



RESEARCH ARTICLE

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Pressure Destabilizes Oxygen Vacancies in Bridgmanite

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Key Points:

- MgFeO_{2.5}, FeFeO₃, and total Fe³⁺ contents in bridgmanite decrease with increasing pressure
- Fe³⁺-linked oxygen vacancies in bridgmanite are destabilized by increasing pressure
- MgFeO_{2.5} can be formed in Fe³⁺-rich bridgmanite under the topmost lower mantle conditions

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Bridgmanite may contain a large proportion of ferric iron in its crystal structure in the forms of FeFeO₃ and MgFeO_{2.5} components. We investigated the pressure dependence of FeFeO₃ and MgFeO_{2.5} contents in bridgmanite coexisting with MgFe₂O₄-phase and with or without ferropericlae in the MgO-SiO₂-Fe₂O₃ ternary system at 2,300 K, 33 and 40 GPa. Together with the experiments at 27 GPa reported in Fei et al. (2020, <https://doi.org/10.1029/2019GL086296>), our results show that the FeFeO₃ and MgFeO_{2.5} contents in bridgmanite decrease from 7.6 to 5.3 mol % and from 2 to 3 mol % to nearly zero, respectively, with increasing pressure from 27 to 40 GPa. Accordingly, the total Fe³⁺ decreases from 0.18 to 0.11 pfu. The formation of oxygen vacancies (MgFeO_{2.5} component) in bridgmanite is therefore dramatically suppressed by pressure. Oxygen vacancies can be produced by ferric iron in Fe³⁺-rich bridgmanite under the topmost lower mantle conditions, but the concentration should decrease rapidly with increasing pressure. The variation of oxygen-vacancy content with depth may potentially affect the physical properties of bridgmanite and thus affect mantle dynamics.

Plain Language Summary Bridgmanite is the most abundant mineral in the Earth's lower mantle. Although its basic chemical formula is MgSiO₃, large amounts of Fe³⁺ can be added in the following two ways: (1) Two Fe³⁺ replace Mg²⁺ and Si⁴⁺ and form the FeFeO₃ component. This is called charge-coupled substitution because the overall charge does not change. (2) One Fe³⁺ replaces one Si⁴⁺ and forms the MgFeO_{2.5} component. Here the loss of positive charge is compensated by a loss of oxygen and is therefore called oxygen-vacancy substitution. In this study, we measured the effect of pressure on the abundance of these two components of bridgmanite. We found that the MgFeO_{2.5} content decreases greatly with increasing pressure. Some oxygen sites may therefore be vacant in bridgmanite at the top of lower mantle, but the concentration of oxygen vacancies should decrease rapidly in deeper regions. The decrease of oxygen-vacancy concentration in bridgmanite will change the nature of the lower mantle, for example, rocks will become harder, and electrical conductivity will decrease with increasing depth.

1. Introduction

It is known that the disproportionation reaction of iron from Fe²⁺ to Fe³⁺ and Fe⁰ can occur in Earth's deep lower mantle (Armstrong et al., 2019; Frost et al., 2004). In particular, the separation of metallic iron and Fe³⁺-bearing silicate magma during core formation would raise the Fe³⁺/ΣFe ratio in silicate magma, resulting in high proportion of Fe³⁺ in deep mantle minerals that precipitated from the magma ocean (e.g., Andraut et al., 2018; Armstrong et al., 2019; Boujibar et al., 2016; Frost et al., 2008). On the other hand, the redox-induced density contrast may produce locally Fe³⁺-rich regions (Gu et al., 2016), whereas slabs may transport oxidized components into the deep mantle by subduction (Zhao et al., 2021). Therefore, it is expected that minerals in the deep mantle may contain large amount of Fe³⁺ (Fe³⁺/ΣFe up to 60% or more), at least locally (e.g., Armstrong et al., 2019; Bindi et al., 2020; Boujibar et al., 2016; Frost et al., 2004; Grocholski et al., 2009; Gu et al., 2016; Jackson et al., 2005; Kuppenko et al., 2015; Kurnosov et al., 2017; Lauterbach et al., 2000; Li et al., 2006; McCammon, 1997; Piet et al., 2016; Prescher et al., 2014; Shim et al., 2017; Sinmyo et al., 2011), although they are under relatively reducing conditions with oxygen fugacity close to the iron-wüstite buffer (Frost & McCammon, 2008). Since Fe³⁺ may affect the chemical and physical properties of minerals by changing their defect chemistry (e.g., Creasy et al., 2020; Fei et al., 1994; Glazyrin et al., 2014; Holzapfel et al., 2005; Liu et al., 2018; Sinmyo et al., 2019;

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Wang et al., 2021), knowledge of mineral phase relations in Fe³⁺-rich systems is critical for investigating the structure, dynamics, and evolution of Earth's mantle.

Bridgmanite is stabilized in the pressure range 23–125 GPa (e.g., Ishii et al., 2018; Murakami et al., 2004) and is the dominant mineral in Earth (e.g., Irifune & Ringwood, 1987a, 1987b). It can incorporate large amounts of trivalent elements such as Al³⁺ and Fe³⁺ in its crystal structure (e.g., Andrault et al., 1998; McCammon, 1997; Navrotsky, 1999; Navrotsky et al., 2003; Shim et al., 2017) by the formation of XXO₃ and MgXO_{2.5} components (X is Fe³⁺ or Al³⁺) via charge-coupled and oxygen-vacancy mechanisms, respectively (e.g., Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021; Lauterbach et al., 2000; Liu, Akaogi, & Katsura, 2019; Liu, Ishii, & Katsura, 2017; Liu, Boffa-Ballaran, et al., 2019; Liu et al., 2020; Navrotsky, 1999; Navrotsky et al., 2003; Nishio-Hamane et al., 2005, 2008; O'Neill & Jeanloiz, 1994). The different substitution mechanisms thus produce different types of defect species. The defect-controlled physical properties of bridgmanite such as atomic diffusivity, elasticity, plasticity, and electrical conductivity will depend on the substitution mechanisms (e.g., Andrault et al., 2007, 2001; Boffa-Ballaran et al., 2012; Brodholt, 2000; Creasy et al., 2020; Daniel et al., 2004; Frost & Langenhorst, 2002; Saikia et al., 2009; Xu et al., 1998; Yagi et al., 2004; Yoshino et al., 2016; Zhang & Weidner, 1999).

The Al³⁺ substitution mechanism in Fe³⁺-free bridgmanite has been systematically studied (e.g., Andrault et al., 1998; Brodholt, 2000; Grüninger et al., 2019; Kojitani, Katsura, & Akaogi, 2007; Liu, Akaogi, & Katsura, 2019; Liu, Ishii, & Katsura, 2017; Liu, Boffa-Ballaran, et al., 2019; Navrotsky et al., 2003; Panero et al., 2006; Stebbins et al., 2003; Walter et al., 2004, 2006; Yamamoto et al., 2003). It has been found that the MgAlO_{2.5} component is formed in MgO-excess systems, but not in SiO₂-excess systems (Liu, Akaogi, & Katsura, 2019; Liu, Boffa-Ballaran, et al., 2019). The concentration of AlAlO₃ increases with pressure and temperature, whereas the MgAlO_{2.5} content increases with temperature but decreases with pressure (Brodholt, 2000; Liu, Ishii, & Katsura, 2017; Liu, Nishi, et al., 2017; Liu, Akaogi, & Katsura, 2019).

In contrast to Al³⁺ substitution, the Fe³⁺ substitution mechanism in bridgmanite has been less studied. The majority of previous studies focused on Fe³⁺-Al³⁺ coupling (e.g., Frost & Langenhorst, 2002; Liu, Dubrovinsky, et al., 2019; Liu et al., 2020; Mohn & Trønnes, 2016; Nishio-Hamane et al., 2005; Richmond & Brodholt, 1998; Saikia et al., 2009; Vanpeteghem et al., 2006; Walter et al., 2004), and only a few studies examined Fe³⁺ substitution in Fe³⁺-rich systems. Earlier studies regarding Fe³⁺ substitution in Fe³⁺-rich bridgmanite show a dominance of the charge-coupled substitution mechanism (Andrault & Bolfan-Casanova, 2001; Catalli et al., 2010). However, recent studies with well-constrained chemical compositions (Fei et al., 2020; Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Hummer & Fei, 2012; Sinmyo et al., 2014) show that bridgmanite can contain 2–3 mol % of the MgFeO_{2.5} component in addition to the FeFeO₃ component in the presence of ferropericlase at 25–27 GPa, that is, relatively low-pressure conditions of the bridgmanite stability field. It was also demonstrated that the FeFeO₃ content increases with increasing temperature, whereas the MgFeO_{2.5} content is independent of temperature (Fei et al., 2020). However, the pressure dependence of Fe³⁺ substitution in bridgmanite is still unclear.

In this study, we investigated the substitution mechanism of Fe³⁺ in Al³⁺-free bridgmanite using a recently developed ultrahigh-pressure (>25 GPa) multianvil technique with tungsten carbide anvils (Ishii et al., 2016, 2019) at 33 and 40 GPa at 2300 K. Although bridgmanite in the lower mantle contains Al³⁺, which could affect the Fe³⁺ substitution as mentioned above, we investigated the Al³⁺-free system to provide basic understanding of the roles of trivalent cations in bridgmanite chemistry. To maximize the MgFeO_{2.5} content in bridgmanite, experiments were performed in the MgO-SiO₂-Fe₂O₃ system where bridgmanite coexists with MgFe₂O₄-phase, and with/without ferropericlase. Together with our recent work at 27 GPa (Fei et al., 2020), we show that the concentrations of both FeFeO₃ and MgFeO_{2.5} in bridgmanite, and thus the total Fe³⁺ content, decrease with increasing pressure. Even coexisting with ferropericlase, the formation of oxygen vacancies is completely suppressed at about 40 GPa. Our results provide basic knowledge about the phase relations and Fe³⁺ substitution mechanisms in bridgmanite under Fe³⁺-rich conditions.

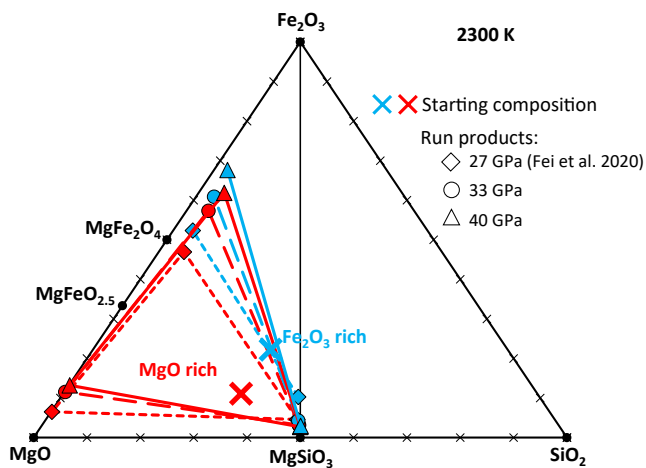


Figure 1. Chemical compositions of MgO-rich and Fe₂O₃-rich starting materials and run products in the ternary phase diagram with endmembers of Fe₂O₃, MgO, and SiO₂. The 27 GPa run was already reported in Fei et al. (2020).

2. Experimental Procedure

2.1. High-Pressure Multianvil Experiments

The starting materials used in this study were identical to those in Fei et al. (2020), that is, mixtures with compositions of 5MgO + 3SiO₂ + 1Fe₂O₃ (MgO-rich sample) and 4MgO + 3SiO₂ + 2Fe₂O₃ (Fe₂O₃-rich sample) prepared from SiO₂, MgO, and Fe₂O₃ oxides (Figure 1). The purity of each oxide was >99.9%. Platinum chambers with inner diameter of 0.3 mm, outer diameter of 0.4 mm, and length of 0.3 mm were used as sample capsules, which were placed in a Al₂O₃ sleeve in the LaCrO₃ furnace. A Cr₂O₃-doped MgO octahedron with edge length of 5.7 mm was used as the pressure medium (Figure 2).

High pressures were generated by tungsten carbide anvils with truncation edge lengths of 1.5 mm using the 15 MN multianvil press, IRIS-15, at the University of Bayreuth (Ishii et al., 2016). The experimental pressures were 33 and 40 GPa (Table 1). The temperature and annealing duration were 2,300 K and 24 hr, respectively. After annealing, the heating power supplier was switched off, by which the temperature decreased to less than 800 K within 1 s and to less than 400 K within 2–4 s. Afterward, the pressure was decreased to ambient conditions over durations exceeding 15 hr.

2.2. Sample Analysis

- (1) *Scanning Electron Microscopy (SEM)*. Cross sections of the recovered assemblies were prepared and analyzed by SEM. Backscattered electron images (BSE) were taken on the cross sections (Figure 3). The presented phases on the cross sections were examined by an energy dispersive detector
- (2) *X-ray Diffraction*. Microfocus X-ray diffraction analyses were performed using a microfocus X-ray diffractometer (Bruker AXS D8 Discover) with a microfocus source of Co-K α radiation. The beam diameter was about 100 μ m focused on the cross sections of the recovered samples. The acceleration voltage and beam current were 40 kV and 500 μ A, respectively. The exposure time was 5–6 hr for each analysis. Examples of the diffraction patterns are shown in Figure 4
- (3) *Mössbauer Spectroscopy*. Synchrotron Mössbauer source (SMS) spectroscopy analyses were performed under ambient conditions on all the samples at beamline BL10XU, SPring-8, Japan. The detailed setup and analytical conditions of SMS spectroscopy are given in Hirao et al. (2020). The spectra were fitted using MossA with Lorentzian doublets (Prescher et al., 2012) (Figure 5)
- (4) *Electron Microprobe Analysis*. The chemical compositions of bridgmanite and coexisting phases were obtained by electron probe microanalyzer (EPMA) at the University of Bayreuth. The acceleration voltage was 15 kV, the beam current was 5 nA, and the counting time was 20 s for each point analysis. An enstatite standard was used for Mg and Si, whereas metallic iron was used for Fe. Tests were also made using a Fe₂O₃-standard for analysis of Fe in the samples, which did not show any meaningful difference compared to results using a metallic-Fe standard. Grains near the Pt capsule wall were avoided in the analyses

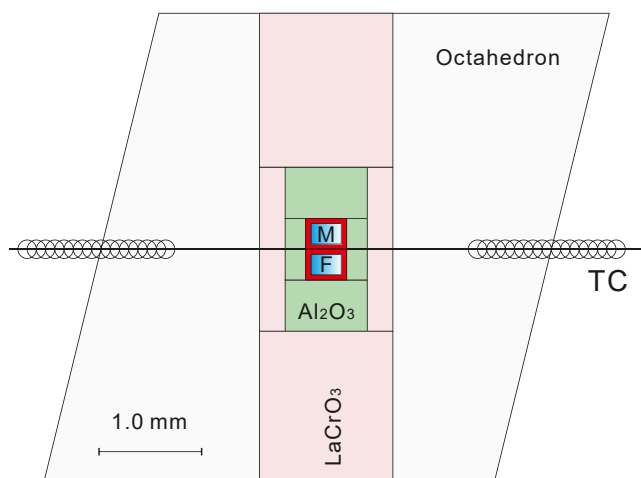


Figure 2. Design of the 5.7/1.5 multianvil cell assembly for 33 and 40 GPa runs. M: MgO-rich starting material. F: Fe₂O₃-rich starting material.

2.3. Calculation of Chemical Formula

Assuming that MgSiO₃ + MgFeO_{2.5} + FeFeO₃ = 100% in the recovered bridgmanite samples, the molar concentrations of the three components were obtained from the equation (Grüniger et al., 2019; Liu, Ishii, & Katsura, 2017),

Table 1
List of Run Conditions and Chemical Compositions of the Run Products

Starting material	Run. No.	Assembly	P (GPa)	T (h)	Phase	N	MgO wt%	SiO ₂ wt%	Fe ₂ O ₃ wt%	Total wt%	Mg pfu	Si pfu	Fe pfu	Bridgmanite (mol %)			MgFe ₂ O ₄ -phase (mol %)			Ferropericlasite (mol %)							
														FeFeO ₃	MgFeO _{2.5}	MgSiO ₃	Mg ₂ SiO ₄	MgFe ₂ O ₄	Fe _{8/7} O ₄	FeO	MgO	FeO					
MgO-rich	I574 (Fei et al., 2020)	7/3	27	9	Bridgmanite	17	35.94 (99)	52.29 (80)	13.47 (42)	101.70 (123)	0.923 (15)	0.902 (13)	0.175 (7)	7.6 (15)	2.2 (27)	90.2 (13)	-	-	-	-	-						
Fe ₂ O ₃ -rich	I574 (Fei et al., 2020)	7/3	27	9	Bridgmanite	15	29.72 (94)	43.57 (194)	26.67 (211)	99.96 (170)	0.821 (18)	0.807 (25)	0.372 (36)	17.9 (18)	1.4 (26)	80.7 (25)	-	-	-	-	-						
Fe ₂ O ₃ -rich	I646 (Fei et al., 2020)	7/3	27	20	Bridgmanite	9	31.45 (94)	46.78 (126)	23.40 (246)	101.63 (67)	0.843 (19)	0.841 (18)	0.316 (35)	15.7 (19)	0.2 (13)	84.1 (18)	-	-	-	-	-						
Fe ₂ O ₃ -rich	I873	5.7/1.5	33	24	Bridgmanite	20	35.50 (83)	52.10 (97)	12.58 (142)	100.18 (95)	0.924 (13)	0.910 (11)	0.166 (20)	7.6 (13)	1.4 (14)	91.0 (11)	-	-	-	-	-						
Fe ₂ O ₃ -rich	I909	5.7/1.5	40	24	Bridgmanite	24	37.67 (66)	56.14 (103)	8.31 (59)	102.12 (134)	0.947 (13)	0.947 (11)	0.106 (8)	5.3 (13)	0.0 (23)	94.7 (11)	-	-	-	-	-						

Note. All experiments were performed at 2,300 K. Runs I574 and I646 at 27 GPa are already reported in Fei et al. (2020). P: pressure. T: annealing time. N: number of analyzed points by electron microprobe. The error bars are one standard deviation of N points from electron microprobe analysis.

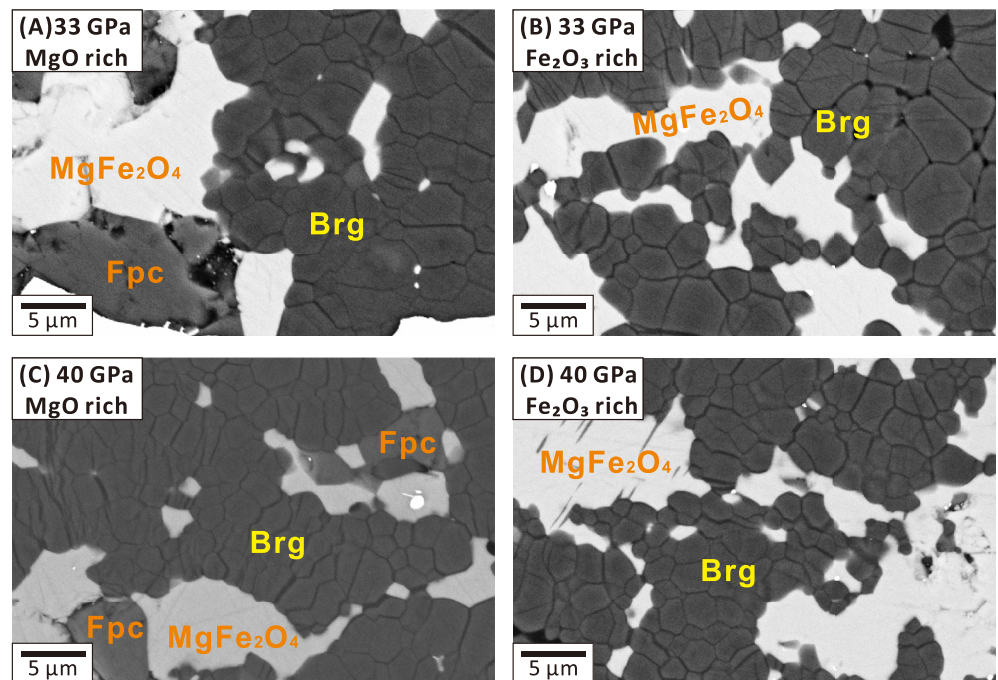


Figure 3. SEM images of samples recovered from 33 (a, b) and 40 GPa (c, d). Brg: bridgmanite. Fpc: ferropericlaase. $MgFe_2O_4$: $MgFe_2O_4$ -phase.

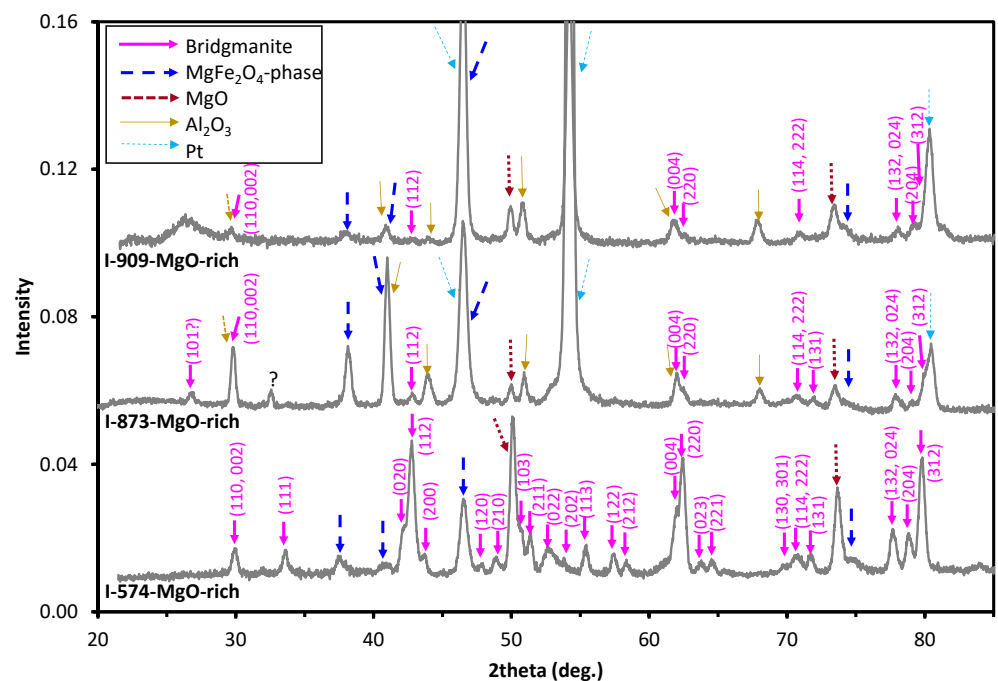


Figure 4. X-ray diffraction spectra of the recovered samples (MgO-rich conditions). Pt and Al_2O_3 peaks are from the sample capsule and the sleeve outside of the capsule in the cell assembly (Figure 2), respectively, owing to the limited spatial resolution of the diffractometer. The $MgFe_2O_4$ -phase show consistent peaks at different pressures, indicating the same structure. The spectra are background subtracted. The identified peaks of bridgmanite are labeled in the figure (hkl), and their d-spacings and fitted lattice parameters are given in the online Supporting Information (Table S1).

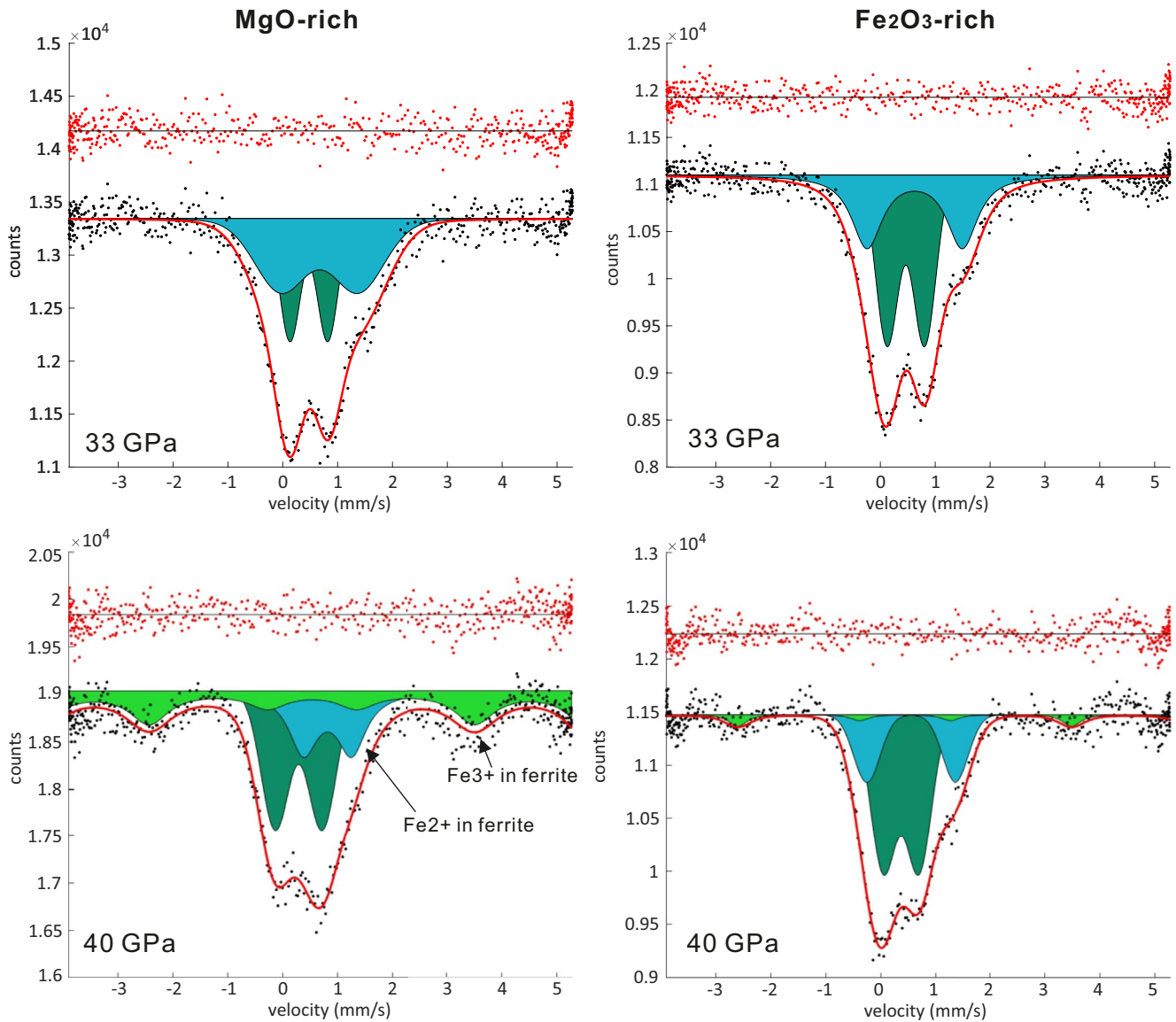


Figure 5. Synchrotron Mössbauer source spectra of the recovered samples. Left: MgO-rich samples. Right: Fe₂O₃-rich samples. A baseline was subtracted from the raw spectra determined from a calibration using the single-line absorber K₂Mg⁵⁷Fe(CN)₆. The dark green doublets correspond to Fe³⁺ in bridgmanite, the blue doublets are Fe³⁺ or Fe^{2.5+} in nonmagnetic MgFe₂O₄-phase, and the light green doublets are Fe³⁺ in magnetic MgFe₂O₄-phase.

$$\text{Mg}_a\text{Fe}_b\text{Si}_c\text{O}_{a+1.5b+2c} = c\text{MgSiO}_3 + (a - c)\text{MgFeO}_{2.5} + \frac{b - a + c}{2}\text{FeFeO}_3 \quad (1)$$

where the atomic ratio of Mg, Fe, and Si ($a : b : c$) in bridgmanite was taken from EPMA. The presence of an MgFeO_{2.5} component can be indicated by higher Mg atomic content than Si ($a > c$), whereas there should be no MgFeO_{2.5} component if $a = c$. The Mg content could be lower than Si ($a < c$) if Fe³⁺ is partially reduced, which is not the case in this study since Fe³⁺/ΣFe ≈ 100% based on Mössbauer analysis as described later.

Similarly, the concentrations of MgFe₂O₄, Mg₂SiO₄, and Fe_{8/3}O₄ components in the MgFe₂O₄-phase were calculated from the EPMA results by assuming Fe³⁺/ΣFe ≈ 100%, whereas MgO and FeO components in ferropericlase were calculated by assuming all Fe as ferrous (Table 1).

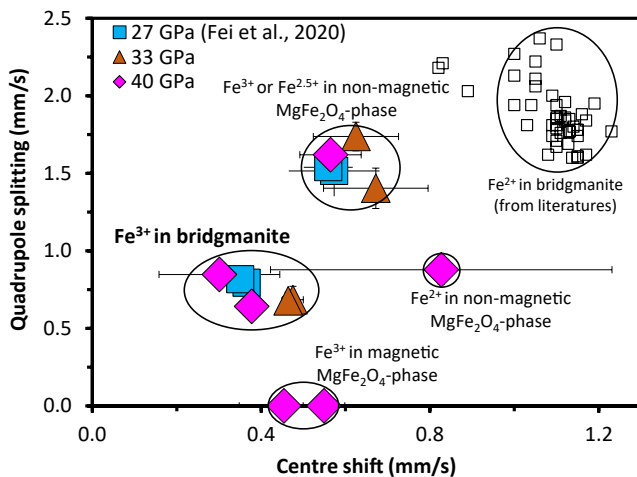


Figure 6. Center shift and quadrupole splitting derived from fits of the Mössbauer spectra. There is no detectable Fe^{2+} in bridgmanite, which should have center shift and quadrupole splitting of about 0.9–1.2 and 1.5–2.5 mm/s, respectively, based on the literature data as shown by open squares (Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Lauterbach et al., 2000; McCammon, 1998; Sinmyo et al., 2019).

and quadrupole splitting (QS) of 0.9–1.2 and 1.5–2.5 mm/s, respectively (e.g., Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Hummer & Fei, 2012; Lauterbach et al., 2000; McCammon, 1998; Sinmyo et al., 2019), was not detected in any plausible fit. Instead, doublets of Fe^{3+} or $\text{Fe}^{2.5+}$ in nonmagnetic MgFe_2O_4 -phase were identified in the run products from all high-pressure conditions, whereas Fe^{2+} in nonmagnetic MgFe_2O_4 -phase and Fe^{3+} in magnetic MgFe_2O_4 -phase were fitted in the 40 GPa samples (Figures 5 and 6). Because of the small proportion of ferropericlasite, doublets of ferropericlasite are not observed within the experimental data scatter.

3.3. Composition of Bridgmanite, MgFe_2O_4 -Phase, and Ferropericlasite

By comparison of bridgmanite compositions at 33 and 40 GPa with that at 27 GPa from Fei et al. (2020), it is found that the Fe^{3+} content in bridgmanite under MgO-rich conditions decreases dramatically from ~ 0.17 pfu at 27 GPa (Fei et al., 2020) to ~ 0.11 pfu at 40 GPa (Figure 7a). As expected, the Fe_2O_3 -rich samples have higher Fe^{3+} content than the MgO-rich samples, and Fe^{3+} content decreases from 0.37 to 0.12 pfu at 27–40 GPa (Figure 7a). The Mg/Si ratios in bridgmanite are slightly higher than unity in the MgO-rich samples, whereas they are essentially unity in the Fe_2O_3 -rich samples (Table 1).

The composition of the MgFe_2O_4 -phase deviates from the MgFe_2O_4 endmember (Figure 1). With increasing pressure from 27 to 40 GPa, the Fe^{3+} content increases from 1.9 to 2.3 pfu, and the Mg content decreases from 0.9 to 0.5 pfu. The Si content is low but detectable (~ 0.1 pfu) (Figure 7b). Additionally, up to 13.2 mol % Fe was found in ferropericlasite (Figure 7c).

4. Discussion

4.1. Fe^{3+} and Fe^{2+} Partitioning Between Bridgmanite and Ferropericlasite

The Fe contents [$\text{Fe}/(\text{Fe} + \text{Mg})$] in ferropericlasite of the MgO-rich samples are 6.5–13.2% (Figure 7c). If all Fe were ferrous in ferropericlasite, the partition coefficient of Fe^{2+} between bridgmanite and ferropericlasite would be nearly zero based on the absence of Fe^{2+} in the current bridgmanite samples. The partition coefficient is thus much smaller than that suggested by previous studies (e.g., Nakajima et al., 2012; Prescher et al., 2014; Xu et al., 2017), who reported values of 0.2–0.4 at 25–40 GPa. We emphasize that this discrepancy cannot be caused by undetectable Fe^{2+} in our bridgmanite samples. If the Fe^{2+}/Mg partition coefficient given by previous

3. Experimental Results

3.1. Phase Assemblages in the Recovered Samples

The recovered MgO-rich and Fe_2O_3 -rich samples contain bridgmanite, a phase close to MgFe_2O_4 composition (hereafter MgFe_2O_4 -phase), and either with (MgO-rich samples) or without (Fe_2O_3 -rich samples) ferropericlasite (Table 1 and Figure 1), as demonstrated by the backscattering images (Figure 3) and X-ray diffraction (Figure 4). No observable inhomogeneity of phase compositions was found throughout the capsules, indicating that chemical equilibrium was reached.

The MgFe_2O_4 -phase was previously assigned to be a CaMn_2O_4 -type structure (Andrault & Bolfan-Casanova, 2001; Fei et al., 2020) or CaTi_2O_4 -type structure (Greenberg et al., 2017), and recently suggested to be a new structure (modified Na-Fe-Ti oxide-type) of post-spinel (Ishii et al., 2020). Our study primarily focused on the bridgmanite phase without considering the structural complexities of the MgFe_2O_4 -phase.

3.2. $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the Run Products

Mössbauer spectra unambiguously indicate the predominance of Fe^{3+} in bridgmanite (Figures 5 and 6). Although fitting models are not unique due to the high degree of line overlap, the Fe^{2+} in bridgmanite as $\text{Fe}^{2+}\text{SiO}_3$ component, whose hyperfine parameters are expected to have center shift (CS)

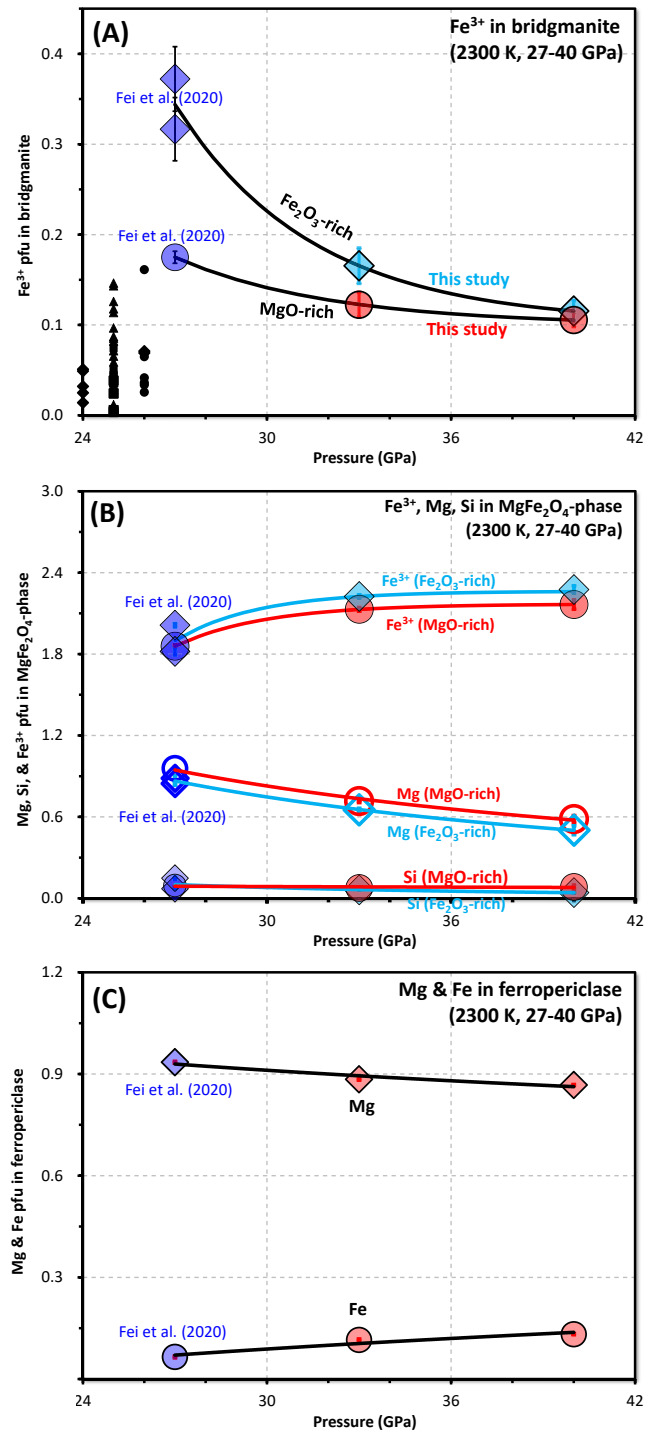


Figure 7. Chemical composition of bridgmanite, ferropericlasite, and MgFe₂O₄-phase in run products. (a) Fe³⁺ content in bridgmanite calculated to O = 3. (b) Mg, Si, and Fe³⁺ contents in the MgFe₂O₄-phase calculated to O = 4. (c) Mg and Fe content in ferropericlasite from MgO-rich samples calculated to O = 1 assuming that all Fe is ferrous in ferropericlasite. Black symbols represent the Fe³⁺ content in bridgmanite that coexists with ferropericlasite reported in previous studies (Frost & Langenhorst, 2002; Frost et al., 2004; Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Hummer & Fei, 2012; Lauterbach et al., 2000), all of which are lower than this study because their experimental temperatures are lower, and/or MgFe₂O₄-phase did not appear (namely Fe³⁺ is not saturated). The data points with blue symbols at 27 GPa are from Fei et al. (2020). The error bars represent one standard deviation of the analyzed points by electron microprobe as shown in Table 1.

studies were followed by our samples, $\text{Fe}^{2+}/\Sigma\text{Fe}$ should be 15–50% in bridgmanite. Such a significant fraction of Fe^{2+} would definitely be detectable by both in-house (Fei et al., 2020) and synchrotron (this study) Mössbauer spectroscopy because the hyperfine parameters of Fe^{2+} doublets in bridgmanite are well known and would not overlap with other components in our spectra (e.g., Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Sinmyo et al., 2019; Yoshino et al., 2016, Figure 6). Therefore, the appearance of 6.5–13.2 mol % FeO in ferropericlase does not suggest the presence of Fe^{2+} in bridgmanite. Since the experiments in previous studies (e.g., Nakajima et al., 2012; Prescher et al., 2014) were mostly performed under relatively reducing conditions with high $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios, one explanation for this discrepancy is that Fe^{2+} is almost entirely incorporated into ferropericlase when the bulk Fe^{2+} content in the system is extremely low, that is, the partition coefficient may have a substantial compositional dependence.

4.2. Fe^{3+} Content in Bridgmanite

Based on the phase rule, the Fe^{3+} content in bridgmanite under MgO-rich conditions should be uniquely constrained because three phases coexist in the system. Although some Fe_2O_3 might be reduced to FeO in high-pressure experiments as indicated by the presence of Fe in ferropericlase in MgO-rich samples (Figure 7a), the number of components in bridgmanite is still three because the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio is close to 100% in bridgmanite as demonstrated by Mössbauer spectroscopy.

The Fe_2O_3 -rich samples in this study and some other studies (e.g., Andrault & Bolfan-Casanova, 2001; Liu et al., 2018; Wang et al., 2021) show much higher Fe^{3+} contents in bridgmanite (up to 1.0 pfu) than the current MgO-rich bridgmanite samples. However, these high Fe^{3+} -content bridgmanite samples did not coexist with ferropericlase (bridgmanite + MgFe_2O_4 -phase in Fe_2O_3 -rich samples in this study and only bridgmanite in Andrault & Bolfan-Casanova, 2001, Liu et al., 2018, and Wang et al., 2021). When bridgmanite coexists with ferropericlase, the Fe^{3+} content in bridgmanite will be limited because of the formation of the MgFe_2O_4 -phase from FeFeO_3 and MgO (Andrault & Bolfan-Casanova, 2001). When bridgmanite does not coexist with MgO, the Fe^{3+} content in bridgmanite depends on the starting material. If the bulk Fe^{3+} content in the starting material is high, the Fe^{3+} content in bridgmanite can accordingly be high based on the phase relations in Figure 1, for example, Fe^{3+} can reach 1.0 pfu as shown in Liu et al. (2018) and Wang et al. (2021). This is understandable because the molar volume of hematite ($30.5 \text{ cm}^3/\text{mol}$) is slightly larger than the FeFeO_3 component in bridgmanite ($29.55 \text{ cm}^3/\text{mol}$, Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021). Therefore, Fe^{3+} may tend to be incorporated in bridgmanite by a MgSiO_3 - Fe_2O_3 solid solution instead of forming hematite, consequently, the Fe^{3+} solubility in bridgmanite is high. The upper limit of Fe^{3+} content should be obtained in the system with coexistence of bridgmanite and hematite, which was not investigated in this study. Additionally, the formation of the FeAlO_3 component will also increase the Fe^{3+} content in Al-bearing bridgmanite, which causes the high Fe^{3+} content (about 0.7 pfu) in Liu, Dubrovinsky, et al. (2019) and Liu et al. (2020).

The MgFe_2O_4 -phase may have structural complexities (e.g., Andrault & Bolfan-Casanova, 2001; Greenberg et al., 2017; Ishii et al., 2020), which may affect Fe^{3+} partitioning between bridgmanite and the MgFe_2O_4 -phase and thus affect the Fe^{3+} content in bridgmanite. Some studies reported phase transitions among polymorphs of MgFe_2O_4 at high temperatures below 25 GPa (e.g., Ishii et al., 2020; Uenver-Thiele et al., 2017), and at ambient temperature in the pressure range 25–40 GPa (Greenberg et al., 2017). However, no phase transition of MgFe_2O_4 has been reported at the conditions of our experiments, that is, 2,300 K and 27–40 GPa. The absence of a phase transition of the MgFe_2O_4 -phase in this study has also been indicated by X-ray diffraction of the recovered samples (Figure 4). Therefore, the systematic decrease of Fe^{3+} content in bridgmanite is not expected to be caused by complex polymorphism of MgFe_2O_4 .

4.3. Pressure Dependence of Fe^{3+} Substitution in Bridgmanite

In the MgO-rich samples, the FeFeO_3 content in bridgmanite decreases from 7.7 to 5.3 mol %, whereas the $\text{MgFeO}_{2.5}$ content decreases from 2.2 to ~0% at 27–40 GPa (Figure 8a). The extrapolation of data agrees well with the maximum $\text{MgFeO}_{2.5}$ content of 3.5% reported by Hummer and Fei (2012) at 25 GPa and 1,970–2,070 K (Figure 8a). In contrast, Fe_2O_3 -rich samples have FeFeO_3 contents ranging from 17.9% to 5.9%, which is higher than the MgO-rich samples, and have $\text{MgFeO}_{2.5}$ contents that are essentially zero within error over the entire investigated pressure range (Figure 8b).

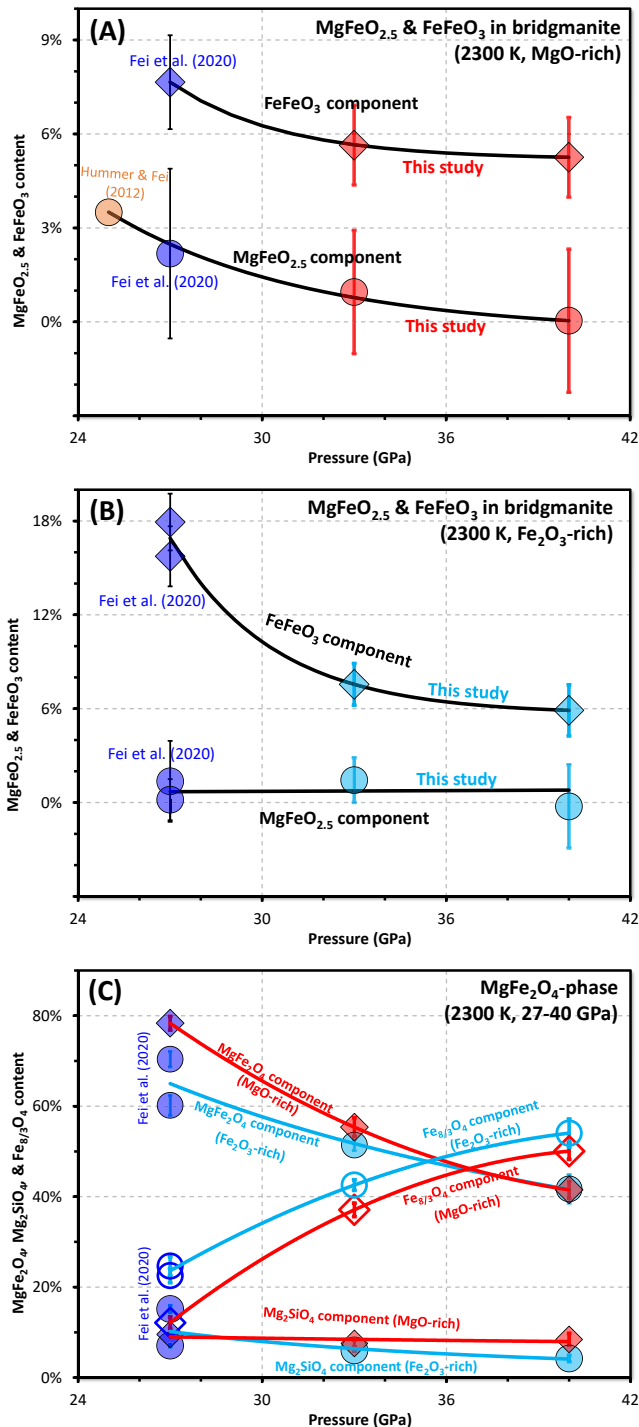
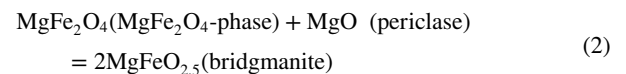


Figure 8. Substitution mechanisms in bridgmanite and MgFe₂O₄-phase. (a) Fe³⁺ substitution in bridgmanite under MgO-rich conditions. The maximum MgFeO_{2.5} content reported by Hummer and Fei (2012) at 25 GPa, 1,970–2,070 K is also shown for comparison. (b) Fe³⁺ substitution in bridgmanite under Fe₂O₃-rich conditions. (c). Substitution mechanisms in the MgFe₂O₄-phase. The data points with blue symbols at 27 GPa are from Fei et al. (2020). The error bars represent one standard deviation of the analyzed points by electron microprobe as shown in Table 1.

Note that smaller Pt capsules were used in the runs at 33 and 40 GPa in this study compared to the 27 GPa runs in Fei et al. (2020). Because Pt capsules may absorb Fe from the samples and thus release O₂, more O₂ might be released in 33 and 40 GPa runs relative to sample volumes. However, the O₂ formed by Fe dissolution in Pt should not cause MgFeO_{2.5} content to decrease with increasing pressure. Since Fe³⁺/ΣFe ≈ 100% in bridgmanite in all runs, the chemistry of bridgmanite in MgO-rich samples is uniquely constrained with maximized Fe³⁺ content and maximized Fe³⁺/ΣFe ratio. Excess O₂ cannot further oxidize bridgmanite. Therefore, the chemistry of bridgmanite from MgO-rich samples in this study will not be affected by excess O₂. Although the excess O₂ may produce peroxide components (Hu et al., 2016; Zhu et al., 2019), it requires pressures >70 GPa, which is not the case in this study.

Because of the uncertainties in the Mg, Si, and Fe contents obtained from EPMA analysis (Table 1), the error bars are relatively large for the relatively small MgFeO_{2.5} contents (Figure 7a). Additionally, the reproducibility of MgFeO_{2.5} content obtained in different runs under the same pressure and temperature conditions is about ±0.3–1.25 mol % (Table 1 and Fei et al., 2020), which is not negligible. These problems make it challenging to obtain a definite conclusion regarding the pressure dependence of the MgFeO_{2.5} content. However, plots of Mg and Si contents in bridgmanite versus Fe³⁺ content show that data at 27 GPa and 1,700–2,300 K under MgO-rich conditions clearly deviate from the theoretical Mg and Si contents of pure FeFeO₃ substitution, whereas they essentially follow the trend of the pure FeFeO₃ substitution mechanism in Fe₂O₃-rich samples (Figure 9 and Fei et al., 2020). This behavior demonstrates the presence of MgFeO_{2.5} components at 27 GPa under MgO-rich conditions. In contrast to the 27-GPa data, the 33-GPa data are closer to the pure FeFeO₃ substitution, and the 40-GPa data are exactly on the trend of pure FeFeO₃ substitution even in MgO-rich samples (Figure 9), which suggests a decrease of MgFeO_{2.5} content with increasing pressure. Therefore, the reduction of MgFeO_{2.5} content with increasing pressure is convincing despite relatively large uncertainties of absolute MgFeO_{2.5} contents.

The suppression of Fe³⁺-linked oxygen vacancies with increasing pressure can be understood by the volume increase associated with MgFeO_{2.5} formation. Partial molar volume of the MgFeO_{2.5} component in bridgmanite is estimated to be 27.65 cm³/mol (Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021), whereas the molar volume of the MgFe₂O₄-phase is 41.4 cm³/mol (Ishii et al., 2020), and that of MgO is 11.25 cm³/mol at ambient conditions (Dorogokupets, 2010; Tange et al., 2012). Thus, the volume change in the reaction,



is about +2.7 cm³/mol at ambient conditions. This volume change will be even larger (4.3–4.7 cm³/mol) by adjusting the pressure to 27–40 GPa using reported equation of states (Dorogokupets, 2010; Ishii et al., 2020; Tange et al., 2012), because the MgFe₂O₄-phase has a much smaller bulk modulus (164 GPa) than bridgmanite (257 GPa) (Ishii et al., 2020; Tange et al., 2012). The reaction should thus be significantly suppressed by increasing pressure. As a result, the concentration of MgFeO_{2.5} content decreases rapidly with increasing pressure.

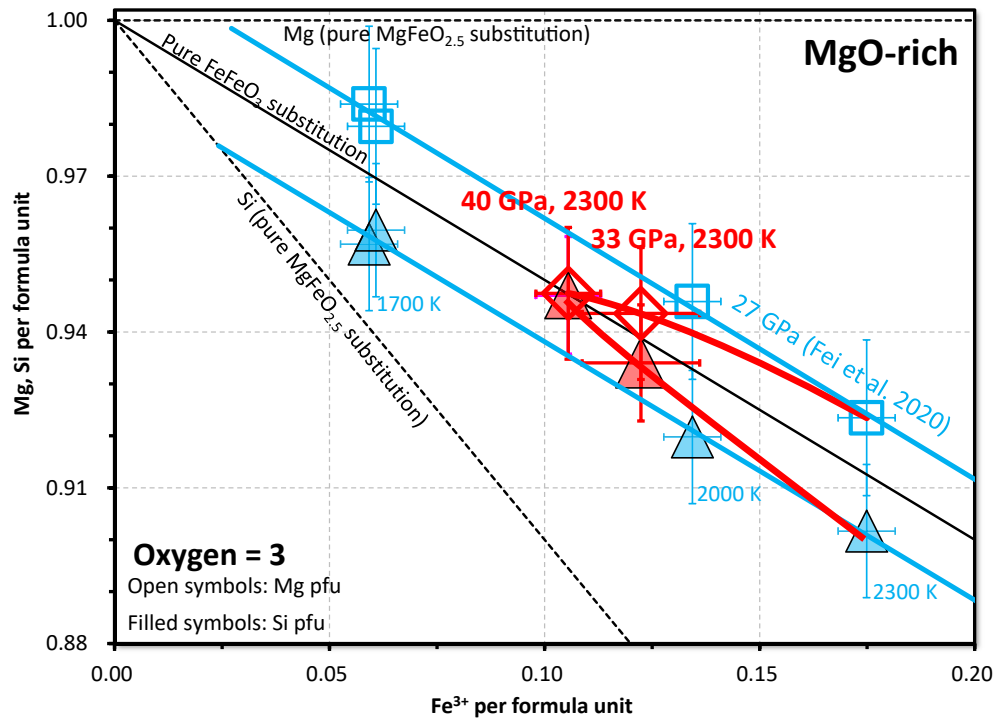
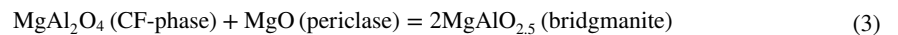


Figure 9. Mg and Si contents (per formula unit) as a function of Fe^{3+} content in bridgmanite in MgO-rich samples. The data points at 27 GPa are from Fei et al. (2020) at 1,700–2,300 K, whereas those at 33 and 40 GPa are from this study with a temperature condition of 2,300 K. The theoretical Mg and Si contents with pure FeFeO_3 substitution and pure $\text{MgFeO}_{2.5}$ substitution mechanisms are shown by thin solid and dashed lines, respectively. The error bars represent one standard deviation of the analyzed points by electron microprobe as shown in Table 1.

The negative pressure dependence of $\text{MgFeO}_{2.5}$ content is identical to that of the $\text{MgAlO}_{2.5}$ content in the $\text{MgO-SiO}_2\text{-Al}_2\text{O}_3$ system (Liu, Ishii, & Katsu, 2017), which can also be understood by the positive volume change of the reaction:



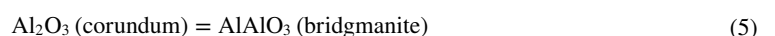
in which $\text{MgAlO}_{2.5}$ and MgAl_2O_4 have molar volume of 26.6 and 36.5 cm^3/mol , respectively (Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021; Kojitani, Hisatomi, & Akaogi, 2007; Liu, Akaogi, & Katsura, 2019; Sueda et al., 2009).

The FeFeO_3 content in our samples decreases with increasing pressure as well. The reaction of Fe^{3+} between bridgmanite and MgFe_2O_4 -phase can be written as:



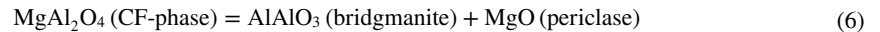
The FeFeO_3 component has a molar volume of 29.55 cm^3/mol (Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021). Although the volume change of the above reaction is negative at ambient conditions ($\Delta V = -0.6 \text{ cm}^3/\text{mol}$), it becomes positive (+0.5 to +0.8 cm^3/mol) after adjusting to 27–40 GPa using the equation of state for each phase (Dorogokupets, 2010; Ishii et al., 2020; Tange et al., 2012). As a result, the FeFeO_3 content in bridgmanite decreases with pressure.

In contrast to the FeFeO_3 component in bridgmanite, the AlAlO_3 content in Fe^{3+} -free bridgmanite increases with increasing pressure (Liu et al., 2016; Liu, Nishi, et al., 2017). Since bridgmanite coexists with corundum (Al_2O_3) in Liu, Ishii, and Katsura (2017) and Liu, Nishi, et al. (2017), the exchange of Al between bridgmanite and corundum can be written as:



Al₂O₃ (corundum) and AlAlO₃ (bridgmanite) have nearly identical molar volumes (25.6 and 25.8 cm³/mol, respectively) (Dewaele & Torrent, 2013; Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021; Liu, Akaogi, & Katsura, 2019).

On the other hand, in the case that bridgmanite coexists with MgAl₂O₄ and MgO, the AlAlO₃ component in bridgmanite can be formed by,



which has a small, but positive volume change ($\Delta V = +0.5$ cm³/mol at ambient conditions) using the molar volume of each component reported previously (Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021; Kojitani, Hisatomi, & Akaogi, 2007; Liu, Akaogi, & Katsura, 2019; Sueda et al., 2009). Thus, the small but positive volume changes of reactions (5) and (6) suggest that the AlAlO₃ content in bridgmanite should slightly decrease or be nearly constant with increasing pressure, which contradicts the tendency reported by Liu et al. (2016) and Liu, Nishi, et al. (2017). A possible cause for this discrepancy could be a large uncertainty in the reported molar volume of AlAlO₃ component in bridgmanite since it is extrapolated from the volume of bridgmanite with relatively low AlAlO₃ content (up to 14 mol %) (Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021; Liu, Akaogi, & Katsura, 2019; Liu, Boffa-Ballaran, et al., 2019), or that the AlAlO₃ component has a much smaller bulk modulus than MgSiO₃-bridgmanite since Al³⁺ has a smaller ionic radius than Mg²⁺ (0.50 Å versus 0.65 Å), leading to negative ΔV for reactions (5) and (6) at high pressures. In contrast, Fe³⁺ has a comparable ionic radius (0.64 Å) with Mg²⁺ and larger than Si⁴⁺ (0.42 Å). Therefore, the FeFeO₃ component should be less compressible than AlAlO₃ and MgSiO₃ components.

4.4. Chemistry of MgFe₂O₄-Phase

The detailed substitution mechanism of the MgFe₂O₄-phase is unknown, but it is assumed to be composed of MgFe₂O₄, Mg₂SiO₄, and Fe³⁺_{8/3}O₃ (or Fe²⁺Fe³⁺₂O₄) components (Huang, 2020; Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Liu, Akaogi, & Katsura, 2019). The Mg₂SiO₄ substitution mechanism occurs by replacement of two Fe³⁺ sites by Mg²⁺ and Si⁴⁺. Fe²⁺Fe³⁺₂O₄ substitution might have occurred instead of Fe³⁺_{8/3}O₄ if significant Fe in the MgFe₂O₄-phase were ferrous.

Based on the atomic contents of Mg, Si, and Fe from EPMA analysis (Table 1), the concentration of each component can be obtained by assuming the MgFe₂O₄-phase to be composed of MgFe₂O₄, Mg₂SiO₄, and Fe_{8/3}O₄. As shown in Figure 8c, the Fe_{8/3}O₄ content increases significantly from 12–25% to ~50% with increasing pressure from 27 to 40 GPa. Correspondingly, the MgFe₂O₄ content decreases from 60–80% to ~40% (Figure 8c). The variation of Fe_{8/3}O₄ and MgFe₂O₄ contents in MgFe₂O₄-phase could be caused by the reaction of FeFeO₃ (bridgmanite) = $\frac{3}{4}$ Fe_{8/3}O₄ (MgFe₂O₄-phase) or MgFe₂O₄ (MgFe₂O₄-phase) = $\frac{3}{4}$ Fe_{8/3}O₄ (MgFe₂O₄-phase) + MgO (periclase). The Mg₂SiO₄ content has a much smaller pressure dependence than the Fe_{8/3}O₄ content: it slightly decreases from 7–15 to 4–8 mol % with increasing pressure from 27 to 40 GPa (Table 1). These observations imply that the negative pressure dependence of Fe³⁺ content in bridgmanite is dominated by dissolution of Fe³⁺ from bridgmanite and formation of the Fe_{8/3}O₄ component in the MgFe₂O₄-phase, but the replacement of Fe³⁺ in bridgmanite by Mg²⁺ and Si⁴⁺ released from the MgFe₂O₄-phase also partially contributes to the decrease of Fe³⁺ in bridgmanite.

4.5. Implications for Chemistry of Fe³⁺-Rich Bridgmanite

4.5.1. Fe³⁺-Bearing and Al-Free System

Because bridgmanite coexists with ferropericlase and MgFe₂O₄-phase in the MgO-SiO₂-Fe₂O₃ ternary system under MgO-rich conditions, the experimentally determined MgFeO_{2.5}, FeFeO₃, and total Fe³⁺ contents should represent their maximum contents in Al-free bridgmanite when ferropericlase is present. Fei et al. (2020) demonstrated that the concentration of FeFeO₃ component increases with increasing temperature, whereas the MgFeO_{2.5} content has no clear temperature dependence when bridgmanite coexists with ferropericlase at 27 GPa. On the other hand, the MgFeO_{2.5}, FeFeO₃, and total Fe³⁺ contents are found to decrease with increasing pressure in the present study (Figures 7a and 8a). By combining the pressure and temperature effects following the geotherm in the lower mantle (Katsura et al., 2010), the MgFeO_{2.5} content in Al-free bridgmanite coexisting with

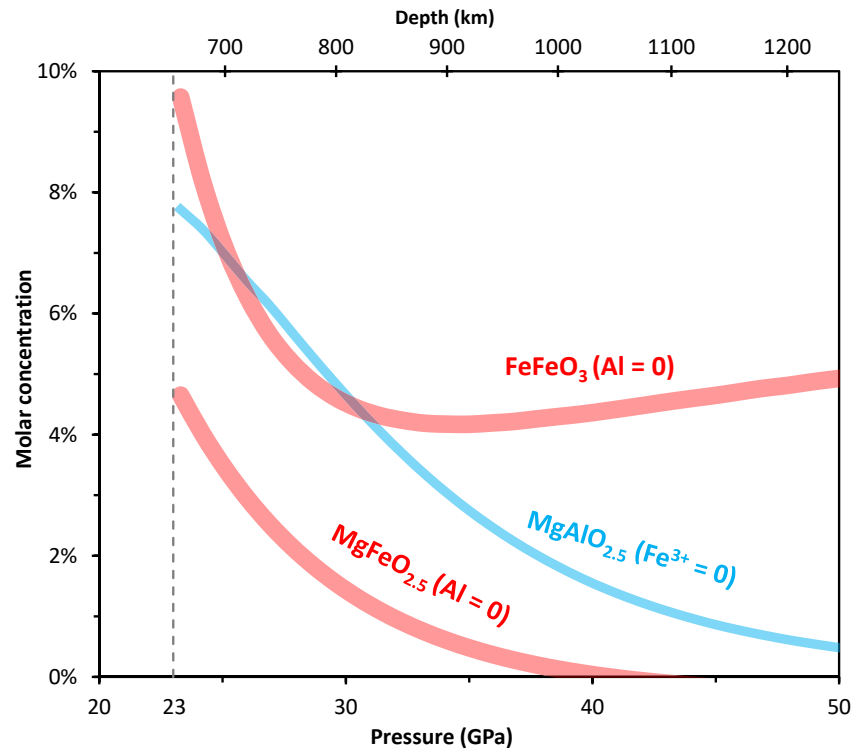


Figure 10. FeFeO_3 and $\text{MgFeO}_{2.5}$ contents as a function of depth according to the pressure dependences determined in this study, temperature dependences given by Fei et al. (2020), and geotherm from Katsura et al. (2010). The $\text{MgAlO}_{2.5}$ content in Fe^{3+} -free bridgmanite is based on the pressure and temperature dependences given by Liu, Ishii, and Katsura (2017) and Liu, Akaogi, & Katsura (2019).

ferropericline decreases rapidly by more than two orders of magnitude from 4 to 5 mol % at the topmost lower mantle to nearly zero at 1,000–1,200 km depth. In contrast, the FeFeO_3 content decreases from 8% at 700 km depth to a minimum of ~4% at about 800 km depth, and is nearly constant or slightly increases to 5% at 1,200 km depth because of the negative and positive pressure and temperature dependences, respectively (Figure 10).

4.5.2. Fe^{3+} and Al-Bearing System

The pure Fe^{3+} -bearing ($\text{MgO-SiO}_2\text{-Fe}_2\text{O}_3$) system is ideal model for understanding the chemistry of bridgmanite. A more realistic approach for bridgmanite in the lower mantle considers both Fe^{3+} and Al^{3+} (e.g., Frost & McCammon, 2008; Irifune, 1994). The substitution mechanism will be controlled by the ratio of Al^{3+} and Fe^{3+} because of the formation of the FeAlO_3 component (e.g., Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Liu et al., 2020; Mohn & Trønnes, 2016; Richmond & Brodholt, 1998; Walter et al., 2006; Zhang & Oganov, 2006). When the $\text{Al}^{3+}/\text{Fe}^{3+}$ atomic ratio is larger than unity, all Fe^{3+} will be consumed by the FeAlO_3 component, whereas excess Al^{3+} will form the AlAlO_3 and $\text{MgAlO}_{2.5}$ components (Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021; Mohn & Trønnes, 2016). In contrast, when the $\text{Al}^{3+}/\text{Fe}^{3+}$ ratio is smaller than unity, excess Fe^{3+} will form the FeFeO_3 and $\text{MgFeO}_{2.5}$ components in addition to the FeAlO_3 component (Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Mohn & Trønnes, 2016).

Although the Fe^{3+} content in bridgmanite under deep lower mantle conditions is considered to be relatively low in comparison with Al^{3+} (Frost & McCammon, 2008; Irifune & Ringwood, 1987a; Kurnosov et al., 2017; Lauterbach et al., 2000; Liu et al., 2020; Nakajima et al., 2012; Prescher et al., 2014; Shim et al., 2017; Sinmyo et al., 2019) and therefore Fe^{3+} should mainly form FeAlO_3 , $\text{Fe}^{3+}/\text{Al}^{3+}$ could be larger than unity in some regions. For example, bridgmanite in the topmost lower mantle has relatively high Fe^{3+} solubility (Fei et al., 2020; Liu et al., 2018; Wang et al., 2021) but low Al^{3+} solubility (Liu et al., 2016; Panero et al., 2006), subducted slabs may have relatively high oxygen fugacity conditions and thus should be Fe^{3+} -enriched (Zhao et al., 2021), and harzburgitic rocks are depleted in Al^{3+} (e.g., Irifune & Ringwood, 1987b). All of these regions may have

relatively high Fe^{3+} content in bridgmanite, and thus $\text{MgFeO}_{2.5}$ and FeFeO_3 components could be formed. Their concentrations should decrease rapidly with increasing pressure because of the negative pressure dependence of their solubilities as determined in this study.

4.6. Implications for Lower Mantle Dynamics

The presence of $\text{MgFeO}_{2.5}$ and FeFeO_3 components in bridgmanite may affect its physical and chemical properties as predicted from the effects of $\text{MgAlO}_{2.5}$ and AlAlO_3 components (e.g., Andrault et al., 2001, 2007; Boffa-Ballaran et al., 2012; Brodholt, 2000; Daniel et al., 2004; Frost & Langenhorst, 2002; Saikia et al., 2009; Xu et al., 1998; Yagi et al., 2004; Zhang & Weidner, 1999). Because the $\text{MgFeO}_{2.5}$ component contains oxygen vacancies, the atomic diffusivity, which is proportional to the defect concentration, is expected to be enhanced. On the other hand, although the FeFeO_3 component does not produce vacancies, it should strongly distort the crystal structure of bridgmanite by substitution of Fe^{3+} on the Si site compared to other components such as MgSiO_3 , AlAlO_3 , FeSiO_3 , and FeAlO_3 due to the much larger ionic radius of Fe^{3+} compared to Si^{4+} and Al^{3+} . As a result, the FeFeO_3 component is expected to enhance element diffusivities as well. Therefore, the decrease of both FeFeO_3 and $\text{MgFeO}_{2.5}$ content with pressure may cause decreasing atomic diffusivities in bridgmanite, which may affect diffusion-controlled physical and chemical processes and thus affect the mantle dynamics.

One example is mantle rheology. The creep of minerals is controlled by diffusion of the slowest species (e.g., Herring, 1950; Nabarro, 1967). Although the viscosity of bridgmanite is controlled by Mg and Si diffusion rather than O because Mg and Si diffuse slower than O (e.g., Dobson et al., 2008; Holzapfel et al., 2005; Xu et al., 2011; Yamazaki et al., 2000), both Mg and Si are fully surrounded by O in polyhedrons. The hopping of Mg and Si ions from/into the polyhedron should become easier when an oxygen ion is missing. Hence, oxygen vacancies may enhance the diffusion of Mg and Si and thus reduce the viscosity. Therefore, it is predicted that the decrease in both FeFeO_3 and $\text{MgFeO}_{2.5}$ contents in bridgmanite from 700 to $\sim 1,000$ – $1,200$ km depth could suppress Mg and Si diffusivities in bridgmanite, which may contribute to the large viscosity increase in the midmantle inferred from geoid analysis (Rudolph et al., 2015).

Another example is electrical conductivity in the lower mantle. The electrical conductivity of bridgmanite is dominated by the ionic conduction mechanism at relatively high temperatures (e.g., Dobson, 2003; Xu & McCammon, 2002; Yoshino et al., 2016), which is controlled by atomic diffusion of the fastest species, that is, O in bridgmanite (Dobson et al., 2008). Therefore, based on the Nernst-Einstein relation, the ionic conductivity of bridgmanite should be enhanced by the presence of the $\text{MgFeO}_{2.5}$ component. The decreasing of $\text{MgFeO}_{2.5}$ content with depth may contribute to the decrease in observed conductivity at >800 km depth based on magnetotelluric sounding (e.g., Civet et al., 2015; Civet & Tarits, 2013).

The above examples are based on qualitative interpretation. To constrain the role of $\text{MgFeO}_{2.5}$ and FeFeO_3 components on mantle dynamics in more detail, further investigations about their effects on the physical and chemical properties of bridgmanite are required. Additionally, as mentioned above, bridgmanite in the lower mantle contains Al^{3+} , which could affect the substitution mechanism of Fe^{3+} (e.g., Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš & Frost, 2021; Huang, Boffa-Ballaran, McCammon, Miyajima, & Frost, 2021; Liu et al., 2020). More experimental studies on the pressure and temperature dependences of Fe^{3+} substitution in both Fe^{3+} and Al^{3+} bearing bridgmanite are therefore necessary following the pattern of the detailed investigated in Huang, Boffa-Ballaran, McCammon, Miyajima, Dolejš and Frost (2021); Huang, Boffa-Ballaran, McCammon, Miyajima, and Frost (2021); at a single condition (25 GPa, 1970 K) corresponding to the topmost lower mantle.

Data Availability Statement

The EPMA, XRD, and Mössbauer data for this paper are given in Zenodo (<https://doi.org/10.5281/zenodo.5661686>).

Acknowledgments

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