Thermal Equations of State of Corundum and Rh$_2$O$_3$ (II)-Type Al$_2$O$_3$ up to 153 GPa and 3400 K

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Abstract In this study, we present new experimental constraints on the thermal equations of state of corundum and Rh$_2$O$_3$ (II)-type Al$_2$O$_3$ up to 153 GPa and 3400 K using synchrotron X-ray diffraction in laser-heated diamond anvil cells. Corundum was observed to transform into a mixture of corundum and Rh$_2$O$_3$ (II)-type Al$_2$O$_3$ at 106 GPa and 2300 K, accompanied by a strong kinetic barrier. The Rh$_2$O$_3$ (II)-type Al$_2$O$_3$ further transforms into the CaIrO$_3$-phase at 156 GPa and 3700 K. The transition from corundum to Rh$_2$O$_3$ (II)-type Al$_2$O$_3$ along a normal mantle geotherm could lead to a 1.9(5)% increase in density ($\rho$) but a 0.6(3)% reduction in $V_p$. Al$_2$O$_3$ is one of the major components of the anorthositic crust once this old crust was subducted to the deep mantle. Using the obtained thermoelastic parameters, we further modeled $\rho$ and $V_p$ profiles of primordial anorthositic crust and found that the subducted fate of the primordial anorthositic crust depended strongly on its temperature. Our modeling reveals that primordial anorthositic crust along a normal mantle geotherm could descend to the transition zone but be trapped at the topmost lower mantle with a greater $V_p$. Sinking of the anorthositic crust to the lower mantle can only occur along a 500–1000 K colder slab geotherm.

Plain Language Summary Al$_2$O$_3$ is an important constituent in the Earth’s crust and mantle. The overall weight percentages of Al$_2$O$_3$ in the pyrolitic mantle and subducted mid-ocean ridge basalt are estimated to be ~4% and ~16%, respectively. Moreover, Al$_2$O$_3$ is also one of the major components of the primordial anorthositic crust formed by crystallization of the magma ocean. Experimental constraints on the physical properties for the high-pressure phases of Al$_2$O$_3$ are thus critical for understanding the current mantle composition and deciphering the fate of the primordial anorthositic crust on the Earth. Here we have investigated the thermal equations of state of corundum and Rh$_2$O$_3$ (II)-type Al$_2$O$_3$ at the relevant pressure and temperature conditions of the Earth’s lower mantle. Combining the thermal equations of state of Al$_2$O$_3$ determined in this study and literature results, we have further modeled the density and bulk sound velocity profiles of the anorthositic crust from 10 to 120 GPa along different mantle geotherms and discussed the subducted fate of primordial anorthositic crust. The modeling results are critical to identify the seismic signature of the oldest anorthositic crust in the mantle.

1. Introduction

Aluminum oxide (Al$_2$O$_3$) is an important constituent in the Earth’s crust and mantle (Irfune & Ringwood, 1993; Ringwood, 1975; Taylor & McLennan, 1985). The overall weight percentages of Al$_2$O$_3$ in the pyrolitic mantle and subducted mid-ocean ridge basalt (MORB) are estimated to be ~4% and ~16%, respectively (Green, 1979; Sun, 1982). Al$_2$O$_3$ is mainly accommodated in mantle garnet or bridgmanite. However, recent petrological studies of diamond inclusions in mantle xenoliths revealed that Al$_2$O$_3$ could also be a separate phase in the Earth's mantle (Hutchison et al., 2001, 2004). Moreover, Al$_2$O$_3$ is one of the major components of the primordial anorthositic crust formed by crystallization of the magma ocean (Shearer et al., 2006; Wieczorek et al., 2006; Wood et al., 1970). Although anorthosite is widely distributed in the lunar crust, geological evidence for the existence of this primordial crust on Hadean Earth is lacking (Harrison & Wielicki, 2016; Rino et al., 2008). Some studies have thus proposed that the missing anorthositic crust on the Earth may have been removed from the surface to the deep interior (Kawai et al., 2009; Komabayashi et al., 2009; Nishi et al., 2018; Rino et al., 2008). Experimental constraints on the phase stability and thermoelastic properties of Al$_2$O$_3$ at high pressures and temperatures
Al$_2$O$_3$ crystallizes in the corundum structure with space group $\overline{R}3c$ at ambient conditions (Green, 1979). Corundum is stable up to 106 GPa at 300 K and transforms into the Rh$_2$O$_3$-(II)-type structure (space group: $Pbca$) upon heating at 1,800 K with a Clapeyron slope of $-6.5 \pm 1.5$ MPa/K (Kato et al., 2013; Tsuchiya et al., 2005). The forward and reversal transition between corundum and Rh$_2$O$_3$-(II)-type Al$_2$O$_3$ was observed in in Kato et al. (2013) which provided crucial constrains on the phase boundary between these two phases. Rh$_2$O$_3$-(II)-type Al$_2$O$_3$ was observed to further transform into the CaIrO$_3$-type structure (space group: $Cmcm$) at $\sim$130 GPa and 1,500 K, other high P-T experiments observed a stable Rh$_2$O$_3$-(II)-phase up to 170 GPa and 2,300 K (Oganov & Ono, 2005; Ono et al., 2006). The phase boundary between Rh$_2$O$_3$-(II)-type and CaIrO$_3$-type Al$_2$O$_3$ is thus controversial (Kato et al., 2013; Oganov & Ono, 2005; Ono et al., 2006; Tsuchiya et al., 2005).

More importantly, experimental constraints on the thermal equations of state (EoS) of high-pressure Al$_2$O$_3$, which are important for modeling the density ($\rho$) and velocity profiles ($V_\varphi$) of alumina-bearing rocks in the Earth's deep interior, are lacking. Most previous high-pressure experiments on the thermal EoS of corundum were performed at 300 K (Chung & Simmons, 1968; d’Amour et al., 1978; Dewaele & Torrent, 2013; Jephcoat et al., 1988; Richet et al., 1988). Although the thermal EoS of corundum have been determined up to 65 GPa and 1,500 K by Dubrovinsky et al. (1998), experimental pressures at high temperatures were determined from the luminescence of ruby at 300 K by assuming no changes in pressure inside the diamond anvil cells (DACs) during every heating-cooling cycle. This may result in large uncertainties in the obtained thermoelastic parameters (Yen et al., 2020). Furthermore, there are no experimental constraints on the thermoelastic parameters of Rh$_2$O$_3$-(II)-type Al$_2$O$_3$. The EoS of Rh$_2$O$_3$-(II)-type Al$_2$O$_3$ have only been theoretically predicted at 0 K (Marton & Cohen, 1994; Oganov & Ono, 2005; Thomson et al., 1996). The effect of temperature on the thermoelastic parameters of Rh$_2$O$_3$-(II)-type Al$_2$O$_3$ is still unknown.

In this study, we have determined the thermal EoS of corundum and Rh$_2$O$_3$-(II)-type Al$_2$O$_3$ up to 153 GPa and 3,400 K using synchrotron X-ray diffraction (XRD) in laser-heated DACs. The obtained results were used to constrain the density ($\rho$) and bulk sound velocity ($V_\varphi$) of Al$_2$O$_3$ along different mantle geotherms. Furthermore, our experimental results were applied together with literature data to discuss the fate of the primordial anorthositic crust by comparing the modeled $\rho$ and $V_\varphi$ profiles of anorthositic crust with those of the surrounding mantle at high P-T conditions. These are essential for deciphering the fate of the oldest crust on the Earth.

2. Experiments

Corundum powder with a purity of 99.9% and grain size of $\sim$1 µm purchased from Alfa Aesar Corporation was used as the starting material. The starting corundum was mixed with 7.5 wt % platinum (Pt) powder, which served as the laser absorber and pressure calibrant (Fei et al., 2007). The sample mixture was pressed into foils with a thickness of $10–15$ µm using a symmetric DAC equipped with a pair of 500-µm culet diamonds. The sample foils were broken into small pieces with diameters of 30–60 µm by a tungsten carbide (WC) needle. Two symmetric DACs equipped with a pair of 200-µm culet diamonds were used for experiments below 90 GPa. Experiments above 90 GPa were conducted using three DACs equipped with a pair of beveled diamonds 150 µm in diameter. Rhenium gaskets were pretrained into a thickness of 25–30 µm. The sample pieces were sandwiched between two NaCl layers of $\sim$5 µm in thickness. The NaCl layers used as the pressure medium and thermal insulator were dried for 8 hr to remove the potential moisture (Uts et al., 2013).

High P-T XRD experiments were conducted up to 156 GPa and 3,800 K at the GeoSoilEnviroConsortium (GSECARS) of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). An X-ray beam of
The X-ray wavelength was 0.3344 Å. Representative XRD patterns of Al$_2$O$_3$(II)-type Al$_2$O$_3$. The temperature was determined by fitting the thermal radiation spectrum with the Planck radiation function under the Graybody approximation (Prakapenka et al., 2008). The uncertainty in the temperature was estimated by multiple measurements from both sides of the sample (Prakapenka et al., 2008). For corundum, we always cold compressed the sample to the target pressure and heated a fresh sample spot up to 100 GPa and 3,000 K (Figure 1). XRD patterns at 300 K were collected after quenching because laser heating at high temperatures can greatly reduce the deviatoric stress inside the DACs (Uts et al., 2013). The heating time was extended to 30 min above 90 GPa close to the phase transition boundary between corundum and the Rh$_3$O$_3$(II)-phase to help overcome the potential kinetic barrier (Funamori & Jeanloz, 1997; Kato et al., 2013; Lin et al., 2004). Once the Rh$_3$O$_3$(II)-phase was present, we also collected the XRD patterns during temperature quenching from the maximum temperature to 1,200 K at intervals of 100–300 K to better constrain the thermal EoS of the Rh$_3$O$_3$(II)-phase. To test the stability of CaIrO$_3$-type Al$_2$O$_3$, we also heated the corundum + Rh$_3$O$_3$(II)-phase mixture up to 3,800 K between 129 and 156 GPa.

3. Results

Experimental P-T points are shown in Figure 1. At 103 GPa up to 2,300 K, we only observed corundum plus Pt and NaCl in our XRD patterns. Elevating the temperature above ~2,300 K transformed corundum to a corundum + Rh$_3$O$_3$(II)-phase mixture (Figures 1 and 2). Increasing the heating time to ~30 min did not cause obvious changes in the intensities of the XRD peaks for corundum or the Rh$_3$O$_3$(II)-phase. We kept increasing the laser power at 104 GPa and 3,300 K, which led to a significant laser flash and the formation of a single Rh$_3$O$_3$(II)-phase (Figure 2). The temperature for the formation of this single phase was not well constrained due to the significant laser flash. However, we did not observe the back-transition of the Rh$_3$O$_3$(II)-phase to corundum when lowering the temperature from 3,400 to 1,200 K between 104 and 119 GPa which could be caused by a fast quench speed. The CaIrO$_3$-phase appeared when we heated the corundum + Rh$_3$O$_3$(II)-phase mixture at 156 GPa and 3,700 K (Figures 1 and 2).

At least 5–8 and 9–15 diffraction peaks were used to determine the lattice parameters of corundum and Rh$_3$O$_3$(II)-type Al$_2$O$_3$, respectively (Figure 2). XRD patterns collected during quenching from the maximum temperature to 300 K were also analyzed to constrain the lattice parameters of both phases (Figure S1, Tables S1 and S2 in Supporting Information S1). NaCl was used as the pressure calibrant for one cell equipped with a pair of 200-µm culet diamonds when the diffraction peaks of Pt were too weak. We compared the pressure determined by NaCl to that determined by Pt in the second 200-µm culet DAC (Fei et al., 2007). The difference in the pressures determined by NaCl and Pt was within 1 GPa between 35 and 67 GPa up to 3,000 K (Figure S2 in Supporting Information S1). Pt was used as the pressure calibrant when fitting the thermal EoS of the Rh$_3$O$_3$(II)-phase (Fei et al., 2007). The thermoelastic parameters of corundum and the Rh$_3$O$_3$(II)-phase were derived by fitting the obtained pressure-volume-temperature data using the Mie-Grüneisen EoS (Jackson & Rigden, 1996). At high temperature, the total pressure, $P$, can be expressed by the Mie-Grüneisen formulation:

$$P(V, T) = P_0(T) + \Delta P_0(V, T)$$

(1)

where $P_0(T)$ represents the pressure at a reference temperature, $T_0$, and can be derived by the Murnaghan EoS (Birch, 1938):

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**Figure 2.** Representative XRD patterns of Al$_2$O$_3$ at high pressures and temperatures. Purple ticks: Pt; green ticks: NaCl-B2 phase; blue ticks: corundum; red ticks: Rh$_3$O$_3$(II)-type Al$_2$O$_3$; orange ticks: CaIrO$_3$-type Al$_2$O$_3$. The X-ray wavelength was 0.3344 Å.
Table 1
Thermoelastic Parameters of Corundum and Rh$_2$O$_3$(II)-Type Al$_2$O$_3$

|                | $K_{T0}$ (GPa) | $K'_{T0}$ | $V_0$ (Å$^3$) | $K_{T0}$ (GPa) | $K'_{T0}$ | $V_0$ (Å$^3$) | $\theta_D$ (K) | $\gamma_0$ | $q$ |
|----------------|----------------|------------|---------------|----------------|------------|---------------|----------------|------------|-----|
| **Corundum**   |                |            |               |                |            |               |                |            |     |
| This study     | 246(2)         | 4(fixed)   | 255.1(fixed)* |                |            |               | 1,100(fixed)   | 1.32(7)   | 0.8(4) |
| Dubrovinsky et al. (1998) | 258(2)         | 4.88(4)    | 255.05(20)    |                |            |               |                |            |     |
| Dewaele et al. (2013) | 254(8)         | 4.00(13)   | 255.45(52)    | 246(1)*        | 4(fixed)   | 255.96(19)*   |                |            |     |
| Richet et al. (1988) | 255(15)        | 5.1(9)     | 255.05(7)     | 277(3)*        | 4(fixed)   | 255.05(fixed) |                |            |     |
| d’Amour et al. (1978) | 255             | 4.23       | 255.89(12)    |                |            |               |                |            |     |
| Wang and Wu (2018)* | 249             | 3.96       | 250.13        |                |            |               |                |            |     |
| Oganov and Ono (2005)c | 253             | 4.24       | 254.57        |                |            |               |                |            |     |
| **Rh$_2$O$_3$(II)-type phase** |            |            |               |                |            |               |                |            |     |
| This study     | 256(6)         | 4(fixed)   | 165.2(7)      |                |            |               | 600(200)       | 1.47(5)   | 1(fixed) |
| Marton and Cohen (1994)* | 261             | 3.97       | 163.36        |                |            |               |                |            |     |
| Thomson et al. (1996) | 262             | 3.93       | 165.08        |                |            |               |                |            |     |
| Oganov and Ono (2005) c | 258             | 4.14       | 165.69        |                |            |               |                |            |     |

*Ambient volume of corundum from Lutterotti and Scardi (1990). *bResults obtained by reanalyzing the P-V data in the literature by recalculating the pressures using the self-consistent pressure scales of Fei et al. (2007) and Dewaele et al. (2004). *cTheoretical results.

\[
P_{T0}(V) = \frac{3}{2} K_{T0} \left[ \left( \frac{V}{V_0} \right)^{-\frac{7}{3}} - \left( \frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \cdot \left\{ 1 + \frac{3}{4} \left( K'_{T0} - 4 \right) \left( \frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right\}
\]

where $K_{T0}$ and $V_0$ are the isothermal bulk modulus and molar volumes at ambient conditions, respectively. $K'_{T0}$ is the pressure derivative of the bulk modulus and is fixed to 4 when fitting the thermal EoS. \(\Delta P_{th}(V,T)\) represents the thermal pressures and can be expressed by:

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

where $E_{th}(V,T)$ and $E_{th}(V,T_0)$ are the internal energies at $T$ and $T_0$, respectively. $\gamma$ is the Grüneisen parameter. The internal energy can be derived by:

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

where $n$ is the number of atoms in the chemical formula ($n = 5$ for both corundum and the Rh$_2$O$_3$(II)-phase), $R$ is the gas constant, and $\theta_D$ is the Debye temperature. $\gamma$ and $\theta_D$ can be described by:

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

\[
\theta_D = \theta_{D0} \exp \left( -\frac{\gamma - \gamma_0}{q} \right)
\]

where $q$ represents the volume dependence of $\gamma$. $\theta_{D0}$ and $\gamma_0$ are the Debye temperature and Grüneisen parameter at ambient conditions, respectively. The obtained thermoelastic parameters of corundum and the Rh$_2$O$_3$(II)-phase are listed in Table 1, and the fitting residuals are shown in Figure S3 in Supporting Information S1. The differential stress in our sample chamber was evaluated by the $S_t$ value of Pt ($S$ is the elastic anisotropy factor and $t$ is the uniaxial stress component) (Figure S4 in Supporting Information S1). $S_t$ varies between 0.005 and 0.005, indicating a small differential stress in our sample chamber (Shim et al., 2000).
Figure 3. Pressure-volume (per formula) relationships of Al$_2$O$_3$ at high pressures and 300 K. Blue: corundum; red: Rh$_2$O$_3$(II)-type Al$_2$O$_3$; circles: this study; upper triangles: Dewaele et al. (2013); lower triangles: d'Amour et al. (2013); hexagons: Lin et al. (2004). Circles with crosses represent pressures determined by NaCl. Pressures in Dewaele et al. (2013), Richet et al. (1988), Lin et al. (2004) and Ono et al. (2006) have been reanalyzed using self-consistent pressure scales (Dewaele et al., 2004; Fei et al., 2007).

Kato et al., 2013; Ono, 1998). The transition from the Rh$_2$O$_3$(II)-phase to CaIrO$_3$-phase observed in this study occurred at a greater pressure than that reported in Ono et al. (2006) but was in agreement with the results of Kato et al. (2013). Ono et al. (2006) first synthesized the CaIrO$_3$-phase at ∼170 GPa and 1,500–2,500 K. The back-transition to the Rh$_2$O$_3$(II)-phase was observed by decompressing the CaIrO$_3$-phase to 130 GPa and heating at 1,500 K. Since this transition is sluggish, the transition from the CaIrO$_3$-phase to Rh$_2$O$_3$(II)-phase could be easier to occur at low pressures. Although the phase boundary between the Rh$_2$O$_3$(II)-phase and the CaIrO$_3$-phase needs to be further constrained by future studies, it is more likely that CaIrO$_3$-type Al$_2$O$_3$ may not exist in the Earth’s lower mantle.

4. Discussion

4.1. Phase Transition of Al$_2$O$_3$

In this study, we observed the presence of the Rh$_2$O$_3$(II)-phase coexisting with corundum at 103 GPa above ∼2,300 K (Figure 1). Increasing the heating time to 30 min did not promote the further formation of the Rh$_2$O$_3$(II)-phase. The phase boundary between corundum and the Rh$_2$O$_3$(II)-phase with a negative Clapeyron slope of −6.5 ± 1.5 MPa/K was determined based on the relative intensity changes of the corundum 104 XRD line and the Rh$_2$O$_3$(II)-phase 211 and 021 lines in previous forward and backward experimental study (Kato et al., 2013). However, corundum was not observed to transform completely into Rh$_2$O$_3$(II)-type Al$_2$O$_3$ in the previous study, indicating a strong kinetic barrier for this phase transition (Kato et al., 2013). Here, we continued increasing the laser power at 103 GPa and 3,300 K and observed the formation of a single Rh$_2$O$_3$(II)-phase after a significant laser flash. Since the temperature cannot be well constrained during the laser flash, the P-T condition for the formation of a single Rh$_2$O$_3$(II)-phase between 104 and 119 GPa is not shown in Figure 1. On the other hand, the Rh$_2$O$_3$(II)-phase was present at a greater temperature between 103 and 135 GPa than that shown in Kato et al. (2013), which could be caused by the short heating time in this study. At 129 GPa, we heated the mixture of corundum and the Rh$_2$O$_3$(II)-phase. A single Rh$_2$O$_3$(II)-phase was formed above 2,100 K at 132 GPa (Figure 1 and Figure S5 in Supporting Information S1). In addition, we did not observe the back-transition from the Rh$_2$O$_3$(II)-phase to corundum during quenching from 3,500 to 1,200 K at pressures between 104 and 119 GPa, potentially due to our fast quench speed.

Rh$_2$O$_3$(II)-type Al$_2$O$_3$ was proposed to undergo a further phase transition to the CaIrO$_3$-phase, yet previous experimental and theoretical studies yielded conflicting results for the phase boundary (Caracas & Cohen, 2005; Kato et al., 2013; Oganov & Ono, 2005; Ono et al., 2006; Tsuchiya et al., 2005). Here, we observed the transition from the Rh$_2$O$_3$(II)-phase to the CaIrO$_3$-phase at 156 GPa and 3,700 K. To compare this with the literature results, we have reanalyzed the pressures in previous experiments using a self-consistent pressure scale of Fei et al. (2007) (Figure S5 in Supporting Information S1).

4.2. Thermal Elastic Properties of Al$_2$O$_3$

To better compare our EoS to those in previous experimental studies, we first recalculated the pressures in previous studies using self-consistent pressure scales of Fei et al. (2007) and Dewaele et al. (2004) (Dewaele & Torrent, 2013; Lin et al., 2004; Ono et al., 2006; Richet et al., 1988). The pressures in Dubrovinsky et al. (1998) and d’Amour et al. (1978) cannot be recalculated because they either did not provide the reference used for pressure determinations or the wavelength of the ruby $R_1$ luminescent line. In general, our P-V data of corundum at 300 K were in good agreement with the
results of Dawaele and Torrent (2013) but lower than other literature results obtained above 20 GPa (Figure 3; d’Amour et al., 1978; Dubrovinsky et al., 1998; Richet et al., 1988). The volume data used to constrain the EoS of corundum in this study were obtained after laser heating, which can greatly reduce the deviatoric stress inside the DACs (Richet et al., 1988). The difference in volumes between this study and Dubrovinsky et al. (1998) could be caused by the use of different pressure calibrants.

As shown in Table 2, the thermoelastic parameters of corundum are not sensitive to the variation of \( \theta_{D0} \). Varying \( \theta_{D0} \) from 500 to 1,100 K leads to a weak increase in the \( \gamma_0 \) value from 1.21 to 1.32 and does not affect the values of \( K_{T0} \) and \( q \) after considering experimental uncertainties. Using the obtained elastic parameters, we calculated the \( \rho \) and \( V_\Phi \) of corundum at 300 K up to 112 GPa (Figure 4). The obtained \( \rho \) and \( V_\Phi \) from this study at 300 K were consistent with the results of Dewaele et al. (2013). However, compared with other previous studies, our \( \rho \) is greater but \( V_\Phi \) is lower. The calculated \( \rho \) of corundum at 40 GPa using our determined elastic parameters was 1.3–2.0(4)% greater than those in the literature, and this difference increased to \( \sim 2.0–6.3(6)% \) at 112 GPa. Our \( V_\Phi \) was \( \sim 2.1–4.2(5)% \) lower than those in previous studies (d’Amour et al., 1978; Dewaele & Torrent, 2013; Dubrovinsky et al., 1998; Richet et al., 1988). Modeling \( \rho \) and \( V_\Phi \) at relevant P-T conditions of the mantle further showed that elevating the temperature by 500 K led to a 0.6–1.3(2)% reduction in \( \rho \) and a 0.6–1.8(3)% reduction in \( V_\Phi \) between 5 and 95 GPa (Figure 5).

Here, we provide the first experimental constraints on the thermoelastic parameters of Rh\( _2 \)O\( _3 \)(II)-type Al\( \text{2} \)O\( \text{3} \) (Figure 3, Tables 1 and 3). For the Rh\( _2 \)O\( _3 \)(II)-phase, the Gr"uneisen parameter, \( \gamma_0 \), exhibited a strong dependence on the \( q \) value (Table 3). Varying \( q \) from 0.6 to 2.2 caused a 4(1)% increase in \( K_{T0} \) but a 0.8(2)% reduction in \( V_\Phi \), whereas it had a negligible influence on the Debye temperature, \( \theta_{D0} \). \( \rho \) and \( V_\Phi \) of the Rh\( _2 \)O\( _3 \)(II)-phase modeled at 300 K using the derived elastic parameters were in general agreement with the theoretical predictions, although the theoretical calculations were performed at 0 K (Figure S6 in Supporting Information S1; Marton & Cohen, 1994; Oganov & Ono, 2005; Thomson et al., 1996). At the bottom lower mantle, varying the temperature by 500 K led to a 0.5(3)% changes in both \( \rho \) and \( V_\Phi \) of the Rh\( _2 \)O\( _3 \)(II)-phase. Furthermore, we modeled the \( \rho \) and \( V_\Phi \) profiles of Al\( \text{2} \)O\( \text{3} \) along different geotherms using the thermoelastic parameters of corundum and the Rh\( _2 \)O\( _3 \)(II)-phase. Compared with the results of Dubrovinsky et al. (1998) along a normal mantle geotherm, our corundum had a 2.0(3)% higher \( \rho \) but a 3.0(6)% lower \( V_\Phi \) at 100 GPa. Our modeling results showed that the phase transition from corundum to the Rh\( _2 \)O\( _3 \)(II)-phase caused a sudden 1.9(4)% increase in \( \rho \) but a 0.6(5)% decrease in \( V_\Phi \).
Temperature had a negligible effect on $\rho$ and $V_\Phi$ changes across this phase transition.

5. Geophysical Implications

$\text{Al}_2\text{O}_3$ is one of the major components of the anorthositic crust once this old crust was subducted into the Earth’s deep mantle. To decipher the fate of anorthositic crust which was proposed to once exist on the Earth’s surface, we have modeled the $\rho$ and $V_\Phi$ profiles of anorthositic crust from 10 to 120 GPa along different mantle geotherms using the obtained thermal EoS of $\text{Al}_2\text{O}_3$ and literature results (Figure 7 and Figures S7, S8 in Supporting Information S1). The phase diagram of anorthosite has been well studied by (Figure 6). Temperature had a negligible effect on $\rho$ and $V_\Phi$ changes across this phase transition.

### Table 3

|                      | Model 1 | Model 2 | Model 3 | Model 4 | Model 5 |
|----------------------|---------|---------|---------|---------|---------|
| $K_{T0}$ (GPa)       | 253(6)  | 256(6)  | 259(6)  | 262(6)  | 262(6)  |
| $K_{T0}'$            | 4(fixed)| 4(fixed)| 4(fixed)| 4(fixed)| 4(fixed)|
| $V_0$ ($\text{Å}^3$) | 165.5(7)| 165.2(7)| 164.8(7)| 164.5(6)| 164.2(6)|
| $\theta_{D0}$ (K)    | 600(200)| 600(200)| 600(200)| 600(200)| 500(200)|
| $\gamma_0$          | 1.33(5) | 1.47(5) | 1.62(6) | 1.79(7) | 1.97(7) |
| $q$                  | 0.6(fixed)| 1(fixed)| 1.4(fixed)| 1.8(fixed)| 2.2(fixed)|

**Corundum**

- **a. $\Delta \rho/\rho$**
  - $0.8\%$
  - $-0.4\%$

- **b. $\Delta V_\Phi/V_\Phi$**
  - $0$
  - $0$

**Rh$_2$O$_3$(II)**

- **c. $\Delta \rho/\rho$**
  - $0.4\%$
  - $-0.4\%$
  - $-0.2\%$

- **d. $\Delta V_\Phi/V_\Phi$**
  - $0$
  - $0$
  - $0$

*Figure 5.* Influence of temperature on the $\rho$ and $V_\Phi$ of corundum (a and b) and Rh$_2$O$_3$(II)-type Al$_2$O$_3$ (c and d), respectively. $\rho$ and $V_\Phi$ of corundum (Rh$_2$O$_3$(II)-type Al$_2$O$_3$) at high pressures along a normal mantle geotherm were used as the reference. The contour shows the change in $\rho$ ($V_\Phi$) by varying temperature or pressure relative to the $\rho$ ($V_\Phi$) of corundum (Rh$_2$O$_3$(II)-type Al$_2$O$_3$). Here, $\Delta \rho/\rho = (\rho_{P,T} - \rho_{P,MT})/\rho_{P,MT} \times 100\%$, where $\rho_{P,MT}$ is the density of corundum (Rh$_2$O$_3$(II)-type Al$_2$O$_3$) along a normal mantle geotherm. $\Delta V_\Phi/V_\Phi = (V_\Phi(P,T) - V_\Phi(P,MT))/V_\Phi(P,MT) \times 100\%$, where $V_\Phi(P,MT)$ is the bulk sound velocity of corundum (Rh$_2$O$_3$(II)-type Al$_2$O$_3$) along a normal mantle geotherm.
Figure 6. Influence of the transition from corundum to the Rh$_3$O$_7$(II)-phase on the $\rho$ and $V_\phi$ of Al$_2$O$_3$ at high pressures and temperatures. Solid line: corundum and Rh$_3$O$_7$(II)-phase from this study; dashed line: corundum from Dubrovinsky et al. (1998); red: along a normal mantle geotherm (Brown & Shankland, 1981); orange: along a 500-K colder slab geotherm; blue: along a 1,000-K colder slab geotherm; vertical ticks: calculation error bars.

In contrast to previous large-volume press and DAC experiments (Nishi et al., 2018). Here, we followed the phase diagram in the literature by considering changes in the proportions of each phase at high pressures and temperatures (Akaogi et al., 2009; Nishi et al., 2018). The thermoelastic parameters of the minerals used for modeling are listed in Table S3 in Supporting Information S1. We first calculated $\rho$ and $V_\phi$ of individual phase at high P-T conditions. For a multiphase assemblage, the density and bulk modulus were computed following (Cottaar et al., 2014):}

$$\rho = \sum \rho_i V_i$$

$$M = \frac{1}{2} \left[ \sum V_i M_i + \left( \sum V_i M_i^{-1} \right)^{-1} \right]$$

where $V_i, \rho_i$, and $M_i$ are the volume percentage, density, and bulk modulus of the $i$th phase, respectively. $V_\phi$ of a multiphase assemblage was computed with:

$$K_S = (1 + \alpha T) K_T$$

$$V_\phi = \sqrt{\frac{K_S}{\rho}}$$

where $K_S$ is the adiabatic bulk modulus, $K_T$ is the isothermal modulus, $\alpha$ is the thermal expansion coefficient, and $\gamma$ is the Grüneisen parameter.

In general, our $\rho$ modeled along a normal mantle geotherm was $\sim 0.6(3)$% lower than the modeling results of Nishi et al. (2018) at pressures less than 24 GPa but became $\sim 0.8$–1.5(4)% greater above 24 GPa (Figure S9 in Supporting Information S1). The difference in $\rho$ between our model and the work of Nishi et al. (2018) should be caused by the use of different thermal EoS parameters for mantle minerals (Table S3 in Supporting Information S1). In the transition zone, garnet in anorthosite is formed by a solid solution of 54 mol % grossular, 33 mol % pyrope, and 13 mol % almandine (Nishi et al., 2018). Here, the thermoelastic parameters of garnet were calculated following the method used in a previous study (Wei et al., 2021). In contrast, Nishi et al. (2018) used the thermoelastic parameters of majorite to represent garnet. In the lower mantle, the thermal EoS parameters of davemaite (CaSiO$_3$ perovskite, Ca-Pv), bridgmanite, and calcium ferrite-type phase (CF phase) were from the most recent experimental results, which contributed to the difference in $\rho$ between our modeling results and Nishi et al. (2018) (Sueda et al., 2009; Sun et al., 2016, 2018). More importantly, we have considered the influence of Fe on the thermoelastic parameters of bridgmanite in the lower mantle (Sun et al., 2016, 2018). Furthermore, the transition from corundum to the Rh$_3$O$_7$(II)-phase was shown to produce a $\sim 2$% jump in $\rho$ at $\sim 88$ GPa (2,000-km depth; Nishi et al., 2018). However, $\rho$ of anorthositic crust calculated using our obtained thermal EoS has shown that this phase transition should occur at $\sim 103$ GPa and has a negligible influence on the $\rho$ of anorthosite. The effect of the transition from corundum to the Rh$_3$O$_7$(II)-phase on the density profile of anorthositic crust should be overestimated in the previous study (Nishi et al., 2018).

At 10 GPa, anorthosite, mainly composed of garnet, CaAl$_2$Si$_2$O$_8$-rich phase (CAS) and stishovite, has a density $10.4(2)$% greater than that of the pyrolitic mantle, but the difference in $\rho$ between these two compositions decreases to 3.0(2)% at 23 GPa due to the phase transition of olivine polymorphs in the transition zone in the pyrolitic mantle (Akaogi et al., 2009; Nishi et al., 2018). Our modeling further revealed that although both anorthositic crust and the subducted oceanic crust are denser than the pyrolitic mantle up to the bottom transition zone, $V_\phi$ of anorthositic crust is $3.4$–$15.8(4)$% greater than that of the pyrolitic mantle, in contrast to the subducted oceanic crust which has a $V_\phi$ lower than that of the pyrolitic mantle in the bottom transition zone between 520 and 660 km depth (Irifune & Ringwood, 1993; Ricolleau et al., 2010). It indicates that the primordial anorthositic crust could descend at least to the bottom of the transition zone with a $V_\phi$ greater than that of the normal mantle (Figure 7; Nishi et al., 2018). At the topmost lower mantle, anorthositic crust becomes less dense than the pyrolitic mantle, which could lead to the stagnation of anorthositic crust at this depth, although previous study proposed that
anorthositic crust may subduct to the lower mantle by strong mantle vertical downflow or coupling with dense KREEP basalt (Nishi et al., 2018).

Figure 7. Modeled $\rho$ and $V_\Phi$ of anorthosite, pyrolitic mantle and MORB. Red line: anorthosite along a normal mantle geotherm (Brown & Shankland, 1981); orange line: anorthosite 500 K colder than the normal mantle; blue line: anorthosite 1000 K colder than the normal mantle; black line: pyrolitic mantle; gray line: MORB. The blue region represents depths above 660 km, while the orange region indicates depths below 660 km. Error bars are added as the vertical ticks on the right.

Subduction of anorthositic crust together with MORB to the lower mantle can only occur when it is at least 500–1,000 K colder than the normal mantle (Figure 7). In this case, CAS is no longer stable, and anorthosite is mainly composed of garnet, kyanite, corundum and stishovite at 10 GPa (Akaogi et al., 2009; Nishi et al., 2018). Along a slab geotherm 500 K colder than the normal mantle, further increasing the pressure to 14 GPa can lead to the decomposition of kyanite into corundum and stishovite (Akaogi et al., 2009; Nishi et al., 2018). Due to the different mineralogical composition, anorthositic crust along this cold slab geotherm would have a $\rho$ indistinguishable from that of the anorthositic crust along a normal mantle geotherm and a lower $V_\Phi$ up to the bottom transition zone. Compared to the pyrolitic mantle, $\rho$ and $V_\Phi$ of the anorthositic crust along the cold slab geotherm are 10.3(2)% and 12.5(4)% greater than those of the pyrolitic mantle at 10 GPa, respectively, but the difference in $\rho$ and $V_\Phi$ between the anorthositic crust and the pyrolitic mantle decrease to 2.3(2)% and 2.2(4)% at the bottom transition zone, respectively. As with the subducted oceanic crust, anorthositic crust becomes less dense than the
surrounding mantle when ringwoodite and majoritic garnet in the pyrolitic mantle transformed into lower-mantle minerals. However, once garnet in anorthosite completes the transition into dawsonite and bridgmanite, \( \rho \) and \( V_p \) of anorthositic crust will be 3.4(2)% and 5.3(4)% greater than those of the surrounding mantle, respectively. This suggests that the anorthositic crust along a cold slab geotherm could accumulate around 660 km to form a “megatholith” of sufficient thickness like the subducted oceanic crust but could finally descend to the lower mantle (Hirose et al., 1999).

However, the difference in \( \rho \) between the normal mantle and anorthositic crust along this 500-K colder slab geotherm gradually decreases with increasing depth in the lower mantle. As a result, the anorthositic crust cannot penetrate the lower mantle at depths greater than 1,900 km (84 GPa; Figure 7). Sinking of the anorthositic crust to the bottom lower mantle can occur unless it is 1,000 K colder than the surrounding mantle. Here, our modeling has shown that the transition from corundum to the Rh\(_3\)O\(_3\)(II)-phase in anorthosite can lead to a 0.6(2)% increase in \( \rho \) at 107 GPa (2,400-km depth) along a 1,000-K colder slab geotherm. This phase transition can further promote the sinking of anorthositic crust to the bottom lower mantle. Meanwhile, the cold anorthositic crust in the lower mantle has a greater \( V_p \) than the pyrolitic mantle. Its \( V_p \) along a 500-K colder slab geotherm is 1.5–5.3(4)% greater than that of the pyrolitic mantle at a depth of 660–1,400 km. The difference in \( V_p \) between the anorthositic crust and the pyrolitic mantle slightly decreases to 0.9(4)% due to the transition from stishovite to the CaCl\(_2\)-type SiO\(_2\) in anorthosite at a depth of 1,500 km but could be as large as 3.3(4)% at a 2,200 km depth due to the spin transition of ferropericlase in the pyrolitic mantle. The \( V_p \) of anorthositic crust along a 1,000-K colder slab geotherm will be 2.2–4.4(4)% greater than that of the pyrolic mantle in the lower mantle.

### 6. Conclusion

In summary, we have determined the thermal EoS of corundum and Rh\(_3\)O\(_3\)(II)-type Al\(_2\)O\(_3\) using synchrotron XRD up to 153 GPa and 3,400 K in laser-heated DACs. Due to the strong kinetic barriers across the transition from corundum to the Rh\(_3\)O\(_3\)(II)-type Al\(_2\)O\(_3\), we observed the coexistence of Rh\(_3\)O\(_3\)(II)-type Al\(_2\)O\(_3\) with corundum at 106 GPa and 2,300 K. The Rh\(_3\)O\(_3\)(II)-type Al\(_2\)O\(_3\) further transformed into the CaO\(_2\)-type phase at 156 GPa and 3,700 K. Using our obtained thermal EoS of corundum and Rh\(_3\)O\(_3\)(II)-type Al\(_2\)O\(_3\) together with the literature results, we further modeled the \( \rho \) and \( V_p \) profiles of the anorthositic crust from 10 to 120 GPa along different mantle geotherms. Along a normal mantle geotherm, anorthositic crust is denser than the pyrolitic mantle up to 660 km and has a greater \( V_p \), whereas it would be buoyant at the topmost lower mantle because of the post-spinel transformation in the pyrolitic mantle. Sinking of the anorthositic crust to the lower mantle will only occur when its temperature is 500–1,000 K lower than that of the surrounding mantle. Once the phase transition of garnet completes in the anorthositic crust, the cold anorthositic crust with a greater \( V_p \) value can sink to a depth of 2,100 km in the lower mantle along a 500-K colder slab geotherm or even to the bottom lower mantle along a 1,000-K colder slab geotherm.

### Data Availability Statement

Data used to generate the figures seen in this report can be found in the online supporting information. They can also be downloaded online (from https://zenodo.org/record/5771198).

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