

Phase relations in the system MgSiO_3 - Al_2O_3 up to 2300 K at lower-mantle pressures

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Key Points:

- Phase relations in the system MgSiO_3 - Al_2O_3 were determined at temperatures up to 2300 K and pressures up to 45 GPa.
- The solubility of Al_2O_3 in bridgmanite and that of MgSiO_3 in corundum increase with increasing temperature.
- The Al_2O_3 cannot be fully accommodated in the coldest parts of subducted slabs in the shallow part of the lower mantle.

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Abstract

Phase relations in the system $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ were investigated at pressures of 27–45 GPa and temperatures of 1700, 2000 and 2300 K using sintered diamond and tungsten carbide anvils in a multi-anvil apparatus. The bulk compositions in the $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ binary system crystallize a phase assemblage of pyrope and corundum at pressures below 27 GPa and an assemblage of bridgmanite and corundum at pressures above 27 GPa regardless of temperatures. The solubility of Al_2O_3 in bridgmanite and that of MgSiO_3 in corundum increase significantly with increasing temperature. The solubility of Al_2O_3 in bridgmanite increases from 6.7 mol% at 1700 K to 21.8 mol% at 2500 K under a constant pressure of 27 GPa. Bridgmanite becomes more aluminous with increasing pressure from 27 to 45 GPa at a given temperature. The MgSiO_3 content in corundum increases with increasing pressure at pressure lower than 27 GPa, while it decrease at pressure higher than 27 GPa. Our results suggest that bridgmanite can incorporate a considerably higher Al_2O_3 content than that of the pyrope composition (25 mol% Al_2O_3). The present study further suggests that the entire Al_2O_3 component is accommodated into bridgmanite in the pyrolite lower mantle. However, Al_2O_3 cannot be fully accommodated into bridgmanite in the coldest parts of subducted slabs in the shallow part of the lower mantle, and therefore additional phases such as MgAl_2O_4 with calcium ferrite-type structure are necessary to host the excess Al_2O_3 .

Keywords: phase relations, bridgmanite, Al_2O_3 , subducted slabs, lower mantle

1. Introduction

Al_2O_3 is the fourth most abundant component in the Earth's mantle [Ringwood, 1975; MacDough and Sun, 1995]. It has been put in the spotlight because of its importance for understanding the mineralogy of the Earth's mantle. Al_2O_3 makes up about 4 wt% in the pyrolite mantle [Sun, 1982] and as much as about 16 wt% in the mid-oceanic ridge basalt (MORB) layers in subducted slabs [Green *et al.*, 1979]. From the upper mantle to the transition zone, Al_2O_3 is primarily accommodated into garnet solid solutions in both pyrolite and MORB compositions [Ringwood, 1967; Irifune, 1987]. Under lower-mantle conditions, the entire Al_2O_3 can be incorporated into bridgmanite, the most abundant mineral in the Earth's mantle, in the pyrolite composition [Irifune, 1994]. On the other hand, bridgmanite cannot accommodate all Al_2O_3 in the MORB composition, and some Al_2O_3 may be accommodated in several Al-rich phases in addition to bridgmanite. [e.g., Irifune and Ringwood, 1993; Ono *et al.*, 2001; Hirose and Fei, 2002]. Moreover, the incorporation of Al_2O_3 can greatly change the crystal chemistry of bridgmanite [e.g., McCammon, 1997]; and thereby significantly affect its physical properties such as elastic properties [Zhang and Weidner, 1999; Brodholt, 2000] and electrical conductivity [Xu *et al.*, 1998]. Therefore, knowledge about the Al_2O_3 effects on the crystal chemistry of bridgmanite is of great significance in mineral physics and geophysics, and is seminal for understanding the mineralogy of the lower mantle.

To understand the Al_2O_3 solubility in bridgmanite better, phase relations in the system $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ have been studied extensively at pressure below 27 GPa [Irifune *et al.*, 1996; Kubo and Akaogi, 2000; Hirose *et al.*, 2001; Akaogi *et al.*, 2002]. These studies suggested that bridgmanite coexists with corundum in this system at pressures above 26 GPa. Recently, Liu *et al.* [2016] demonstrated that the Al_2O_3 solubility in bridgmanite increases from 12 to 29 mol% with increasing pressure from 27 to 52 GPa at a temperature of 2000 K. The pressure dependence at a given temperature, therefore, is now clear, however, the temperature

dependence of the Al_2O_3 incorporation in bridgmanite is still poorly constrained. Irifune *et al.* [1996] suggested that it increases from 11 mol% at 1760 K to 17 mol% at 2030 K at a pressure of 27 GPa, whereas Kubo and Akaogi [2000] experiments showed an increase from 8 to 13 mol% with increasing temperature from 1670 to 2170 K at almost the same pressure. Therefore, these two studies disagree significantly. Moreover, these studies were conducted only at the lowest pressure conditions for the bridgmanite and corundum coexistence, and no studies have reported the temperature effect on the Al_2O_3 solubility in bridgmanite at higher pressures. Temperatures in the subducted slabs should be significantly lower than in the surrounding mantle, but should approach that of the surrounding mantle due to thermal equilibration [e.g., Ringwood, 1991; Irifune and Ringwood, 1993; Kirby *et al.*, 1996]. Consequently, the temperature effects are vital to constrain the slab dynamics. Nevertheless, our limited knowledge about the temperature dependence of the Al_2O_3 solubility in bridgmanite prevents us from understanding the mineralogy in the deep subducted slabs.

The reason for our limited knowledge about the temperature dependence of the Al_2O_3 solubility in bridgmanite is the technical difficulty in high-pressure and high-temperature experiments. Although use of the multi-anvil technique is desired for the determination of phase transitions in multiple-component systems, the pressure ranges of conventional multi-anvil presses are restricted to 27 GPa at high temperatures due to the limited hardness of tungsten carbide (WC) anvils. However, recent development of high-pressure and high-temperature technology using sintered-diamond (SD) anvils in conjunction with *in situ* synchrotron X-ray diffraction observations allows generation of accurate pressures up to 50 GPa routinely at high temperature [Tange *et al.*, 2008; Liu *et al.*, 2016]. By utilizing these techniques, we have investigated phase relations in the system MgSiO_3 – Al_2O_3 at temperatures up to 2300 K and pressures up to 45 GPa. Based on our new results, the Al_2O_3 solubility in bridgmanite and the host phases of Al_2O_3 in the lower mantle are discussed.

2. Experimental methods

A fine-grained oxide mixture of composition En₅₀Cor₅₀ (En: MgSiO₃, Cor: Al₂O₃; the number represents mol%, oxide grain size: 50 nm) and En₇₅Cor₂₅ glass (pyrope composition, hereafter denoted as pyropic glass) along the MgSiO₃–Al₂O₃ join are used as starting materials. Detailed chemical compositions of those two starting materials were reported in Liu *et al.* [2016] and also examined using an electron probe microanalyzer in the present study (see Table S1 in supporting information). The starting materials were put into graphite or platinum capsules and then heated at 800 K for one hour to purge water, and finally put into the cell assembly for the high-pressure and high-temperature experiments.

In situ X-ray diffraction (XRD) experiments were performed at pressures of 32–49 GPa at temperatures of 1700 and 2000 K using SD anvils with 1.5 mm truncation as second-stage anvils in a DIA-type multi-anvil apparatus at the synchrotron radiation facility, SPring-8 (SPEED-Mk. II). The experimental facility for *in situ* XRD measurements was described by Katsura *et al.* [2004], and the ultrahigh pressure cell assembly was identical to that of Tange *et al.* [2009], as also shown in **Figure 1**. Pressures were determined based on the *P*–*V*–*T* equation of state of Au proposed by Tsuchiya [2003]. General relations between the generated pressure and the press load at temperatures of 300, 1700 and 2000 K are shown in **Figure 2a**. Uncertainties in pressure determination in these *in situ* experiments are approximately ± 0.2 GPa. Sample temperatures were measured with a W₉₇Re₃–W₇₅Re₂₅ thermocouple, whose hot junction was placed on the bottom of the sample capsule. The sample was compressed to the target pressure and then heated at the target temperature for 3–5 hours. *In situ* XRD patterns were collected for 3–5 hours at the target pressure and temperature. Then, the run was quenched by turning off the electronic power, and the pressure was released slowly over several hours. Finally, *in situ* XRD patterns of the quenched samples were collected under ambient conditions for one hour.

We also conducted high-pressure quench experiments at the Bayerisches Geoinstitut, University of Bayreuth, Germany. Runs at pressures below 25 GPa were conducted using WC anvils with a 10.0 mm octahedral pressure medium and 4.0 mm anvil truncation in a 12-MN multi-anvil press with a split-sphere guide block (Sumitomo 1200-ton) [Keppler and Frost, 2005]. One run conducted at a pressure of 35 GPa and a temperature of 2300 K was also performed using WC anvils with 1.5 mm truncation with this press. This pressure at 2300 K was estimated from the FeO content in bridgmanite [Tange *et al.*, 2009], in equilibrium with magnesiowüstite and stishovite, using synthetic $(\text{Mg}_{0.7}\text{Fe}_{0.3})\text{SiO}_3$ pyroxene as a starting material (see Text S1 and Figure S1 in supporting information for pressure calibration details). Runs at pressures above 25 GPa were performed using a 7 and 5.7 mm pressure medium and 3 and 1.5 mm truncation, respectively, in a 15-MN press with a DIA-type guide block system (IRIS-15) [Ishii *et al.*, 2016]. **Figure 2b** shows the relationships between pressures and press loads at temperatures of 1700 and 2000 K for IRIS-15, which were calibrated using decomposition of pyrope into aluminous bridgmanite and corundum [Hirose *et al.*, 2001] and the Al_2O_3 solubility in bridgmanite [Liu *et al.*, 2016]. Pressure uncertainties of these quench experiments were on the order of ± 0.5 GPa.

Recovered samples were mounted in epoxy resin, ground to expose the central portion, and then polished using 0.25 μm diamond paste. Phases present in the quench runs were identified using a micro-focused X-ray diffractometer (XRD, Bruker, D8 DISCOVER) equipped with a two-dimensional solid state detector (VANTEC500) and a micro-focus source ($I\mu\text{S}$) with $\text{Co-K}\alpha$ radiation operated at 40 kV and 500 μA . The X-ray beams were focused to 50 μm using a IFG polycapillary X-ray mini-lens. Textural observation was performed using a LEO1530 scanning electron microscope (SEM) operating at an acceleration voltage of 15–20 kV and a beam current of 10 nA. Chemical compositions of each phase present in the quench runs were determined using a JEOL JXA-8200 electron probe microanalyzer (EPMA) operating at

acceleration voltages of 10 or 15 kV and a beam current of 5 nA with standards of enstatite for Mg and Si, and pyrope for Al.

3. Results

Experimental conditions and phases present in the recovered samples are listed in **Table 1**. At pressures below 25 GPa under temperatures of 1700 and 2300 K, the starting material of En₅₀Cor₅₀ transforms into pyrope and corundum (see Figure S2 in supporting information), and these corundum can contain significant amounts of the MgSiO₃ component (see Table S2 in supporting information). The MgSiO₃ solubility in corundum increases with increasing pressure and temperature, e.g., 7.9 ± 0.4 mol% at 20 GPa to 12.6 ± 0.6 mol% at 25 GPa under a temperature of 1700 K and 12.6 ± 0.6 mol% at 1700 K to 26.7 ± 0.7 mol% at 2300 K under a pressure of 25 GPa.

Figure 3a shows representative back-scattered electron images of the quenched samples for En₅₀Cor₅₀ oxide mixture and pyropic glass at a pressure of 27 GPa and at temperatures of 1700 and 2500 K, respectively. The corresponding XRD profiles in **Figure 3b** and Figure S2 (see supporting information) of these run products are consistent with the presence of a mixture of bridgmanite and corundum. As shown in **Table 2**, the chemical compositions of phases in the recovered samples using these two different starting materials are identical within analytical uncertainties, implying that chemical equilibrium was achieved under these conditions.

Figure 4 illustrates the solubility of Al₂O₃ in bridgmanite and that of MgSiO₃ in corundum, respectively, as a function of temperatures at a constant pressure of 27 GPa as determined in the present and previous studies [Irifune *et al.*, 1996; Kubo and Akaogi, 2000; Akaogi *et al.*, 2002; Liu *et al.*, 2016]. The Al₂O₃ solubility in bridgmanite apparently increases linearly with temperature (**Figure 4a**), and this tendency is similar to that for FeO in bridgmanite reported by Fei *et al.* [1996]. In the present study, the Al₂O₃ solubility in bridgmanite reaches 21.7 ± 0.6

mol% at 2500 K. The best fit of all the experimental data to a linear function yields the relation of $X_{\text{Al}_2\text{O}_3} = -0.19 \pm 2 + 1.60 \pm 1 \cdot 10^{-5} \cdot T$, where $X_{\text{Al}_2\text{O}_3}$ is the Al_2O_3 solubility in mole percent in bridgmanite at a pressure of 27 GPa, T is the temperature in Kelvin and the number in parentheses represents standard deviations for the last digit. This equation suggests that bridgmanite with a pyrope composition, i.e., with 25 mol% Al_2O_3 , could form at a temperature of approximately 2750 K at this pressure. **Figure 4b** demonstrates that the MgSiO_3 solubility in corundum also increases with increasing temperature at 27 GPa, and reaches as much as 38.0 ± 0.5 mol% at 2500 K in the present study. The values for corundum reported by Irfune *et al.* [1996] and Kubo and Akaogi [2000] are, however, larger than those in the present study at given the same temperature. One possible reason for this discrepancy may be related to the low resolution of the EPMA due to the small grain sizes of corundum and bridgmanite obtained in earlier studies. The grain size of phases in the runs at 27 GPa in our study is considerably larger than 3 μm in **Figure 3**, the composition is thus accurate due to the grain size is larger than the resolution of the EPMA.

Figure 5 shows selected back-scattered electron images of the quenched samples for the $\text{En}_{50}\text{Cor}_{50}$ oxide mixture and pyropic glass at pressures higher than 27 GPa. Aluminous bridgmanite, corundum, and Au pressure markers are found in these *in situ* runs. **Figure 6a** shows *in situ* synchrotron XRD patterns for $\text{En}_{50}\text{Cor}_{50}$ under 31.9–48.5 GPa at 1700 K. In all XRD patterns, the major peaks are assigned to bridgmanite, corundum, and Au, while the other minor ones can be assigned to stishovite, surrounding diamond capsules, and MgO disks. For the product recovered from the run at 48.5 GPa and 1700 K for two hours, the element mapping by means of analytical transmission electron microscopy (ATEM) reported in Figure S3 further confirms that bridgmanite, corundum and trace amount of stishovite coexist in this sample. However, the TEM mapping combined with energy dispersive X-ray spectroscopy (EDXS) suggest the compositions of these phases are not homogeneous, which may be caused by the

unreached chemical equilibrium due to the short heating time as a result of the instability of the heater in this run (Text S2). **Figure 6b** shows the XRD pattern of the S6615 run. It is found that perovskite with a LiNbO_3 structure with a rhombohedral symmetry coexists with corundum at 35 GPa and 2300 K. EPMA analysis on this LiNbO_3 structure demonstrate that it contains 27.3 ± 0.3 mol% of Al_2O_3 . Its lattice parameters ($a = b = 4.849$ (1); $c = 12.712$ (10)) are slightly higher than those ($a = b = 4.783$ (2); $c = 12.680$ (11)) for the same phase with the pyrope composition obtained by Liu *et al.* [2016], which can be explained by a higher Al_2O_3 content in the present study than that of the latter study. The present result further confirms that bridgmanite with the Al_2O_3 content higher than 25 mol% would transform into the LiNbO_3 structure upon releasing pressure, which is consistent with the result of earlier works [Funamori *et al.*, 1997; Miyajima *et al.*, 1999; Liu *et al.*, 2016; Ishii *et al.*, 2017]. However, Liu *et al.* [2016] also found that the bridgmanite phase containing 29.5 mol% exists in the M1677 run, and this difference may be caused by the effect of nanoscale grain size with a higher surface energy as suggested by Liu *et al.* [2016].

Two experiments were performed using the pyropic glass as the starting material at pressures of 42.3 and 44.5 GPa and at temperatures of 2000 and 1700 K, respectively (**Figure 6c**). *In situ* XRD observations suggest that the phases present in these runs are bridgmanite and corundum. In particular, a trace amount of corundum coexists with bridgmanite at 42.3 GPa and 2000 K, which is also confirmed by the back-scattered electron observations in **Figure 5d**. Composition analysis on several large grains (3 μm) suggests that bridgmanite in this recovered sample contains 21.9 ± 0.6 mol% Al_2O_3 . These results suggest that bridgmanite with the pyrope composition should form at a slightly higher pressure than 42.3 GPa, providing more convincing evidence that the Al_2O_3 solubility exceeds 25 mol% above 45 GPa at 2000 K [Liu *et al.*, 2016]. The composition of bridgmanite in M1677 run (51.8 GPa and 2000 K) in Liu *et al.* [2016] was estimated based on relations between unit-lattice parameters and Al_2O_3 contents.

Here, instead, we determined the accurate compositions of the phases in M1677 run by adjusting the EPMA analytical beam-size to 1 μm , and found that the Al_2O_3 content in bridgmanite is 29.5 ± 0.7 mol%, in excellent agreement with that (29 ± 5 mol%) estimated from its unit-cell lattice parameters. Therefore, for the sample at 44.5 GPa and 1700 K, since the grain size of this run product is smaller than 1 μm , the Al_2O_3 content in bridgmanite has been estimated to be approximately 16 ± 3 mol% from its unit-cell lattice parameters (see Table S3 in supporting information) [Liu *et al.*, 2016].

The lattice parameters and molar volume of aluminous bridgmanite and corundum in the present and previous studies [D'Amour *et al.*, 1978; Weng *et al.*, 1981; Ito *et al.*, 1978, 1998; Irfune *et al.*, 1996; Kubo and Akaogi, 2000; Yagi *et al.*, 2004; Walter *et al.*, 2004; Liu *et al.*, 2016] are shown as a function of the Al_2O_3 and MgSiO_3 content, respectively, in **Figure 7**. It is clearly seen that the value of a , b , and c -axis of aluminous bridgmanite increases almost linearly with increasing Al_2O_3 content within analytical uncertainties in **Figure 7a**. A linear function is adapted to the present data and those of Liu *et al.* [2016], and got the following equations:

$$a = 4.777 (\pm 0.001) + 0.014 (\pm 0.007) \times \chi_{\text{Al}_2\text{O}_3}$$

$$b = 4.928 (\pm 0.002) + 0.109 (\pm 0.011) \times \chi_{\text{Al}_2\text{O}_3}$$

$$c = 6.900 (\pm 0.002) + 0.236 (\pm 0.012) \times \chi_{\text{Al}_2\text{O}_3}$$

where $\chi_{\text{Al}_2\text{O}_3}$ represents the mole fraction of the Al_2O_3 in bridgmanite ($0 \leq \chi_{\text{Al}_2\text{O}_3} < 0.30$). These equations agree well with those obtained in Irfune *et al.* [1996] except that the slope for the change in lattice parameters with the Al_2O_3 content is slightly smaller than that obtained in the latter study. The same equation to corundum produces following results (**Figure 7b**):

$$a = b = 4.764 (2) + 0.023(9) \times \chi_{\text{MgSiO}_3}$$

$$c = 12.991 (6) + 0.136 (3) \times \chi_{\text{MgSiO}_3}$$

where χ_{MgSiO_3} represents the mole fraction of the MgSiO_3 in bridgmanite ($0 \leq \chi_{\text{MgSiO}_3} < 0.4$).

The molar volume of bridgmanite increases almost linearly with increasing Al_2O_3 contents (**Figure 7c**), and can be best expressed as $V(x) = 1.35 (8) \cdot x + 24.468 (12)$, where x is the mole fraction of Al_2O_3 ($0 \leq x < 0.3$), and the number in parentheses represents standard deviations for the last digit. It can be also seen in **Figure 7d** that the molar volume of corundum increases slightly with increasing MgSiO_3 contents, expressed as $V(x) = 0.52 (12) \cdot x + 38.47 (3)$, where x is the mole fraction of MgSiO_3 ($0 \leq x < 0.4$). The effect of MgSiO_3 contents on the volume of corundum is significantly smaller than that of Al_2O_3 for bridgmanite.

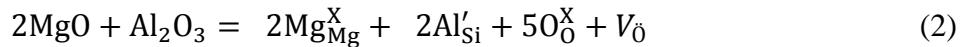
Discussion

4.1 Al substitution mechanism in bridgmanite

It is thought that Al is incorporated into the crystal structure of bridgmanite through two types of possible substitution mechanisms [Hirsch and Shankland, 1991; Richmond and Brodholt, 1998; Navrotsky *et al.*, 1999, 2003; Andrault *et al.*, 2007]: (1) the charge-coupled substitution: substituting of Mg and Si by Al,



(2) the oxygen vacancy substitution: substitution of Al into the Si site and creating an oxygen vacancy,



where subscripts indicate the site and superscripts indicate the charge (X) for neutral, (') for negative charge, (·) for a positive charge (point defect notation from Kröger and Vink [1956]).

Figure 8a shows the cation ratio between Mg and Si (Mg/Si) as a function of the Al pfu in aluminous bridgmanite in the present study and previous works [Irifune *et al.*, 1996; Kubo and

Akaogi, 2000; Liu et al., 2016]. This ratio is mainly along the trend line for the charge-coupled substitution within the analytical uncertainties, while it is far below the trend line of the oxygen vacancy substitution, suggesting the charge-coupled substitution dominates in the aluminous bridgmanite. This result is well consistent with some earlier experimental works on aluminous bridgmanite [Stebbins *et al.*, 2001; Walter *et al.*, 2006]. **Figure 8b** further supports this idea due to the value of Si cation in the bridgmanite is almost along the trend line for the charge-coupled substitution. However, XRD patterns in such as **Figure 3** and **6** demonstrate that trace stishovite coexisted with bridgmanite in some runs, suggesting that trace amounts of the oxygen vacancy substitution may also occurs in the aluminous bridgmanite.

4.2 Phase diagram in the $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ system

Figure 9 shows the phase diagram of the garnet-corundum-bridgmanite transition in the system $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ at pressures of 20–45 GPa and at temperatures of 1700, 2000 and 2300 K. The pressure of the disproportionation of pyrope at various temperatures is estimated from the runs at 1700 and 2000 K in **Figure 2b** together with the study by Hirose *et al.* [2001]. At pressures lower than 25 GPa at these three temperatures, $\text{En}_{50}\text{Cor}_{50}$ crystallizes an assemblage of pyrope plus corundum. Depending on temperatures, pyrope would decompose into bridgmanite and corundum at 25.5–27 GPa. At a pressure of 27 GPa at these temperatures, the two-phase field of bridgmanite and corundum is thus stabilized. At this pressure, the Al_2O_3 solubility in bridgmanite increases from 6.7 ± 0.5 to 21.7 ± 0.6 mol% with increasing temperature from 1700 to 2500 K. In the same temperature range, the MgSiO_3 solubility in corundum also increases from 16.3 ± 0.8 to 38.0 ± 0.5 mol%. Therefore, the two-phase region of bridgmanite and corundum becomes narrower with increasing temperature. The shrinkage of the two-phase region also occurs at higher pressures with increasing temperature. These shrinkages are related to the mixing entropy and enthalpy [Panero *et al.*, 2006].

At a constant temperature, bridgmanite becomes more aluminous with increasing pressure. The Al_2O_3 solubility in bridgmanite increases from 6.7 ± 0.5 to 16 ± 3 mol% with increasing pressure from 27 to 44.5 GPa at 1700 K, from 12.2 ± 0.3 to 21.9 ± 0.6 mol% for pressures from 27 to 42.3 GPa at 2000 K, and from 19.2 ± 0.4 to 27.3 ± 0.3 mol% for pressures from 27 to 35 GPa at 2300 K. In contrast, the MgSiO_3 content in corundum decreases with increasing pressure, e.g., 16.4 ± 0.8 to 7 ± 4.0 mol% at 1700 K and 32.2 ± 0.4 to 21.7 ± 0.5 mol% at 2300 K. Both Al_2O_3 and MgSiO_3 enrichment in bridgmanite and corundum, respectively, can be explained by the cation substitution in the crystal structure of bridgmanite and corundum [e.g., Brodholt, 2000; Kubo and Akaogi, 2000; Walter *et al.*, 2004; Liu *et al.*, 2016].

Increasing proportions of the Al_2O_3 and MgSiO_3 components in bridgmanite and corundum, respectively, increases the lattice parameters of each of the phases (**Figure 7a and 7b**). The lower molar volume of bridgmanite (about 64% of the corundum volume), results in the partitioning of alumina into bridgmanite coexisting with increasingly alumina-rich corundum as pressure increases, accompanied by an increased ratio of bridgmanite to corundum. A simple lever rule analysis of the phase diagram in **Figure 9** rationalizes the variations in phase compositions and proportions as a function of pressure. The opposite situation is seen for the coexisting garnet-corundum assemblage. With bulk system compositions within the two-phase field, the garnet is fixed at the pyrope composition (25 mol% Al_2O_3), and the proportion of garnet decreases with increasing pressure as the MgSiO_3 content of the coexisting corundum increases.

The phase boundaries between bridgmanite and two-phase region of bridgmanite and corundum at 2000 and 2300 K, respectively, reported in the present study are close to those obtained using thermodynamics calculation by Panero *et al.* [2006] and prediction by Irifune and Tsuchiya [2007], respectively, although the rate of the increasing Al_2O_3 content in bridgmanite with increasing pressure in the present study is slightly larger than that in the

calculation and prediction. On the contrary, the phase boundary between this two-phase region and corundum is largely different from that obtained in the mentioned calculation and prediction, which may be caused by the poorly constrained thermodynamics parameters of corundum.

We note that the compositions of the phases in the recovered samples from experiment runs with the pyropic glass as the starting material are identical to those recovered from experiments for the En₅₀Cor₅₀ oxide mixture within analytical errors, as shown in **Figure 9**. This fact suggests that chemical equilibrium was achieved in our study. This idea is also supported by the identical compositions of two phases obtained from a shorter (5 hours, IRIS 232) and longer (15 hours, IRIS266) heating duration at the same conditions.

4.3 Host phases of Al₂O₃ in the lower mantle

Here, we discuss the Al₂O₃ host phases in the lower mantle at depths between 750 and 1250 km, corresponding to pressures of 27 and 50 GPa, respectively. The representative lower-mantle temperatures at these depths are approximately 2000 K [Katsura *et al.*, 2010]. Temperatures in subducted slabs under lower-mantle pressures are unknown, but must be substantially lower than these ambient-mantle temperatures [Kirby *et al.*, 1996].

The pyrolite composition contains about 4 wt% of Al₂O₃ [Sun, 1982]. The phase diagram in **Figure 9** suggests that bridgmanite can contain 13 and 29 wt% of Al₂O₃ at a depth of 750 and 1250 km, respectively. Therefore, all Al₂O₃ should be accommodated in bridgmanite in the majority of the lower mantle, as already suggested by Irifune [1994]. In subducted slabs, the estimated temperature profile may be at least 300 K lower than the ambient mantle depending on whether the slabs are young or old [Kirby *et al.*, 1996]. At these lower temperatures, the Al₂O₃ solubility in bridgmanite is about 7 and 17 wt%, at depth of 750 and

1250 km, respectively. Moreover, the MORB parts of slabs have an Al_2O_3 content up to 16 wt% [Green *et al.*, 1979]. Therefore, all Al_2O_3 cannot be fully accommodated in the cold peridotite parts of subducted slabs at 750 km depth, and one additional aluminous phase such as the CF (a MgAl_2O_4 dominated phase with a calcium ferrite-type structure) [Irifune *et al.*, 1991] may therefore form to host the excess Al_2O_3 in this region. At a depth of 1250 km, however, the Al_2O_3 solubility exceeds 16 wt% even at lower temperature, and therefore CF is expected to disappear with increasing subduction depth.

Although phase relations in the MgSiO_3 – Al_2O_3 system have been determined as a function of pressure and temperature by our advanced multi-anvil experiments using SD technology and *in situ* synchrotron XRD, the chemical systems in the lower mantle and subducted slabs are more complicated. The FeSiO_3 and FeAlO_3 components may change the Al_2O_3 solubility in bridgmanite [*e.g.*, Kesson *et al.*, 1995; Miyajima *et al.*, 1999; Nishio-Hamane *et al.*, 2005]. In particular, the dominance of the FeAlO_3 component in bridgmanite should change the Al_2O_3 solubility relative to that in the MgSiO_3 – Al_2O_3 system [Miyajima *et al.*, 1999; Nishio-Hamane *et al.*, 2005]. The presence of K_2O and Na_2O components would stabilize CF and NAL phases as host phases for the Al_2O_3 component in MORB slabs [*e.g.*, Irifune and Ringwood, 1993; Miyajima *et al.*, 1999, 2001; Ono *et al.*, 2001; Hirose and Fei, 2002; Litasov and Ohtani, 2005], which would decrease the Al_2O_3 contents in bridgmanite. Therefore, further studies of phase relations in Fe-, K- and Na-bearing systems are needed to constrain the host phases of Al_2O_3 and their compositions in the lower mantle.

4. Conclusion

Phase relations in the system $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ were determined at pressures between 27 and 45 GPa and temperatures of 1700, 2000 and 2300 K. At pressure just below 27 GPa, phase assemblages of garnet+bridgmanite and garnet + corundum are stable for compositions of less and more than 25 mol% Al_2O_3 . At pressures above 27 GPa, another assemblage of bridgmanite and corundum is stabilized for bulk compositions within the two-phase field. The Al_2O_3 and MgSiO_3 solubility in bridgmanite and corundum, respectively, increases with increasing temperature. Moreover, bridgmanite becomes more aluminous with increasing pressure and can contain a considerably higher Al_2O_3 component than the pyrope composition. In contrast, the MgSiO_3 solubility in corundum decreases with increasing pressure. Additionally, Al_2O_3 incorporation significantly increases the molar volume of bridgmanite, while MgSiO_3 incorporation only slightly increases the volume of corundum. The present study supports the idea that the entire Al_2O_3 content of 4 wt% can be accommodated into bridgmanite in the pyrolytic lower mantle. On the other hand, the Al_2O_3 solubility in bridgmanite is insufficient to accommodate the entire alumina inventory in subducted slabs in the uppermost part of the lower mantle, owing to the low temperatures and limited pressures, and additional Al phases may therefore be present at these conditions.

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Table 1 Experimental run conditions and products.

Run no.	Starting sample	Pressure (GPa)	Temperature (K)	Duration (hours)	Phases
S6778	En ₅₀ Cor ₅₀ oxide	20	1700	6	Gar + Cor
S6607	En ₅₀ Cor ₅₀ oxide	25	1700	6	Gar + Cor
	En ₇₅ Cor ₂₅ glass				Gar
S6636	En ₅₀ Cor ₅₀ oxide	24	2300	3	Gar + Cor
IRIS232	En ₅₀ Cor ₅₀ oxide	27	1700	5	Al-Brg + Cor
IRIS266	En ₅₀ Cor ₅₀ oxide	27	1700	15	Al-Brg + Cor
	En ₇₅ Cor ₂₅ glass				Al-Brg + Cor + tr (Sti)
IRIS276	En ₅₀ Cor ₅₀ oxide	27	1900*	2	Al-Brg + Cor
IRIS256	En ₅₀ Cor ₅₀ oxide	27	2000	5	Al-Brg + Cor
	En ₇₅ Cor ₂₅ glass				Al-Brg + Cor
IRIS244	En ₅₀ Cor ₅₀ oxide	27	2300	2	Al-Brg + Cor + tr (Sti)
	En ₇₅ Cor ₂₅ glass				Al-Brg + Cor
IRIS300	En ₅₀ Cor ₅₀ oxide	27	2500*	0.5	Al-Brg + Cor+ tr (Sti)
	En ₇₅ Cor ₂₅ glass				Al-Brg + Cor
IRIS252	En ₅₀ Cor ₅₀ oxide	30	2300	1.5	Al-Brg + Cor
M2055	En ₅₀ Cor ₅₀ oxide	31.9	1700	5	Al-Brg + Cor
S6615	En ₅₀ Cor ₅₀ oxide	35	2300	1.5	Al-Pv + Cor
M2037	En ₅₀ Cor ₅₀ oxide	38.5	1700	5.5	Al-Brg + Cor
M2063	En ₅₀ Cor ₅₀ oxide	41.8	1700	6	Al-Brg + Cor
M2080	En ₇₅ Cor ₂₅ glass	44.8	1700	5	Al-Brg + Cor + tr (Sti)
M2106	En ₇₅ Cor ₂₅ glass	42.3	2000	3	Al-Brg + Cor + tr (Sti)
M1610	En ₅₀ Cor ₅₀ oxide	48.5	1700*	2	Al-Brg + Cor + tr (Sti)
M1677#	En ₅₀ Cor ₅₀ oxide	51.8	2000	3	Al-Brg + Cor

* temperature was evaluated from a calibrated power curve derived from the low temperature of 1500 K for IRIS276, and 2400 K for IRIS300.

the run is from Liu et al. [2016].

a: temperature is around 1700-1800 K due to the instability of the heater

Abbreviations: Gar: garnet, Cor: corundum, Sti: stishovite, Al-Brg: aluminous bridgmanite, Al-Pv: aluminous perovskite; tr: trace.

Table 2. Chemical compositions of the coexisting mineral phases in the run products at pressure above 27 GPa

Run	Start Comp	Phases	MgO	Al ₂ O ₃	SiO ₂	Total	Mg	Al	Si	Sum
IRIS23	En ₅₀ Cor ₅₀	Brg (n = 15)	37.79 (62)	6.79 (41)	55.33 (78)	99.11 (115)	3.776 (35)	0.521 (35)	3.722 (19)	8.018 (13)
		Cor (n = 12)	6.73 (33)	82.46 (90)	9.19(69)	98.18 (45)	0.671 (35)	6.706 (48)	0.635 (37)	8.012 (19)
IRIS26	En ₅₀ Cor ₅₀	Brg (n = 15)	37.45 (66)	6.93 (36)	55.33 (88)	99.80 (132)	3.754 (26)	0.548 (32)	3.714 (17)	8.014 (19)
		Cor (n = 12)	6.84 (49)	82.07 (27)	9.91(42)	98.82 (70)	0.699 (56)	6.629 (60)	0.679 (26)	8.006 (17)
IRIS25	En ₅₀ Cor ₅₀	Brg (n = 11)	35.67 (26)	12.49 (27)	52.94 (25)	101.10 (63)	3.523 (48)	0.975 (25)	3.507 (14)	8.005 (19)
		Cor (n = 12)	9.74 (29)	74.98 (17)	14.58 (42)	99.05 (57)	0.989 (28)	6.017 (37)	0.993 (24)	7.999 (12)
IRIS27	En ₅₀ Cor ₅₀	Brg (n = 10)	35.36 (27)	11.66 (14)	52.40 (45)	99.42 (81)	3.552 (10)	0.925 (6)	3.530 (7)	8.007 (5)
		Cor (n = 10)	8.61 (37)	79.26 (28)	12.67 (23)	100.54 (46)	0.864 (34)	6.287 (13)	0.853 (17)	8.004 (17)
IRIS24	En ₅₀ Cor ₅₀	Brg (n = 15)	31.50 (54)	20.60 (24)	49.97 (56)	98.79 (93)	3.243 (33)	1.541 (28)	3.222 (14)	8.007 (12)
		Cor (n = 12)	13.08 (17)	67.41 (29)	18.30 (31)	98.80 (19)	1.335 (15)	5.439 (34)	1.253 (19)	8.027 (4)
	En ₇₅ Cor ₂₅	Brg (n = 15)	33.34 (38)	20.04 (35)	49.37 (27)	102.75 (39)	3.243 (33)	1.541 (28)	3.222 (14)	8.007 (12)
		Cor (n = 12)	11.74 (17)	68.73 (39)	17.51 (31)	98.27 (73)	1.203 (12)	5.586 (34)	1.204 (37)	8.000 (14)
IRIS30	En ₅₀ Cor ₅₀	Brg (n = 15)	31.39 (36)	22.38 (52)	47.46 (51)	101.24 (59)	3.100 (31)	1.735 (49)	3.149 (28)	7.984 (11)
		Cor (n = 12)	15.08 (11)	63.14 (83)	23.09 (28)	101.33 (79)	1.497 (7)	4.953 (33)	1.537 (24)	7.987 (8)
	En ₇₅ Cor ₂₅	Brg (n = 15)	31.25 (49)	22.09 (25)	46.97 (31)	100.28 (76)	3.114 (32)	1.740 (18)	3.138 (16)	7.992 (15)
		Cor (n = 12)	14.69 (42)	63.72 (63)	22.10 (128)	100.21	1.474 (26)	5.034 (93)	1.487 (68)	7.996 (18)
IRIS25	En ₅₀ Cor ₅₀	Brg (n = 15)	32.32 (55)	21.66 (69)	47.58 (79)	101.56	3.183 (31)	1.687 (53)	3.143 (31)	8.013 (11)
		Cor (n = 12)	10.97 (30)	72.26 (74)	15.93 (44)	99.16 (26)	1.115 (32)	5.808 (73)	1.086 (31)	8.009 (11)
S6615	En ₅₀ Cor ₅₀	Brg (n = 8)	29.69 (49)	27.76 (23)	42.55 (32)	100#	2.983 (22)	2.197 (17)	2.861 (38)	8.041 (14)
		Cor (n = 10)	8.82 (19)	77.76 (34)	12.44 (25)	99.01 (37)	0.899 (12)	6.277 (25)	0.854 (15)	8.016 (5)
M2055	En ₅₀ Cor ₅₀	Brg (n = 8)	35.26 (27)	11.76 (24)	52.71 (39)	99.73 (58)	3.530 (29)	0.930 (17)	3.538 (21)	7.997 (13)
		Cor (n = 10)	4.75 (51)	87.84 (45)	6.83 (48)	99.42 (81)	0.482 (29)	7.058 (57)	0.465 (29)	8.006 (3)
M2037	En ₅₀ Cor ₅₀	Brg (n = 8)	34.52 (27)	13.72 (40)	51.82 (56)	99.96 (53)	3.414 (17)	1.195 (23)	3.397 (19)	8.005 (12)
		Cor (n = 10)	4.50 (49)	90.10 (53)	6.72 (51)	101.12 (76)	0.450 (36)	7.118 (48)	0.437 (32)	8.004 (5)
M2063	En ₅₀ Cor ₅₀	Brg (n = 5)	34.27 (77)	15.41 (54)	50.95 (90)	101.64 (89)	3.369 (54)	1.275 (22)	3.359 (22)	8.003 (24)
		Cor (n = 11)	3.61 (28)	92.41 (62)	5.23 (22)	101.37 (51)	0.360 (22)	7.283 (34)	0.358 (15)	8.001 (2)
M2106	En ₇₅ Cor ₂₅	Brg (n = 8)	31.55 (69)	22.35 (82)	46.99 (82)	100.89 (98)	3.127 (57)	1.751 (38)	3.124 (47)	8.001 (33)
M1677	En ₅₀ Cor ₅₀	Brg (n = 12)	28.08 (47)	30.00 (64)	42.57 (69)	100.63 (30)	2.789 (58)	2.357 (48)	2.838 (38)	7.984 (27)
		Cor (n = 16)	4.62 (58)	88.98 (80)	6.40 (52)	100.01 (17)	0.467 (6)	7.110 (60)	0.434 (35)	8.010 (23)

Oxide analyses are reported in wt%. Cations are reported based on the oxygen number is normalised to 12. Number in parentheses represents standard deviation and is placed in the last digit (s). n: the number of analysis points. #: normalized to 100 due to some amounts (~1 wt%) of WO₃ in bridgmanite. Abbreviations: Brg, bridgmanite; Cor, corundum; Comp, composition.

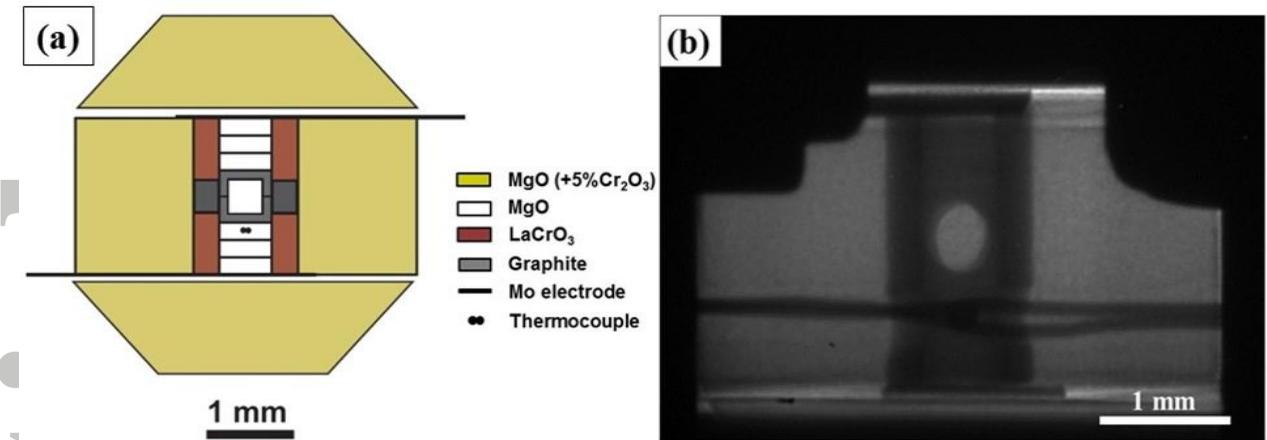


Figure 1. (a) Schematic illustration of the high-pressure cell assembly for *in situ* SD experiments. (b) X-ray radiographic images of SD cell assembly at ambient conditions. The hot junction of the thermocouple was placed at the bottom of the capsule, and the diffracted X-ray signals were acquired through the graphite windows.

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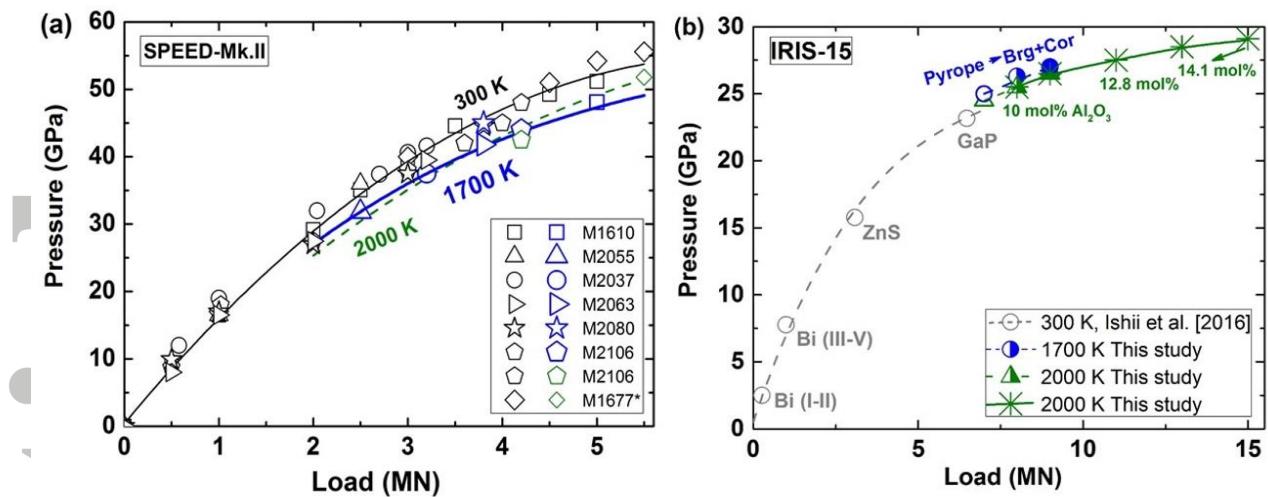


Figure 2. (a) Generated pressure versus the press load at room temperature (300 K, open black symbols), 1700 (blue symbols, this study) and 2000 K (green symbols, this study) for *in situ* XRD experiments using a DIA-type apparatus (SPEED-MK.II) at SPring-8. The black and blue solid lines represent the fitting results of the data at 300 and 1700 K in the present study, and that at 2000 K together with the symbol of M1677 is from Liu *et al.* [2016]. (b) Pressure calibration curve at 1700 (circle) and 2000 K (triangle) for the IRIS-15 multi-anvil apparatus, based on the phase transition of pyrope to bridgmanite and corundum [Hirose *et al.*, 2001] and various Al₂O₃ solubility (mol%) in bridgmanite at 2000 K [Liu *et al.*, 2016]. Pressure calibration at room temperature condition is from Ishii *et al.* [2016].

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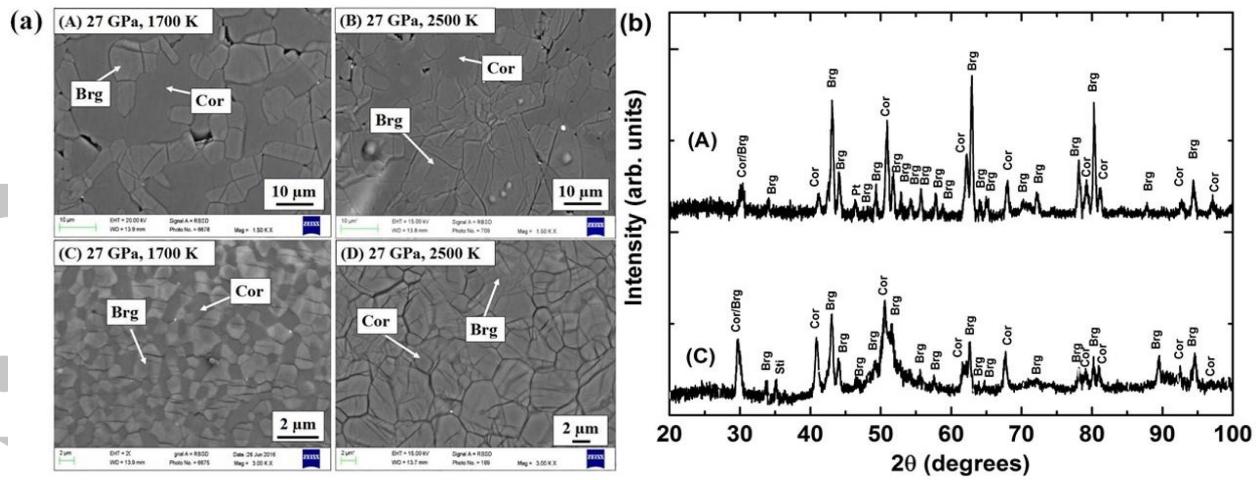


Figure 3. (a) Representative back-scattered electron images of the run products for En₅₀Cor₅₀ (A-B) and pyropic compositions (C-D) synthesized at 27 GPa and 1700 and 2500 K, respectively. (b) Selected XRD patterns of the run products of (A) En₅₀Cor₅₀ and (C) pyropic compositions at 27 GPa and 1700 K, respectively. Abbreviations: Brg, bridgmanite; Cor, corundum; Sti, stishovite.

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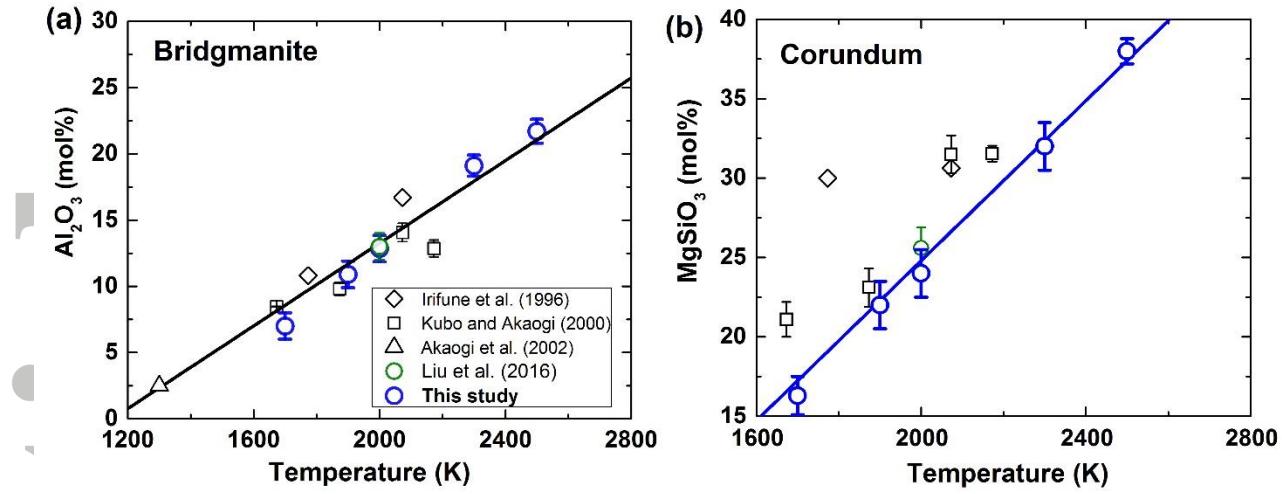


Figure 4. (a) Al_2O_3 solubility in bridgmanite and (b) MgSiO_3 solubility in corundum, respectively, as a function of temperature at a constant pressure of 27 GPa. The solid black and blue lines are the least-squares fitting of all the data and only the data in the present study, respectively.

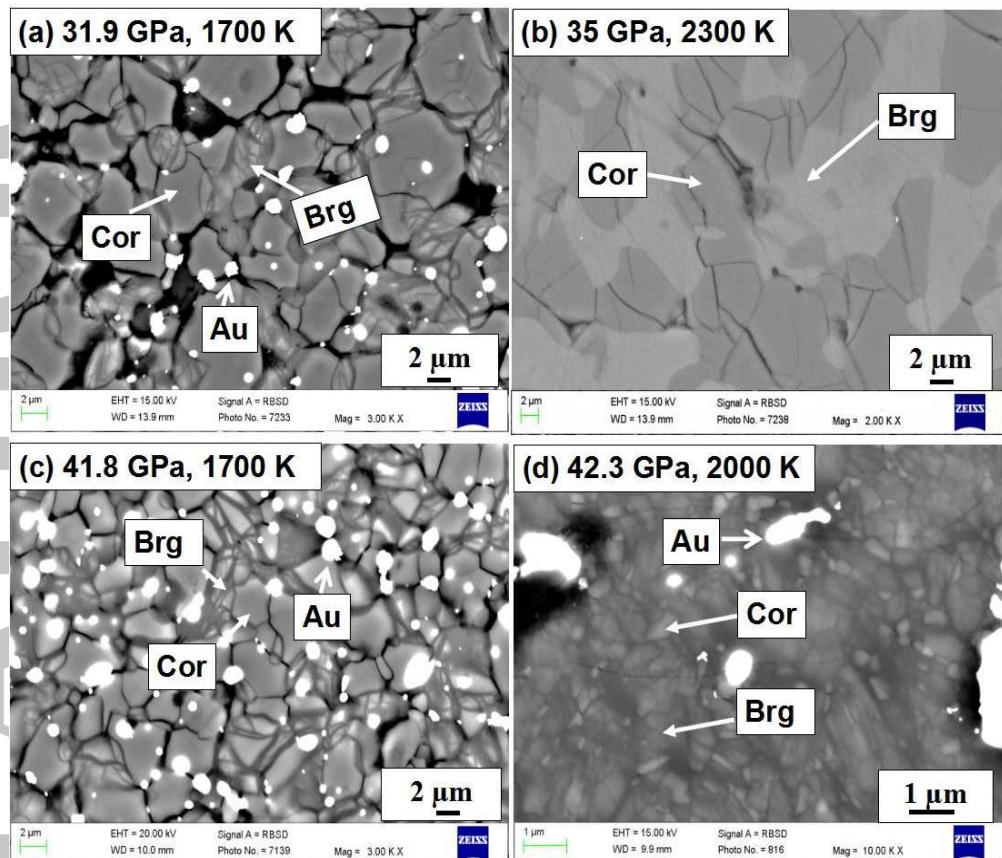


Figure 5. Selected back-scattered electron images of the run products for $\text{En}_{50}\text{Cor}_{50}$ at 31.9–41.8 GPa and 1700 and 2300 K (a–c) and pyropic glass (d) at 42.3 GPa and 2000 K. Abbreviations: Brg, bridgmanite; Cor, corundum; Au: gold.

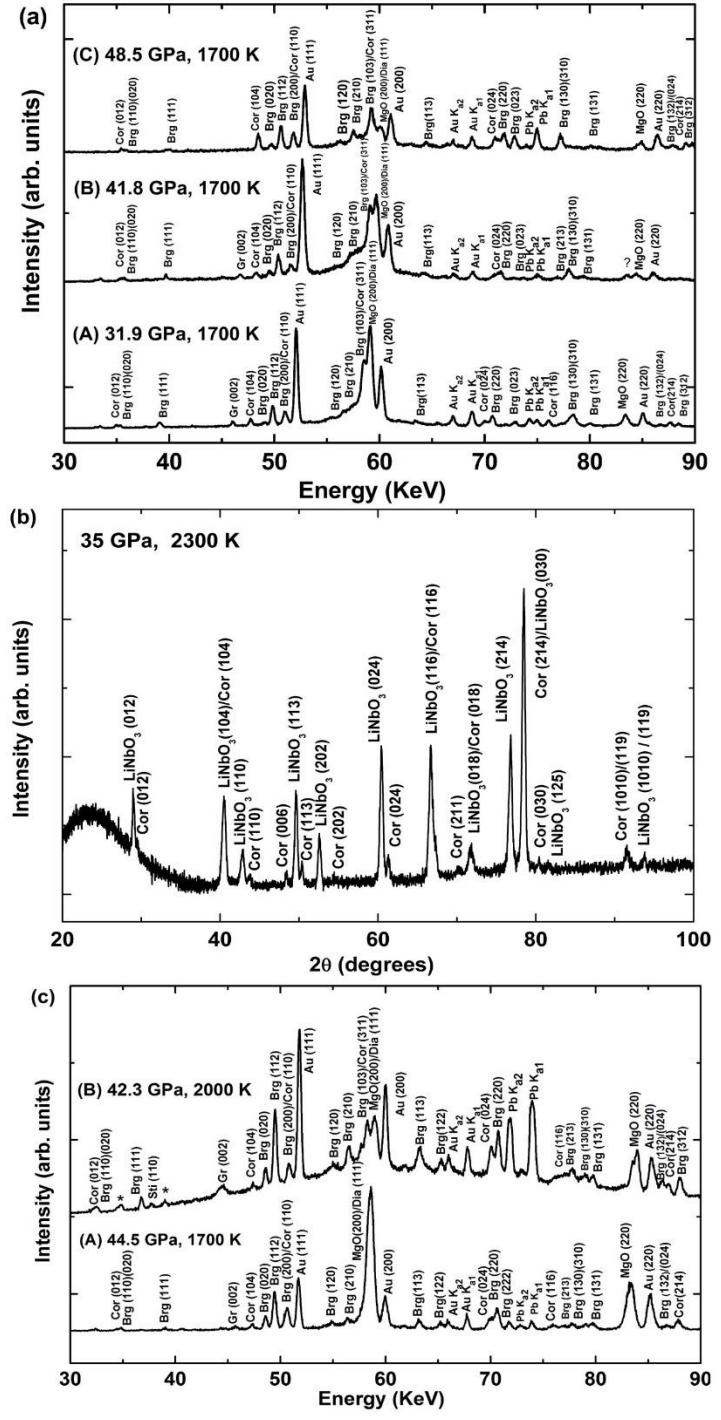


Figure 6. Selected (a) *in situ* and (b) quench XRD profiles of En₅₀Cor₅₀ and (c) *in situ* XRD profiles of the pyropic glass at various pressure and temperature conditions. Abbreviations: Brg, bridgmanite; Cor, corundum; Dia, diamond; Sti, stishovite; Gr: graphite. The stars represent the fluorescence of X-ray beam.

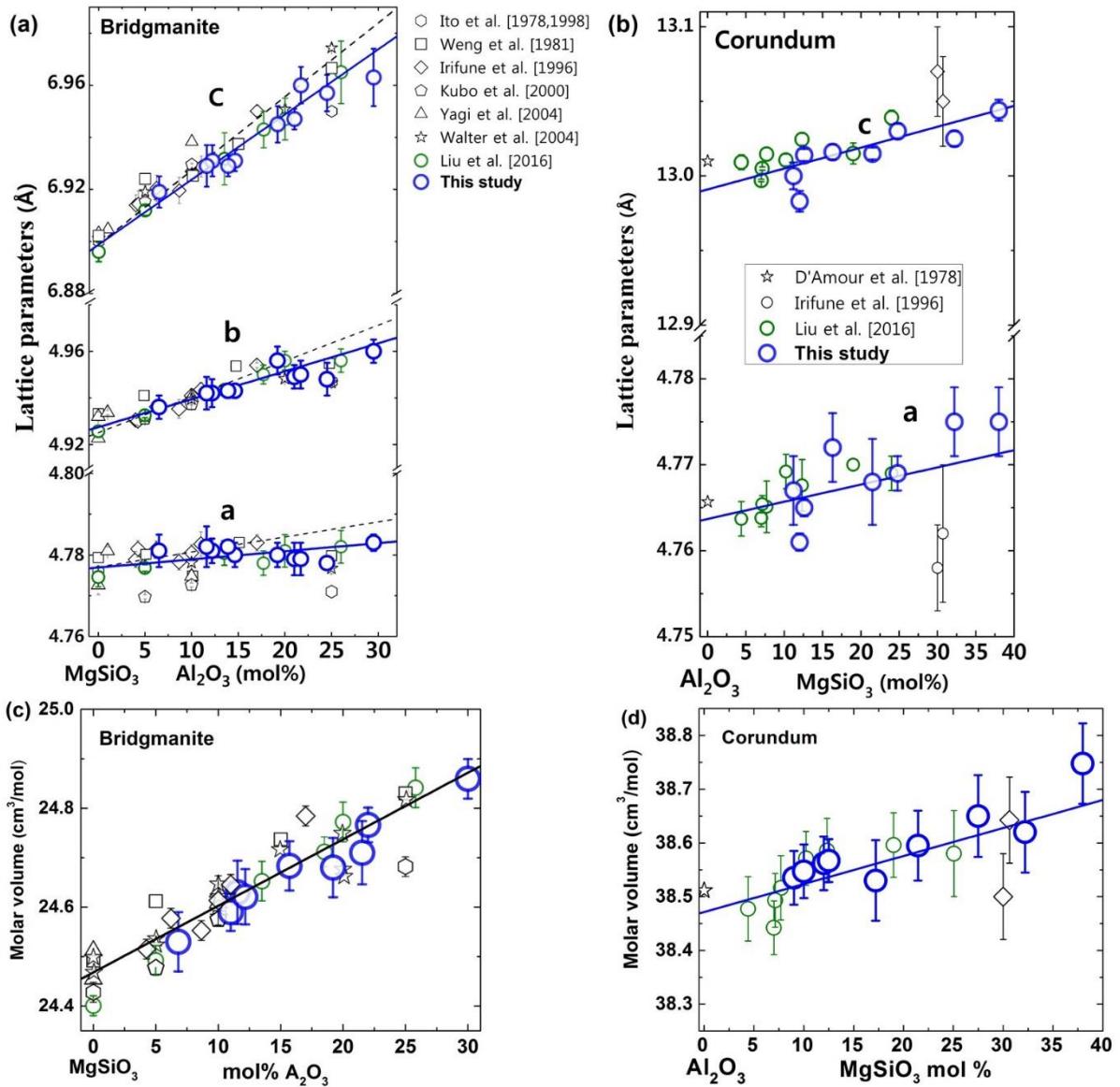


Figure 7. Lattice parameter and molar volume of (a and c) bridgmanite and (b and d) corundum versus the Al_2O_3 and MgSiO_3 content, respectively, in the present and previous work. Solid lines are the linear fitting of the present data and Liu *et al.* [2016], and the dashed lines are results of Irifune *et al.* [1996].

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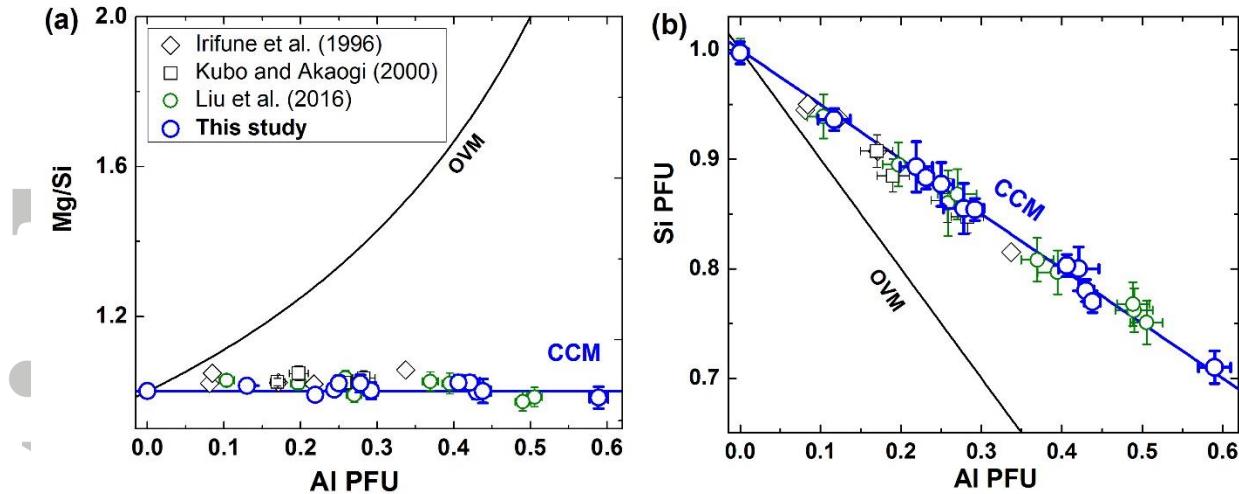


Figure 8. (a) The ratio between Mg and Si cation and (b) Si cation number versus the Al per formula unit (pfu, based on 3 oxygens) in bridgemanite in the present study and previous works [Irifune *et al.*, 1996; Kubo and Akaogi, 2000; Liu *et al.*, 2016]. Solid blue and black lines indicate the trend expected for trivalent cation incorporation by the charge-coupled substitution mechanism (CCM) and oxygen vacancy substitution mechanism (OVM), respectively.

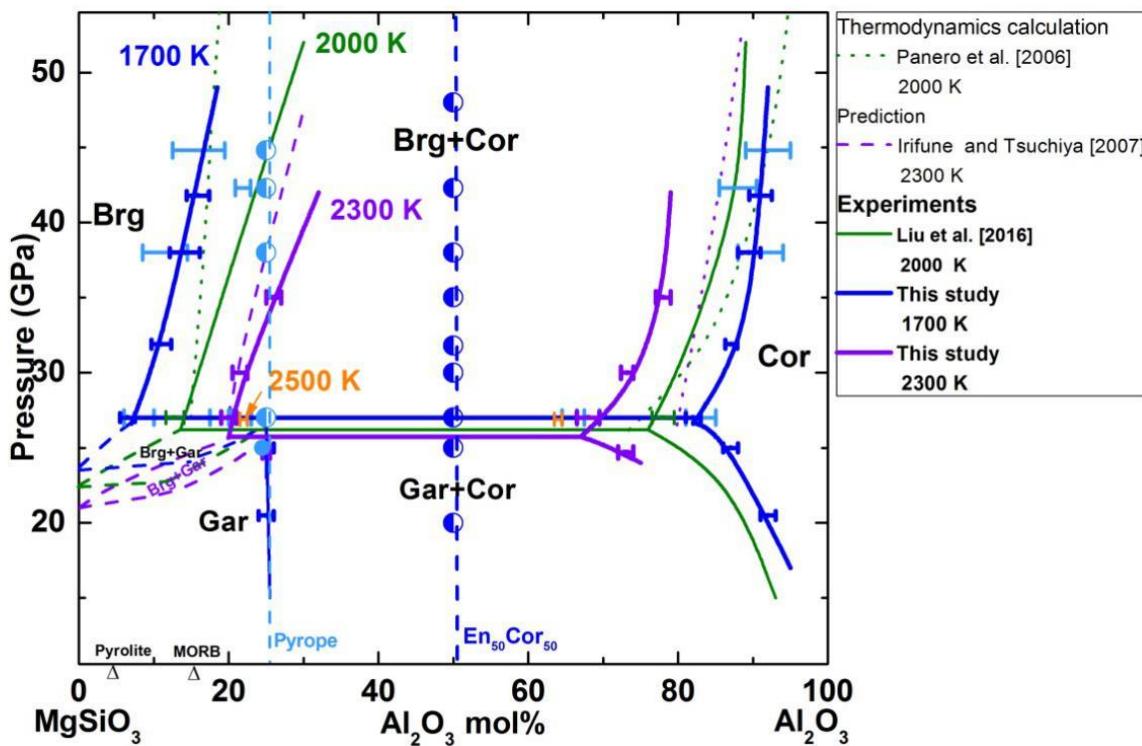


Figure 9. Phase relations in the $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ system at 24–45 GPa and 1700, 2000 and 2300 K in the present and previous studies. Dark and light blue dashed lines represent the chemical compositions of the starting materials in the present study. Dark blue circular symbols indicate the high pressure runs using the $\text{En}_{50}\text{Cor}_{50}$ oxide mixture as the starting material, while light blue circular symbols indicate those for the pyropic glass. The corresponding horizontal-lined symbols mark the compositions of the coexisting phases for the $\text{En}_{50}\text{Cor}_{50}$ oxide mixture and the pyropic glass. The phase loop of bridgmanite plus garnet was referenced from Irfune *et al.* [1996], Kubo and Akaogi [2000] and Irfune and Tsuchiya [2007]. The triangles represent the Al_2O_3 content in the pyrolite and MORB models. Error bars indicate the uncertainties of chemical compositions. Abbreviations: Brg, bridgmanite; Cor, corundum; Sti, stishovite; Gar, garnet.