_\Phi \) profiles of SiO2 in the Earth’s lower mantle (Figure 5) (Wang et al., 2012). \( \rho \) and \( V_\Phi \) of SiO2 were modeled along normal mantle, slab, and cold slab geotherms, respectively (Bina & Navrotsky, 2000; Brown & Shankland, 1981; Eberle et al., 2002; Hernlund et al., 2005). The slab and cold-slab geotherms are 500 and 1000 K lower than the normal mantle geotherm, respectively. Our modeling has shown that elevating temperature by 500 K from the slab to normal mantle geotherm can lead to a 0.8% reduction in \( \rho \) and a 3.7% reduction in \( V_\Phi \) of Stv but only lowers the \( \rho \) and \( V_\Phi \) of CaCl2-type SiO2 by 0.7% and 1%, respectively (Figure 5). Varying temperature thus has a greater effect on the \( \rho \) and \( V_\Phi \) of Stv than CaCl2-type SiO2. In addition, although the difference in \( \rho \) between Stv and CaCl2-
type SiO$_2$ slightly increases with elevating temperature, the weak discontinuity in $\rho$ across the Stv-CaCl$_2$-type phase transition along slab or normal mantle geotherms may not be detected by seismic observation (Figure 5). In contrast, this phase transition can lead to a 10–11% reduction in $V_p$ along slab and mantle geotherms because CaCl$_2$-type SiO$_2$ has a similar density to Stv but a lower bulk modulus (Buchen et al., 2018; Driver et al., 2010; Wang et al., 2012). Considering 20 vol.% SiO$_2$ in the subducted mid-ocean ridge basalt (Perrillat et al., 2006; Ricollet et al., 2010), the reduction in $V_p$ across this phase transition is estimated to be 2–2.2%, which could be related to the observed seismic reflectors in the middle to lower mantle (e.g., Hedlin et al., 1997; Kaneshima, 2018; Kaneshima & Helffrich, 1999, 2003, 2009; Le Stunff et al., 1995; Vinnik et al., 2001). The depth of the velocity heterogeneities could vary between 1,400 and 1,800 km because the phase transition pressure between Stv and CaCl$_2$-type SiO$_2$ shows a positive dependence on temperature.

Since our experimental study cannot provide direct constraints on the phase boundary between seifertite and CaCl$_2$-type SiO$_2$, we used the phase boundary determined by Murakami et al. (2003) to model the $\rho$ and $V_p$ variation across this phase transition. At the bottom lower mantle, the CaCl$_2$-type SiO$_2$ to seifertite phase transition occurs 200–250 km above the core-mantle boundary (Murakami et al., 2003). If free silica exists at the bottom lower mantle and reaches a volume percentage of 20%, this phase transition could cause a ~0.3% increase in $\rho$ and ~0.8% increase in $V_p$ and may contribute to the observed D' discontinuity in some regions at the core-mantle boundary. It should be noted that the lower-mantle SiO$_2$ may contain some Al or even H. Addition of Al and H could influence the transition pressure from CaCl$_2$-type SiO$_2$ to seifertite and their thermal EoS. Future studies are needed to well constrain the thermal EoS and phase transition of the Al and/or H-bearing SiO$_2$ and provide new insights on the complex seismic signature of the D' layer.

In summary, we have studied the phase stability of SiO$_2$ at relevant pressure-temperature of the Earth's lower mantle and determined the thermal EoS of CaCl$_2$-type SiO$_2$ and seifertite. The phase boundary between Stv and CaCl$_2$-type SiO$_2$ determined here is in good agreement with that in literature (Nomura et al., 2010). Considering 20 vol.% SiO$_2$ in the subducted mid-ocean ridge basalt, the phase transition from Stv to CaCl$_2$-type SiO$_2$ can cause a 2–2.2% reduction in $V_p$ but hardly influence the density. Depending on the local temperature of the region in the lower mantle, the change in $V_p$ due to the Stv phase transition should be at depths of 1,400 to 1,800 km, consistent with seismically observed velocity scatters at the corresponding depth Tonga-Fiji and Africa regions (Hedlin et al., 1997; Kaneshima, 2018; Le Stunff et al., 1995). In addition, we synthesized the single-phase seifertite using both SiO$_2$ glass and CaCl$_2$-type SiO$_2$ above 134 GPa and 1400 K. Seifertite was observed to be present together with CaCl$_2$-type SiO$_2$ between 108 and 130 GPa above 2000 K. Due to limited heating time and strong kinetics for this phase transition, our experimental data are not enough to well determine the phase boundary between seifertite and the observed CaCl$_2$-type SiO$_2$. At a given temperature, seifertite which is present at a pressure lower than the phase boundary determined by Murakami et al. (2003) should be metastable. Combining our obtained thermal EoS and literature phase diagram, we also explore the influence of this phase transition on the $\rho$ and $V_p$ of the bottom lower mantle. The CaCl$_2$-type SiO$_2$ to seifertite phase transition could produce a 0.3% and 0.8% increase in the $\rho$ and $V_p$ at the bottom lower mantle considering 20 vol.% SiO$_2$ in the subducted mid-ocean ridge basalt, which may contribute to the formation of the D' discontinuity above the core-mantle boundary.

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References
Andrault, D., Angel, R. J., Mosenfelder, J. L., & Le Bihan, T. (2014). Equation of state of stishovite to lower mantle pressures. Journal of Geophysical Research: Solid Earth, 120, 891–907. https://doi.org/10.1002/2013JB010923
Andrault, D., Angel, R. J., Mosenfelder, J. L., & Le Bihan, T. (2015). Equation of state of stishovite to lower mantle pressures. Journal of Geophysical Research: Solid Earth, 120, 891–907. https://doi.org/10.1002/2013JB010923
Bina, C. R., & Navrotsky, A. (2002). Possible presence of high-pressure ice in cold subducting slabs. Nature, 418(6893), 814–817. https://doi.org/10.1038/418814a
Birch, F. (1938). The effect of pressure upon the elastic parameters of isotropic solids, according to Murnaghan’s theory of finite strain. Journal of Applied Physics, 9(4), 279–288. https://doi.org/10.1063/1.1710417
Brown, J. M., & Shankland, T. J. (1981). Thermodynamic parameters in the Earth as determined from seismic profiles. Geophysical Journal of the Royal Astronomical Society, 66(3), 579–596. https://doi.org/10.1111/j.1365-246X.1981.tb04891.x
"
Buchen, J., Marquardt, H., Schulze, K., Speziale, S., Ballaran, T. B., Nishiyama, N., & Hanfland, M. (2018). Equation of state of polycrystalline stishovite across the tetragonal-orthorhombic phase transition. Journal of Geophysical Research: Solid Earth, 123, 7437–7436. https://doi.org/10.1029/2018JB015835

Carpenter, M. A., Hemley, R. J., & Mao, H. K. (2000). High-pressure elasticity of stishovite and the P4j/mmm reversible arrow Pnnm phase transition. Journal of Geophysical Research, 105(B5), 10,807–10,816. https://doi.org/10.1029/1999JB900419

Černok, A., Marquardt, K., Caracas, R., Bykova, E., Habler, G., Liermann, H. P., et al. (2017). Compressional pathways of alpha-cristobalite, structure of cristobalite X-I, and towards the understanding of seifellite formation. Nature Communications, 8(1), 1–10. https://doi.org/10.1038/scommns15647

Coes, L. (1953). A new dense crystalline silica. Science, 118(3057), 131–132. https://doi.org/10.1126/science.118.3057.131

Driver, K. P., Cohen, R. E., Wu, Z. G., Militzer, B., Rios, P. L., Towler, M. D., et al. (2010). Quantum Monte Carlo computations of phase stability, equations of state, and elasticity of high-pressure silica. Proceedings of the National Academy of Sciences of the United States of America, 107(21), 9519–9524. https://doi.org/10.1073/pnas.0912130107

Dubrovinsky, L., Dubrovinskaia, N., Saxena, S., Tutti, F., Rekhi, S., Le Bihan, T., et al. (2001). Pressure-induced phase transitions in dense silica polymorphs. Physica of the Earth and Planetary Interiors, 134(3-4), 191–202. https://doi.org/10.1016/S0031-9201(02)00157-7

Fei, Y. W., Mao, H. K., Shu, J. F., & Hu, J. Z. (1992). P-V-T Equation of state of magnesiowustite (Mg2MFe2O4). Physics and Chemistry of Minerals, 18, 416–422.

Fei, Y. W., Ricollet, A., Frank, M., Mibe, K., Shu, G. Y., & Prakapenka, V. (2007). Toward an internally consistent pressure scale. Proceedings of the National Academy of Sciences of the United States of America, 104(22), 9182–9186. https://doi.org/10.1073/pnas.0609013104

Fischer, R. A., Campbell, A. J., Chidester, B. A., Reaman, D. M., Thompson, E. C., Pigott, J. S., et al. (2018). Equations of state and phase pressure structural transformations in dense SiO2. Solid State Communications, 114(10), 527–532. https://doi.org/10.1016/S0031-9201(00)00999-5

Herrlund, J. W., Thomas, C., & Tackley, P. J. (2005). A doubling of the perovskite-phase boundary and structure of the Earth's lowermost mantle. Nature, 434(7035), 1891–1894. https://doi.org/10.1038/nature03472

Hirose, K., Takafuji, N., Sata, N., & Ohishi, Y. (2005). Phase transition and density of subducted MORB crust in the lower mantle. Earth and Planetary Science Letters, 237(1-2), 239–251. https://doi.org/10.1016/j.epsl.2005.06.035

Irifune, T., Sekine, T., Ringwood, A. E., & Hibberson, W. O. (1986). The eclogite-facies reaction of garnet peridotite: An in situ X-ray measurement. Geophysical Research Letters, 13, 1914. https://doi.org/10.1029/GL013i006p01914

Kaneshima, S. (2009). Lower mantle scattering precursors under Africa—Evidence for mid-mantle reflectors. Science, 323(5915), 645–648. https://doi.org/10.1126/science.1162207

Kaneshima, S., & Helffrich, G. (1999). Dipping low-velocity layer in the mid-lower mantle: Evidence for geochemical heterogeneity. Science, 283(5409), 1888–1891. https://doi.org/10.1126/science.283.5409.1888

Kaneshima, S., & Helffrich, G. (2003). Subparallel dipping heterogeneities in the mid-lower mantle. Journal of Geophysical Research, 108(B5), 2272. https://doi.org/10.1029/2002JB001596

Kaneshima, S., & Helffrich, G. (2009). Lower mantle scattering profiles and fabric below Pacific subduction zones. Earth and Planetary Science Letters, 282(1-4), 234–239. https://doi.org/10.1016/j.epsl.2009.03.024

Karki, B. B., Warren, M. C., Stixrude, L., Ackland, G. J., & Crain, J. (1997). Ab initio studies of high pressure structural transformations in silica. Physical Review B, 56(6), 3465–3471. https://doi.org/10.1103/PhysRevB.56.3465

Kavner, A., & Duffy, T. S. (2001). Pressure-volume-temperature paths in the laser-heated diamond anvil cell. Journal of Applied Physics, 89(3), 1907–1914. https://doi.org/10.1063/1.1335827

Kingma, K. J., Cohen, R. E., Hemley, R. J., & Mao, H. K. (1995). Transformation of Stishovite to a denser phase at lower-mantle pressures. Nature, 374(6519), 243–245. https://doi.org/10.1038/374243a0

Le Stunff, Y., Wicks, C. W., & Romanowicz, B. (1995). P–p’ precursors under Africa—Evidence for mid-mantle reflectors. Science, 270(5253), 74–77. https://doi.org/10.1126/science.270.5253.74

McLennan, S. M., & Taylor, S. R. (1985). The continental crust: Its composition and evolution. An examination of the geochemical record preserved in sedimentary rocks. Oxford, UK: Blackwell Scientific.

Murakami, M., Hirose, K., Ono, S., & Ohishi, Y. (2003). Stability of CaCl2-type and a α-FeO2-type SiO2 at high pressure and temperature determined by in-situ X-ray measurements. Geophysical Research Letters, 30(5), 1207. https://doi.org/10.1029/2002GL016722

Nesbitt, H. W., Fedo, C. M., & Young, G. M. (1997). Quartz and feldspar stability, steady and non-steady-state weathering, and petrogenesis of siliciclastic sands and muds. The Journal of Geology, 105(23), 173–192. https://doi.org/10.1086/515908

Nis, C., Leinenweber, K., Prakapenka, V., Prescher, T., Tkachev, S., & Shim, S. H. D. (2017). Phase transition and equation of state of dense hydrous silica up to 63 GPa. Journal of Geophysical Research: Solid Earth, 122, 6972–6983. https://doi.org/10.1002/2017JB014055

Nomura, R., Hirose, K., Sata, N., & Ohishi, Y. (2010). Precise determination of post-stishovite phase transition boundary and implications for seismic heterogeneities in the mid-lower mantle. Physics of the Earth and Planetary Interiors, 183(1-2), 104–109. https://doi.org/10.1016/j.pepi.2010.08.004

Oganov, A. R., Gillan, M. J., & Price, G. D. (2005). Structural stability of silica at high pressures and temperatures. Physical Review B, 71, 064104. https://doi.org/10.1103/PhysRevB.71.064104

Ono, S., Hirose, K., Murakami, M., & Ishihiki, M. (2002). Post-stishovite phase boundary in SiO2 determined by in situ X-ray observations. Earth and Planetary Science Letters, 197(3-4), 187–192. https://doi.org/10.1016/S0012-821X(02)00479-X

Perrillat, J. P., Ricoleau, A., Daniel, L., Fiquet, G., Mezouar, M., Guignot, N., & Cardon, H. (2006). Phase transformations of subducted basaltic crust in the uppermost lower mantle. Physics of the Earth and Planetary Interiors, 157(1-2), 139–149. https://doi.org/10.1016/j.pepi.2006.04.001

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12,629

Journal of Geophysical Research: Solid Earth 10.1029/2019JB017853
Prakapenka, V. B., Kubo, A., Kuznetsov, A., Laskin, A., Shkuzikhin, O., Dera, P., et al. (2008). Advanced flat top laser heating system for high pressure research at GSECARS: Application to the melting behavior of germanium. *High Pressure Research, 28*(3), 225–235. https://doi.org/10.1080/08957950802050718

Prakapenka, V. B., Shen, G. Y., Dubrovinsky, L. S., Rivers, M. L., & Sutton, S. R. (2004). High pressure induced phase transformation of SiO2 and GeO2: Difference and similarity. *Journal of Physics and Chemistry of Solids, 65*(8-9), 1537–1545. https://doi.org/10.1016/j.jpcs.2003.12.019

Prescher, C., & Prakapenka, V. B. (2015). DIOPTAS: A program for reduction of two-dimensional X-ray diffraction data and data exploration. *High Pressure Research, 35*(3), 223–230. https://doi.org/10.1080/08957959.2015.1059835

Ricolleau, A., Perrillat, J. P., Fiquet, G., Daniel, I., Matas, J., Addad, A., et al. (2010). Phase relations and equation of state of a natural MORB: Implications for the density profile of subducted oceanic crust in the Earth’s lower mantle. *Journal of Geophysical Research, 115*, B08202. https://doi.org/10.1029/2009JB006709

Sekine, T., Irifune, T., Ringwood, A. E., & Hibberson, W. O. (1986). High-Pressure Transformation of Eclogite to Garnetite in Subducted Oceanic-Crust. *Nature, 319*(6054), 584–586.

Singh, A. K., Andrault, D., & Bouvier, P. (2012). X-ray diffraction from stishovite under nonhydrostatic compression to 70 GPa: Strength and elasticity across the tetragonal - > orthorhombic transition. *Physics of the Earth and Planetary Interiors, 208*, 1–10. https://doi.org/10.1016/j.pepi.2012.07.003

Stishov, S. (1961). A new dense modification of silica. *Geokhimiya, 10*, 837–839.

Sun, N. Y., Wei, W., Han, S. J., Song, J. H., Li, X. Y., Duan, Y. F., et al. (2018). Phase transition and thermal equations of state of (Fe, Al)-bridgmanite and post-perovskite: Implication for the chemical heterogeneity at the lowermost mantle. *Earth and Planetary Science Letters, 490*, 161–169. https://doi.org/10.1016/j.epsl.2018.03.004

Thomson, A., Crichton, W., Brodholt, J., Wood, J., Siersch, N., Muir, J., et al. (2019). Seismic velocities of CaSiO3 perovskite can explain LLSPs in Earth’s lower mantle. *Nature, 572*(7771), 643–647. https://doi.org/10.1038/s41586-019-1483-x

Toby, B. H. (2001). EXPGUI, a graphical user interface for GSAS. *Journal of Applied Crystallography, 34*(2), 210–213. https://doi.org/10.1107/S0021889801002242

Tsuchiya, T., Caracas, R., & Tsuchiya, J. (2004). First principles determination of the phase boundaries of high-pressure polymorphs of silica. *Geophysical Research Letters, 31*, L11610. https://doi.org/10.1029/2004GL019649

Vinnik, L., Kato, M., & Kawakatsu, H. (2001). Search for seismic discontinuities in the lower mantle. *Geophysical Journal International, 147*(1), 41–56. https://doi.org/10.1046/j.1365-246X.2001.05516.x

Wang, F. L., Tange, Y., Irifune, T., & Funakoshi, K. (2012). P-V-T equation of state of stishovite up to mid-lower mantle conditions. *Journal of Geophysical Research, 117*, B06209. https://doi.org/10.1029/2011JB009100

Wedepohl, K. H. (1995). The composition of the continental crust. *Geochemica et Cosmochimica Acta, 59*(7), 1217–1232. https://doi.org/10.1016/0016-7037(95)00038-2

Yamazaki, D., Ito, E., Yoshino, T., Tsujino, N., Yoneda, A., Guo, X., et al. (2014). Over 1 Mbar generation in the Kawai-type multianvil apparatus and its application to compression of (Mg0.92Fe0.08)SiO3 perovskite and stishovite. *Physics of the Earth and Planetary Interiors, 228*, 262–267. https://doi.org/10.1016/j.pepi.2014.01.013