

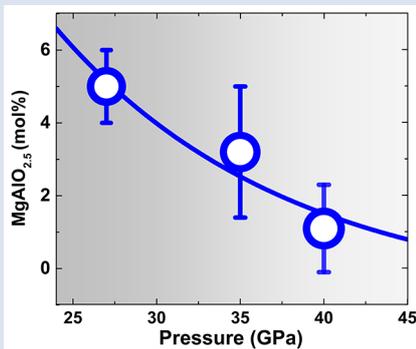
Rapid decrease of MgAlO_{2.5} component in bridgmanite with pressure

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Abstract



The solubility of the MgAlO_{2.5} component in bridgmanite was measured at pressures of 27, 35 and 40 GPa and a temperature of 2000 °K using an ultra-high pressure multi-anvil press. Compositional analysis of recovered samples demonstrated that the MgAlO_{2.5} component decreases with increasing pressure, and approaches virtually zero at 40 GPa. Above this pressure, the MgAlO_{2.5} component, *i.e.* the oxygen-vacancy substitution, becomes negligible, and Al is incorporated in bridgmanite by the charge-coupled substitution only. These results are supported by the volume change associated with the change from the oxygen-vacancy substitution to charge-coupled substitution. The present result may explain the seismically observed slab stagnation in the mid-lower mantle. Although bridgmanite has been put forward as a potential host for water and argon in the lower mantle by trapping them in oxygen vacancies, such capabilities will rapidly decrease with depth and be lost in regions deeper than 1000 km.

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Introduction

Aluminium (Al) is the fifth most abundant element in the Earth's mantle (McDonough and Sun, 1995). Under the Earth's lower mantle conditions, Al³⁺ is mainly accommodated in bridgmanite in a pyrolite mantle (Irifune, 1994). Al substitution in the Mg, Si or both sites modifies the crystal chemistry of bridgmanite, and thereby changes the physical properties of bridgmanite (Zhang and Weidner, 1999; Brodholt, 2000). Therefore, understanding the Al substitution mechanism is essential to investigating the mineralogy and dynamics of the lower mantle.

Two competing Al substitution mechanisms occur in bridgmanite (Hirsch and Shankland, 1991). One is the charge-coupled substitution ($\text{Mg}^{2+} + \text{Si}^{4+} = \text{Al}^{3+} + \text{Al}^{3+}$; components along the MgSiO₃–Al₂O₃ binary system), where two Al cations substitute for one Mg with the roughly 8-fold coordination (A site) and one Si with the 6-fold coordination (B site). The other mechanism is the oxygen-vacancy substitution ($2\text{Si}^{4+} + \text{O}^{2-} = 2\text{Al}^{3+} + \text{V}_\text{O}$, where V_O is an oxygen vacancy; components along the MgSiO₃–MgAlO_{2.5} binary system), where two Al cations replace two Si in the B sites and one oxygen vacancy forms to compensate for the excess negative charges. The oxygen vacancies in bridgmanite have special importance for understanding lower mantle processes because oxygen vacancies may induce water ($\text{V}_\text{O} + \text{O}^{2-} + \text{H}_2\text{O} = 2\text{OH}^{-1}$; Navrotsky, 1999) and noble gases into bridgmanite (Shcheka and Kepler, 2012).

Earlier theoretical calculations investigated whether oxygen vacancies exist in bridgmanite (Brodholt, 2000; Yamamoto *et al.*; 2003; Akber–Knutson and Bukowinski, 2004). Brodholt (2000) suggested that oxygen-vacancy substitution should dominate at pressures only up to 30 GPa. Yamamoto *et al.* (2003) argued oxygen-vacancy substitution should be unfavourable in the entire lower mantle. Furthermore, energetic calculations by Akber–Knutson and Bukowinski (2004) suggested that oxygen-vacancy substitution could only account for 3–4 % and less than 1 % of Al substitutions in the shallower and deeper parts of the lower mantle, respectively.

High pressure and high temperature synthesis (Navrotsky *et al.*, 2003) and nuclear magnetic resonance (NMR) spectroscopy (Stebbins *et al.*, 2003) suggested that oxygen-vacancy substitution dominates in bridgmanite with 5–10 mol. % MgAlO_{2.5} at 27 GPa and 1873 °K. On the other hand, X-ray diffraction measurements in a laser-heated diamond anvil demonstrated that bridgmanite coexisted with periclase from a glass starting material with a composition of 90 mol. % MgSiO₃ and 10 mol. % MgAlO_{2.5} at 40 ± 10 GPa and 2000–2500 °K (Walter *et al.*, 2006), indicating that the MgAlO_{2.5} component was not present in bridgmanite and thereby oxygen-vacancy substitution was unfavoured under these conditions. Note that pressure and temperature uncertainties in this study were relatively large, and the composition of bridgmanite was not determined owing to its very small sample size. Thus, it is still uncertain whether MgAlO_{2.5} can be a dominant component in bridgmanite in the lower mantle.

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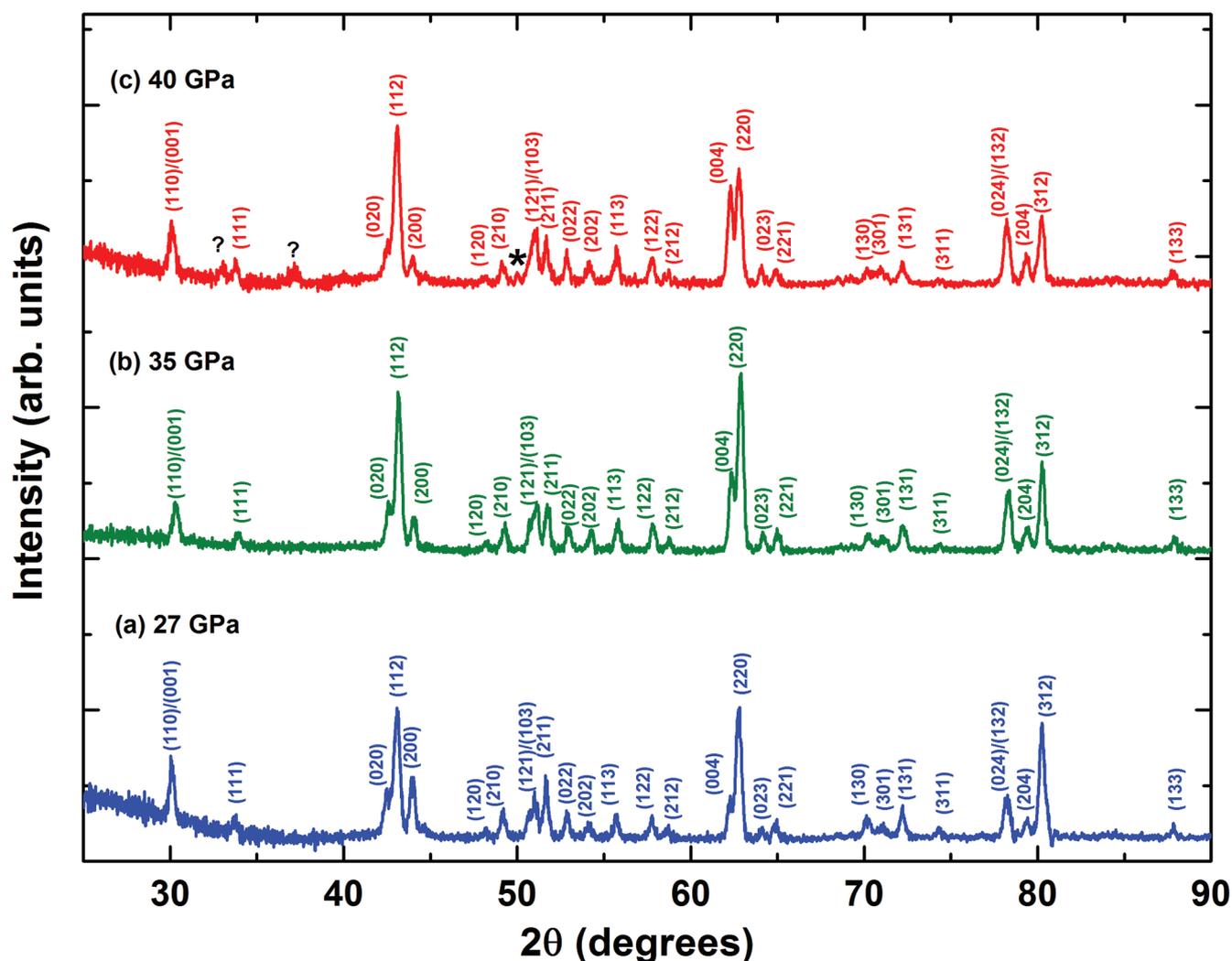


Figure 1 XRD patterns of $\text{En}_{90}\text{Brm}_{10}$ subjected to (a) 27, (b) 35 and (c) 40 GPa and at 2000 °K. Number in parentheses represents the index of bridgmanite. Question marks denote unidentified peaks. Asterisk denotes the probable (200) peak of periclase.

Here, we investigate the solubility of the $\text{MgAlO}_{2.5}$ component in bridgmanite as a function of pressure from 27 to 40 GPa at a constant temperature of 2000 °K and discuss water and noble gas storage capacities in the lower mantle.

Experimental Methods

The starting materials were glasses with $\text{En}_{90}\text{Brm}_{10}$ (En: MgSiO_3 ; Brm: $\text{MgAlO}_{2.5}$; mol. %) and $\text{En}_{95}\text{Cor}_5$ (Cor: Al_2O_3) compositions (see section S-1 in the Supplementary Information for synthesis details and Table S-1 for their compositions). High pressure and high temperature experiments were conducted using ultra-high pressure multi-anvil technology with carbide anvils (Ishii *et al.*, 2016), and detailed techniques can be found in Figures S-1 and S-2 in the Supplementary Information. As shown in Table 1, bridgmanite samples with $\text{En}_{90}\text{Brm}_{10}$ and $\text{En}_{95}\text{Cor}_5$ compositions were first synthesised at 27 GPa and 2000 °K for 3 hours. These samples were annealed at pressures of 35 and 40 GPa and a temperature of 2000 °K for 2 and 3 hours. The recovered samples were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA) (see section S-2 in the Supplementary Information for analytical analyses).

Results

XRD patterns of bridgmanite with the $\text{En}_{90}\text{Brm}_{10}$ starting composition synthesised at 27, 35 and 40 GPa are shown in Figure 1, while those for $\text{En}_{95}\text{Cor}_5$ composition are shown in Figure S-3. All diffraction peaks of the sample for the $\text{En}_{90}\text{Brm}_{10}$ composition synthesised at 27 GPa were assigned to those of bridgmanite (Ito and Matsui, 1978), indicating the formation of a single phase bridgmanite. The diffraction peaks of the $\text{En}_{90}\text{Brm}_{10}$ bridgmanite sample annealed at 35 GPa were also assigned to bridgmanite. For the sample annealed at 40 GPa, the majority of its peaks were assigned to bridgmanite, except for three extra weak peaks with d -spacings of 2.11 ($2\theta = 50.3^\circ$), 2.80 ($2\theta = 37.5^\circ$) and 3.15 ($2\theta = 32.9^\circ$) Å. The peak with d -spacing of 3.15 Å was suggested to result from the presence of a superstructure (Navrotsky *et al.*, 2003). The weak peak with d -spacing of 2.11 Å may correspond to (200) of MgO (periclase), which indicates the coexistence of a trace amount of periclase with bridgmanite at 40 GPa and 2000 °K as consistent with the observation by Walter *et al.* (2006). The sample decomposed to periclase and aluminous bridgmanite, suggesting a lower solubility of the $\text{MgAlO}_{2.5}$ component with increasing pressure.

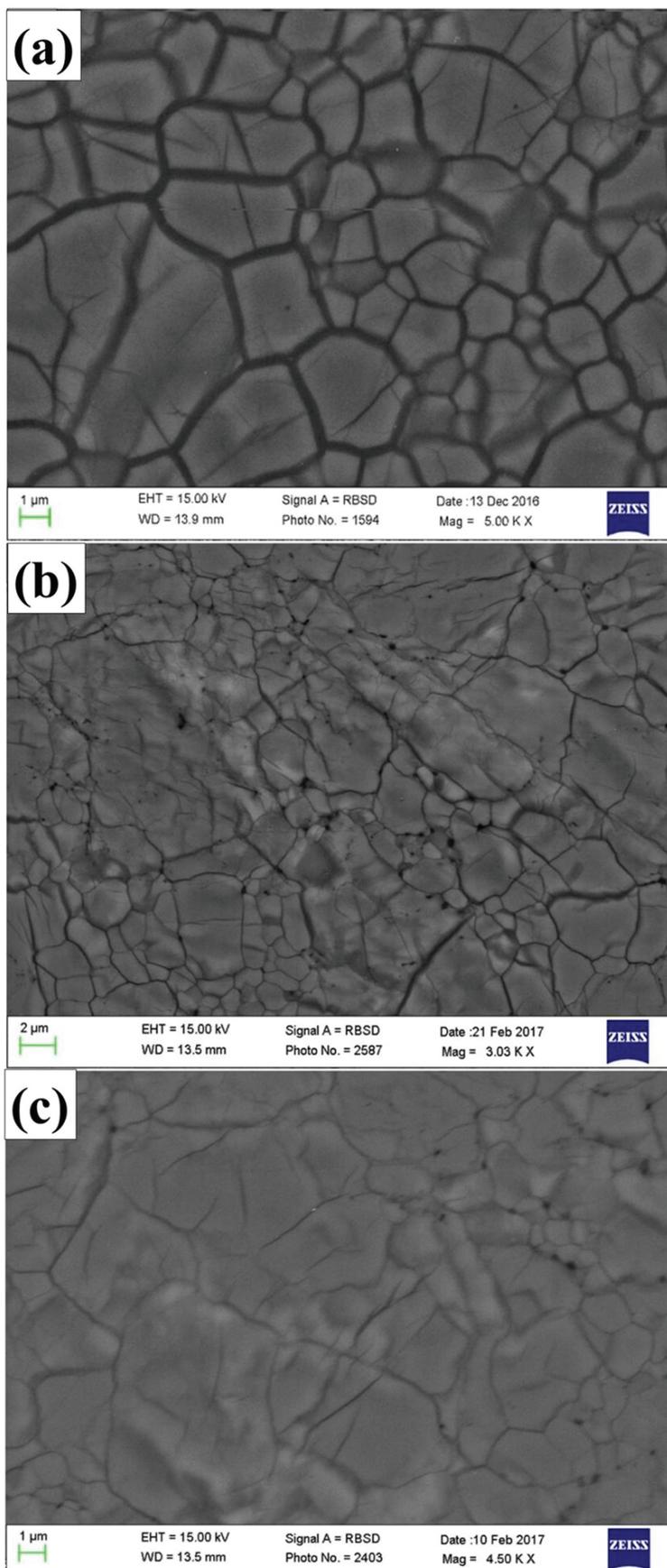


Figure 2 Representative BSE images of $\text{En}_{90}\text{Brm}_{10}$ subjected to (a) 27 GPa, (b) 35 and (c) 40 GPa and 2000 °K.

Textural observations by SEM showed that all samples consist of a single phase. Although the XRD patterns showed the presence of periclase for the sample annealed at 40 GPa, this phase was not detected by back scattered electron (BSE)

observations in Figure 2. Compositions of bridgmanite with grains larger than 3 μm were analysed by EPMA and shown in Table 1, where the total cation numbers were normalised to two to show clearly the variation of oxygen number with pressure.

Table 1 Experimental conditions, run products, and phase compositions.

Start Comp	Phases	MgO	Al ₂ O ₃	SiO ₂	Total	O	Mg	Al	Si
IRIS333 (27 GPa, 2000 °K; 3 hours)									
En ₉₀ Brm ₁₀	Brg [n = 40]	39.82 (23)	5.13 (15)	55.92 (24)	100.86 (14)	2.973 (4)	0.979 (5)	0.100 (3)	0.922 (4)
En ₉₅ Cor ₅	Brg [n = 26]	37.93 (22)	5.11 (12)	56.31 (3)	99.35 (55)	2.998 (2)	0.952 (5)	0.101 (2)	0.948 (4)
IRIS357 (35 GPa, 2000 °K; 2 hours)									
En ₉₀ Brm ₁₀	Brg [n = 52]	39.11 (52)	5.19(13)	56.38 (45)	100.69 (25)	2.984 (7)	0.970 (13)	0.102 (2)	0.938 (7)
IRIS351 (40 GPa, 2000 °K*; 3 hours)									
En ₉₀ Brm ₁₀	Brg [n = 55]	38.01 (40)	5.09 (12)	56.01 (46)	99.11 (65)	2.995 (4)	0.955 (8)	0.101 (2)	0.944 (4)
En ₉₅ Cor ₅	Brg [n = 20]	38.44 (32)	5.12 (16)	57.37 (55)	100.92 (72)	2.999 (3)	0.949 (6)	0.100 (3)	0.950 (3)

Oxide analyses are reported in wt %. n: number of analysis points.

*: temperature was evaluated from a calibrated power curve derived from a lower temperature of 1500 °K.

Number in parentheses represents standard deviation for the last digit (s). Abbreviation: Brg, bridgmanite.

The number of oxygen atoms in bridgmanite from the En₉₀Brm₁₀ and En₉₅Cor₅ compositions in the present and previous studies (Navrotsky *et al.*, 2003; Kojitani *et al.*, 2007) are plotted in Figure 3a. At 27 GPa, the number of oxygens in bridgmanite for the En₉₀Brm₁₀ composition is 2.973 ± 0.004 , which is slightly lower than those in Navrotsky *et al.* (2003) and Kojitani *et al.* (2007) and substantially lower than that of En₉₅Cor₅ bridgmanite. This value shows clearly the presence of oxygen vacancies as consistent with ²⁷Al NMR observations by Stebbins *et al.* (2003). However, the number of oxygens in bridgmanite for the En₉₀Brm₁₀ composition monotonically increases to 2.984 ± 0.007 at 35 GPa, and finally reaches 2.995 ± 0.004 at 40 GPa, which is within the uncertainties of En₉₅Cor₅ bridgmanite at the same pressure, indicating almost no oxygen vacancies at 40 GPa.

Figure 3b shows the variation in the Mg/Si cation ratio in these two kinds of aluminous bridgmanite against pressures. At 27 GPa, this ratio of the sample from the En₉₀Brm₁₀ composition was 1.06 ± 0.01 , which lies between the ideal compositional lines associated with the oxygen-vacancy and charge-coupled substitution. With increasing pressure, it decreases to 1.03 ± 0.02 at 35 GPa, and then to 1.01 ± 0.02 at 40 GPa, which finally lies on the ideal composition line of the charge-coupled substitution for the case of En₉₅Cor₅ bridgmanite.

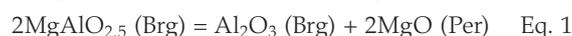
Figure 3c shows the ratios of Al at the A and B sites (Al_B/Al_A) in bridgmanite. This ratio of the sample for En₉₀Brm₁₀ decreases from 3.82 ± 0.53 at 27 GPa to 1.23 ± 0.38 at 40 GPa, which is finally within the uncertainties of unity, the expected result of the charge-coupled substitution. In contrast, this ratio for En₉₅Cor₅ bridgmanite remains almost unchanged with increasing pressure and lies on the line associated with the charge-coupled substitution.

The mass balance calculation implies that 1.2 ± 0.2 and 1.9 ± 0.4 wt. % periclase should coexist with bridgmanite for the En₉₀Brm₁₀ composition at 35 and 40 GPa, respectively. However, XRD patterns exhibited only one peak of periclase from the sample at 40 GPa, and that of the sample at 35 GPa and SEM showed no evidence for the coexistence of periclase. No observation of periclase by SEM could be explained by polishing out tiny interstitial grains.

The results of these observations can be summarised such that the proportion of the MgAlO_{2.5} component in bridgmanite decreases with increasing pressure: 5.7 ± 0.8 mol. % at 27 GPa, 3.2 ± 1.8 mol. % at 35 GPa, and 1.1 ± 1.0 mol. % at 40 GPa (see the detailed calculation in section S-6 in the Supplementary Information). Thus, this component should become negligible at pressures above 40 GPa. Theoretically, the proportion of the MgAlO_{2.5} component should decrease

more rapidly than demonstrated in this study because our starting sample was not ideally saturated with this component (see section S-6 in the Supplementary Information). It is noted that the oxygen fugacity has a negligible effect on the oxygen vacancy for Fe-free minerals (*e.g.*, Smyth and Stocker, 1975; Stocker and Smyth, 1978). Compositions of synthetic Al-bearing bridgmanite being consistent with each other by using different metal capsules (such as gold and rhenium) and also comparable to those of the glass starting materials in the present and previous studies (Navrotsky *et al.*, 2003; Kojitani *et al.*, 2007) further confirms this point. Therefore, pressure is the only factor to result in this rapid decrease of the MgAlO_{2.5} component in bridgmanite.

The present conclusion can be understood by a simple volume comparison based on the following reaction:



The molar volume of periclase (Per) under ambient conditions is 11.27 cm³/mole. The molar volumes of the hypothetical end members of MgAlO_{2.5} and Al₂O₃ bridgmanite (for Al cation number of 0.1 *per* formula unit) under ambient conditions are estimated to be 24.50 and 24.54 cm³/mole, respectively, from the volume composition data in Figure S-4 and Liu *et al.* (2016). Therefore, the molar volume of the left hand side component of Equation 1 is larger than that of the right hand side components by 1.92 cm³/mole, suggesting that the MgAlO_{2.5} component becomes unstable with increasing pressure (see Fig. S-5).

Geochemical Implications

Although the water storage of the lower mantle is uncertain, it has significant impacts on the chemical evolution of the mantle. The oxygen vacancy substitution, one of the most likely mechanisms, in aluminous bridgmanite may provide suitable storage sites to incorporate water in the shallower part of the lower mantle (*e.g.*, Navrotsky, 1999; Brodholt, 2000) according to the following reaction:



Although the volume of the MgHAIO₃ component in bridgmanite is unknown, we could assume that it has a similar volume with the MgAlO_{2.5} component because of an actually zero volume of the proton (Hernández *et al.*, 2013). Hence, H₂O is expected to be incorporated in bridgmanite as MgHAIO₃ in the lower mantle because of high pressures. Murakami *et al.* (2002) and Litasov *et al.* (2003) reported that synthetic Al-Fe-bearing bridgmanite in mantle peridotite can contain 1000–2000 ppm water at 26 GPa and 1500–1923 °K, which is significantly higher than that in synthetic MgSiO₃ bridgmanite at 24–25 GPa and 1573–1873 °K (Bolfan-Casanova *et al.*, 2000;



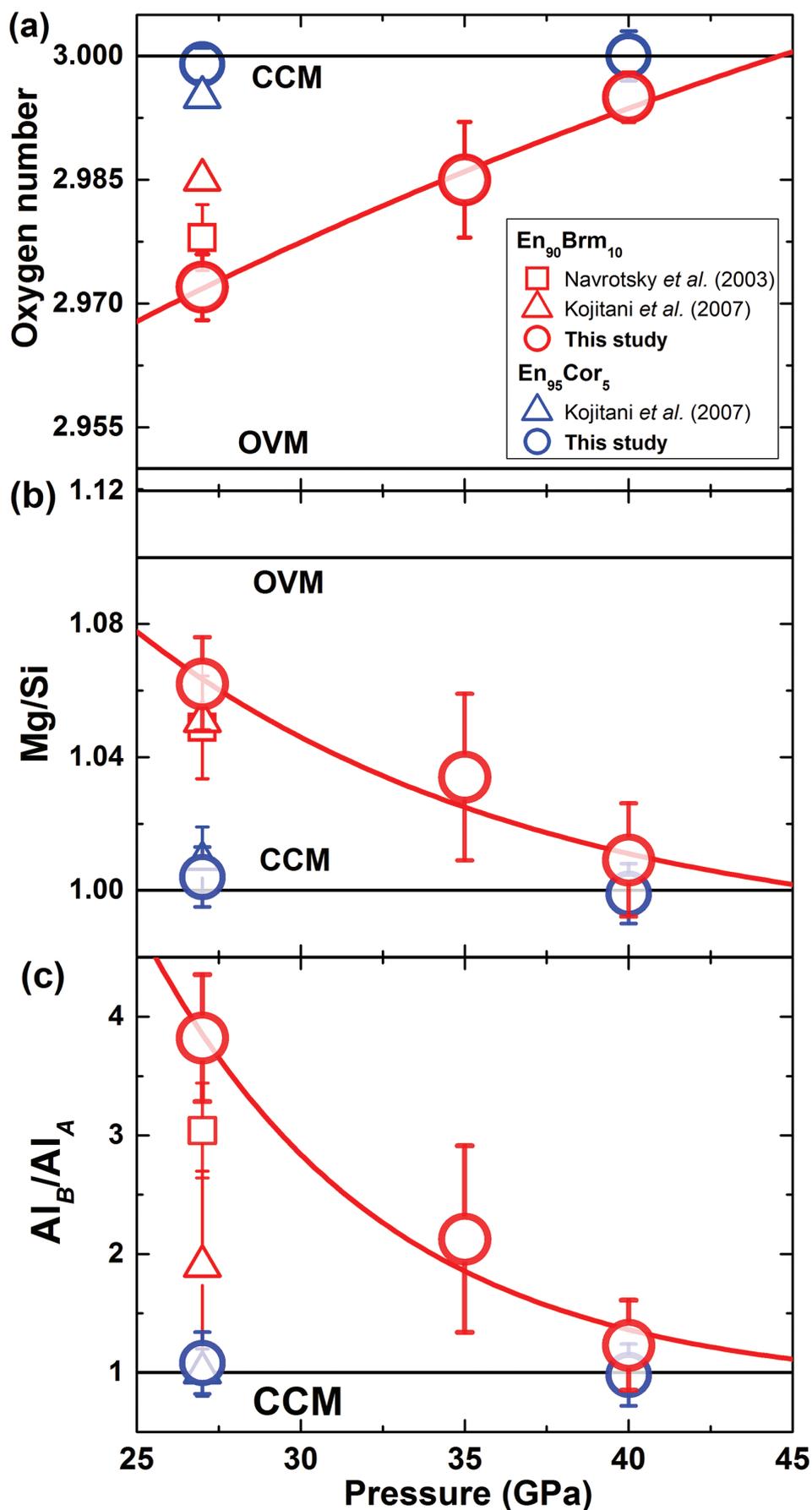


Figure 3 Plots of (a) oxygen number, (b) Mg/Si ratio, and (c) Al ratio in A and B sites (Al_B/Al_A) in bridgmanite for $En_{90}Brm_{10}$ and $En_{95}Cor_5$ versus pressure. The black lines represent the compositions associated with the oxygen-vacancy substitution mechanism (OVM) and charge-coupled substitution mechanism (CCM) for bridgmanite. The red line is the least squares fitting ($Mg/Si = A_{exp}(-P/B) + C$, where P is pressure) of the present data.

Litasov *et al.*, 2003). Following Equation 2, the amount of 2.2 mol. % MgAlO_{2.5} in bridgmanite can explain those reported high water amounts in bridgmanite. In contrast, Bolfan-Casanova *et al.* (2003) and Panero *et al.* (2015) showed that Al-Fe-bearing bridgmanite had a very low water content (<10 ppm) at 24–26 GPa and 1600–2000 °K. Even though bridgmanite contained these amounts of water in their experimental conditions, the water solubility should rapidly decrease with increasing pressure due to a rapid decrease of MgAlO_{2.5} component in bridgmanite. Since bridgmanite has a negligible MgAlO_{2.5} component at pressures above 40 GPa, no water could be stored in regions deeper than 1000 km depth, *i.e.* in the majority of the lower mantle. Furthermore, the ambient lower mantle temperatures (Katsura *et al.*, 2010) are too high for hydrous minerals (Walter *et al.*, 2015), therefore, we conclude that the majority of lower mantle is dry.

Shcheka and Keppler (2012) showed that MgSiO₃ bridgmanite contained ~1 wt. % argon at 25 GPa and 1873–2073 °K dissolved through oxygen-vacancy substitution. Theoretically, Al-bearing bridgmanite may accommodate larger amounts of argon than MgSiO₃ bridgmanite because of the higher proportion of oxygen vacancies in the uppermost part of the lower mantle. With increasing depths, the incorporation capacity of argon quickly diminishes, due to the rapidly decreasing oxygen vacancies in aluminous bridgmanite, and finally vanishes at depths deeper than 1000 km. Therefore, the explanation for the xenon anomaly in the Earth's atmosphere given by Shcheka and Keppler (2012) needs to be further investigated.

Bridgmanite, the most abundant phase in the lower mantle (80 vol. %; Irifune, 1994), dominates the viscosity of this region (Girard *et al.*, 2016). Seismic observation suggests that some slabs stagnate at 600–1000 km depths (Fukao and Obayashi, 2013). Since there are no phase transitions in this region, some special explanations are required. One explanation is the increase of viscosity with depth in this region. Since the viscosity of minerals is controlled by atomic diffusivity (Karato and Wu, 1993), the decrease of oxygen-vacancies in aluminous bridgmanite will cause a decrease in element diffusivity. Therefore, the expected decrease in diffusivity for aluminous bridgmanite should cause a high viscosity, which may explain this mid-lower mantle slab stagnation.

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Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1739

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