Strong correlation of oxygen vacancies in bridgmanite with Mg/Si ratio

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A R T I C L E   I N F O

Article history:
Received 8 October 2018
Received in revised form 4 June 2019
Accepted 27 June 2019
Available online xxxx

Editor: B. Buffett

Keywords:
oxidation vacancy
Mg/Si ratio
bridgmanite
volatile
slab stagnation
lower mantle

A B S T R A C T

The variation of an oxygen vacancy (OV) in the form of an MgAlO2.5 component in bridgmanite with Mg/Si ratios of bulk compositions was clarified using phase relations in the ternary system MgO–Al2O3–SiO2 at a pressure of 27 GPa and a temperature of 2000 K using advanced multi-anvil techniques. Both normal and reversed experiments suggest that significant amounts of the OV component exist in bridgmanite synthesized from bulk compositions with Mg/Si ratios above unity. The OV component significantly decreases with decreasing Mg/Si ratio, and it finally becomes negligible for Mg/Si ratios below unity. In contrast, the charge-coupled (CC) component of Al2O3 becomes more dominant. The ternary phase relations further indicate that bridgmanite in a pyrolic or peridotitic lower mantle will contain certain amounts of OV component, while that in mid-ocean ridge basalts (MORB) will not contain any amount of this component. Our study suggests that significant amounts of volatiles such as argon trapped by the OV of bridgmanite may be induced into the ambient lower mantle, while they cannot be brought into basaltic slabs by bridgmanite but other phases such as hydrous phases. The decrease of the OV in bridgmanite with decreasing Mg/Si ratio may offer a simple explanation for the occurrence of some stagnant slabs in the lower mantle.

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1. Introduction

Bridgmanite, the most abundant phase in the lower mantle (about 80% by volume), can contain significant amounts of aluminum (Al) (Irifune, 1994; Tschauner et al., 2014). Al substitution in bridgmanite can occur in the forms of AlAlO2 and MgAlO2.5. These two components, referred to as the CC (charge-couple) component and OV (oxygen-vacancy) component, respectively, affect differently the chemistry and elastic properties of bridgmanite. The OV component appears to considerably decrease the bulk modulus of bridgmanite (Zhang and Weidner, 1999; Brodholt, 2000; Daniel et al., 2001; Andrault et al., 2007) and it may transport water (Nakovsky, 2000; Murakami et al., 2002) and noble gases (Shcheka and Keppler, 2012) into the lower mantle (Liu et al., 2017a). In contrast, the CC component does not affect the bulk modulus significantly (Walter et al., 2004, 2006), and it cannot incorporate volatiles into the bridgmanite structure. Hence, it is important to investigate the conditions for which each Al substitu-

gation mechanism dominates in order to understand the structure and geochemical circulation in the lower mantle.

In a pyrolic mantle composition with an Mg/Si ratio of 1.3, bridgmanite coexists with ferropericlase (MgO) (Irifune, 1994), whereas it coexists with stishovite (SiO2) for the composition of mid-ocean ridge basalts (MORB) with a very low Mg/Si ratio of 0.5 (Hirose et al., 2005). It is expected that the OV component will dominate in bridgmanite for MgO-rich conditions rather than for SiO2-rich conditions (Navrotsky, 1999; Walter et al., 2006; Andrault et al., 2007). Navrotsky et al. (2003), Kojitani et al. (2007) and Liu et al. (2017a) indeed showed that the OV component was prevalent in the system MgSiO3–MgAl2O4 that corresponded to MgO-rich conditions, at pressures corresponding to the uppermost part of the lower mantle. Petrological studies on the system MgSiO3–Al2O3 (Irifune et al., 1996; Kubo and Akao, 2000; Liu et al., 2016, 2017b), which provided more Si-rich conditions, suggested that the CC component becomes dominant in the deeper lower mantle, while the OV component becomes negligible. Furthermore, Walter et al. (2006) studied phase relations in MgSiO3–MgAl2O4, MgSiO3–MgAl2O4, and MgSiO3–Al2O3 systems using a laser-heated diamond anvil cell (LHADC) combined with in-situ X-ray diffraction, suggesting that the OV component plays a negligible role even in MgO-rich systems in the lower mantle.

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https://doi.org/10.1016/j.epsl.2019.06.037
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Thus, it is still unclear what effect the bulk composition has on the substitution mechanism of Al in bridgmanite.

In this study, we systematically investigated the content of the OV and CC component in bridgmanite with varying Mg/Si ratios for the bulk compositions in ternary system MgO–Al2O3–SiO2 using a multi-anvil press with tungsten carbide anvils. The pressure and temperature condition in this study were 27 GPa and 2000 K in order to avoid the presence of majorite, which may have cause additional complication in the phase relations. With these experiments, we could constrain the OV content in bridgmanite in the uppermost part of the lower mantle, and then discuss its implications for the mineralogy, dynamics, and geochemical cycling in the lower mantle.

2. Materials and methods

We prepared eight different starting compositions, which are shown in Fig. 1. The starting materials A, C, E, and G are glasses with compositions of En90Brm10 (Brm: MgAl2O4 brownmillerite), En95Sp5 (Sp: MgAl2O4 spinel), En95Cor5 (Cor: Al2O3 corundum), and En95Ky5 (Ky: Al2SiO5 kyanite), while B, D, F, and H are fine-grained oxide mixtures of En52Brm48, En95Sp50, En95Cor50, and En95Ky50. Their general features are as follows. The compositions of A (Mg/Si = 1.06) and B (Mg/Si = 1.75) mixtures are on the tie line of MgSiO3 to MgAl2O4. The C (Mg/Si = 1.02) and D (Mg/Si = 1.76) mixtures are on the tie line of MgSiO3 to MgAl2O4, those of mixtures E (Mg/Si = 1.00) and F (Mg/Si = 0.99) are on the tie line of MgSiO3 to Al2O3. Finally, the G (Mg/Si = 0.92) and H (Mg/Si = 0.48) mixtures are on the tie line of MgSiO3 to Al2O3. The glasses were prepared from oxide mixtures of reagent-grade MgO, SiO2, and Al2O3, which were fused at a temperature of 2000 K for 1 h, quenched into cold water and ground into fine-grained powder. This process was repeated three times in order to obtain homogeneous glass starting material. The fine-grained oxide mixtures were prepared from reagent-grade oxide chemically with very small grain sizes of \( \sim 100 \) nm in order to enhance reactions at 27 GPa and 2000 K (Liu et al., 2016, 2017b). The compositions of these starting materials were measured with an electron probe microanalyzer (see Supplementary Table S1). The starting materials were put into platinum capsules, and heated at 800 K for 1 h before being used in the high-pressure cell assembly in order to minimize the amount of adhesive water.

Synthesis experiments at 27 GPa and 2000 K were performed using a Cr2O3-doped MgO octahedra with 7-mm edge length and a LaCrO3 sleeve for heating in combination with tungsten carbide cubes with 3-mm truncated edge lengths in a Kawai-type multi-anvil apparatus with a press load of 15 MN at the Bayerisches Geoinstitut, University of Bayreuth (IBIS-15) (Ishii et al., 2016). Pressure calibrations at 2000 K were calibrated based on the solubility of Al2O3 in bridgmanite coexisting with corundum (Liu et al., 2017b). The pressure uncertainties of these experiments are \( \pm 0.5 \) GPa.

Textural observations and chemical analyses of the recovered samples were performed using an LEO1530 scanning electron microscope (SEM) and a JEOL JXA-8200 electron probe microanalyzer (EPMA) operating at an acceleration voltage of 15 kV and a beam current of 5 nA with enstatite and forsterite for Mg and Si standards, respectively, and corundum for Al. We measured the composition of pure MgSiO3 bridgmanite (Liu et al., 2016) using the same setting as a benchmark analysis. The phases present were identified using a micro-focused X-ray diffractometer (MF-XRD), a Bruker D8 DISCOVER equipped with a two-dimensional solid state detector (VANTEC500), and a micro-focus source (Ips) with Co-Kα radiation operated at 40 kV and 500 μA. The X-ray beam was focused to 50 μm using an IFG polycapillary X-ray mini-lens. XRD profiles of each sample were collected for two hours. The Bragg angles of (2θ) of the MF-XRF were calibrated using MgSiO3 bridgmanite as an external standard.

3. Results

3.1. Phase assemblages

Experimental conditions and phases present in the recovered samples are summarized in Table 1. The starting materials with compositions near pure-MgSiO3 (A, C, and E) produce a single-phase of bridgmanite except for the SiO2-rich system (G), which crystallizes to a bridgmanite + stishovite assemblage from XRD and SEM observations (Figs. 2 and 3). The run products from starting materials with a larger secondary component (B, D, F, and H) consist of bridgmanite plus one or two additional phases (Figs. 2 and 3). The coexisting phases change from periclase + CF phase (B) to CF phase + corundum (D) to corundum (F) and finally to corundum + stishovite (G).

3.2. Composition

Compositions of bridgmanite in the recovered samples are shown in Table 2, and those of additional phases coexisted with bridgmanite are shown in Supplementary Table S2. Bridgmanite for A, C, E, and G contains almost the same Al2O3 content (5 wt.%), which is also comparable with that of their glass starting material. The Mg/Si ratio of these synthesized bridgmanite is almost close to that of the bulk starting materials within analytical uncertainties except G. The Mg/Si ratio of bridgmanite from G is 0.99, which is significantly higher than that of the starting material (0.92) due to the existence of some amount of minor stishovite in this sample. The Al2O3 content in bridgmanite increases from 8.1 wt.% for B to 10.5 wt.% for D and to 12.6 wt.% for F and then decrease to 10.9 wt.% for H. It’s found that the appearing CF phase in B and D
contains significant amounts of the Mg$_2$SiO$_4$ component, and this component would decrease from 34 mol% from B to 30 mol% for D. The corundum in samples D, F, and H contains 19, 21, and 20 mol% Mg$_2$SiO$_4$ component, respectively. The periclase and stishovite in B and H, respectively, also contain small amounts of Al$_2$O$_3$ component of 0.3 and 2.0 mol%. We also did one reversed experiment in the run IRIS478 for the powder sample of the run products of B and D, which were synthesized at 27 GPa and 2000 K for 22–26 h in the runs IRIS427 and IRIS446, for additional 20–26 h at the same pressure and temperature. Bridgmanite from B and D in this reversed run contains about 8.3 and 10.9 wt.% Al$_2$O$_3$, respectively, which are comparable to those [8.1 and 10.5 wt.-%] for B and D in the synthesized runs IRIS427 and IRIS446. The CF phase, corundum, and periclase also show nearly consistent compositions with those in the above synthesis runs within analytical uncertainties. This fact suggests that chemical equilibrium was achieved for experiments at 27 GPa and 2000 K for keeping 22–26 h in our experiments.

The content of the OV (MgAlO$_{2.5}$) and CC (AIAI0$_3$) components in bridgmanite were derived from the reaction of Mg$_2$Al$_2$Si$_2$O$_7$, O$_{4+x+y+2z}$ = y MgSiO$_3$ + (x - y) MgAlO$_{2.5}$ + (z - x + y)$_2$Al$_2$O$_3$ (x + y + z = 2, Liu et al., 2017a). Fig. 4a shows the variation of the OV and CC content in the synthesized bridgmanite with Al pfu (pfu: per formula units) of 0.1 as a function of the Mg/Si ratio. It was noted that the OV content in bridgmanite rapidly decreases from 4.9 mol% to approximately zero with the Mg/Si ratio decreasing from 1.05 for bridgmanite synthesized from A to 1.00 for that from G. In contrast, the corresponding CC content increases from 2.6 to 5.6 mol%. This fact suggests that both OV and CC mechanisms take place in the MgO-rich systems, with OV being dominant with respect to CC. However, with increasing Si content from A to G, the excess Si relative to Mg in the starting compositions favors the substitution of Al to form the CC component rather than the OV component. In addition, the OV and CC components suppress each other because the Al content in bridgmanite is nearly constant with changing Mg/Si ratio from A to G.

For bridgmanites with Al pfu above 0.1 that coexisted with one or two additional phases in B, D, F, and H, the OV gradually decreases from 2.0 mol% to nearly zero with a decreasing Mg/Si ratio from 1.02 to 1.00 for these synthesized bridgmanite (Fig. 4b). On the contrary, the CC content significantly increases with decreasing Mg/Si ratio in these bridgmanites. However, the slope of the dependence of the OV decreasing versus Mg/Si ratios for Al-rich bridgmanite is slightly lower than that for bridgmanite with Al pfu of 0.1, suggesting that the high Al might disfavor OV in Al-rich bridgmanite. These results can be explained by the decomposition of the MgAlO$_{2.5}$ and MgAl$_2$O$_4$ component in the latter discussion.

### 3.3. Molar volume

The unit-cell lattice parameters of all phases present in the recovered samples are shown in Supplementary Table S3, and the molar volume of bridgmanite with Al pfu of 0.1 is plotted versus the Mg/Si ratio of the synthesized bridgmanite from different starting materials in Fig. 5a. In general, the molar volume of bridgmanite decreases with decreasing Mg/Si ratios. In more detail, the molar volume (24.59 cm$^3$/mol) of bridgmanite synthesized in the En-Brm system, namely Mg-rich systems is significantly higher than those (24.50 cm$^3$/mol) of bridgmanite crystallized in the more Si-rich systems such as En-Cor and En-Ky systems. In Fig. 5b, a linear function was used to fit the data for CC-bearing bridgmanite synthesized from the En-Cor and En-Ky systems by fixing the endmember of MgSiO$_3$ bridgmanite. The following equation was obtained: $V(X) = 24.44 + 0.0135(5) \cdot X_{\text{AlAlO}3} \cdot (0 < X_{\text{AlAlO}3} \leq 15)$, where $V$ is the molar volume, $X_{\text{AlAlO}3}$ is the mole content of AlAlO$_3$ in bridgmanite, and the number in parentheses represents the standard deviation for the last digits. After that, we fitted the pure OV-bearing bridgmanite by subtracting the effect of the CC component and got $V(X) = 24.44 + 0.023(2) \cdot X_{\text{AlAlO}3} \cdot (0 < X_{\text{AlAlO}3} < 6)$, where $X_{\text{AlAlO}3}$ is the mole content of MgAlO$_{2.5}$ in bridgmanite. This fact suggests that 1 mol% OV would increase by 2 times higher for molar volume than the same content of CC component.

### 4. Discussions

#### 4.1. Al substitution reactions in bridgmanite in the ternary system MgO–AlO$_{1.5}$–SiO$_2$

The compositions of bridgmanite, CF phase, periclase, corundum, and stishovite obtained in the present study are summarized in the phase diagram in the ternary system MgO–AlO$_{1.5}$–SiO$_2$ (Fig. 6a). In the En-Brm system, the majority of the Brm component in the starting material A (En$_{50}$Brm$_{10}$) forms the OV component in bridgmanite, which can be explained by the following equation:

$$\text{MgAlO}_{2.5} = \text{MgAlO}_{2.5}(\text{OV})$$

(1)

Since a small amount of the CC component is also contained in this bridgmanite, the following reaction should have occurred:

$$2\text{MgAlO}_{2.5} = \text{AlAlO}_{3}(\text{CC}) + 2\text{MgO}$$

(2)

The starting material B (En$_{52}$Brm$_{48}$) produced periclase and a calcium-ferrite type (Mg,Al,Si)$_3$O$_4$ (CF) in addition to bridgmanite
Fig. 2. XRD profiles of run products from various starting materials. The number in parentheses represents miller indices of the first appearing phase. Abbreviations: Brg, bridgmanite; Cor, corundum; CF, calcium ferrite-type structure of MgAl₂O₄; Sti, stishovite; Per, periclase.

(Figs. 2 and 3), which can be explained by the following reaction:

$$2\text{MgAlO}_2 + \text{MgSiO}_3 = \text{Mg}_2\text{SiO}_4(\text{CF}) + \text{MgAl}_2\text{O}_4(\text{CF})$$  \hspace{1cm} (3)

Both equation (2) and (3) suggest that end-member MgAlO₂₅ bridgmanite cannot exist in the lower mantle, and it will decompose into the CF phase or corundum and periclase. Thus, the OV component in bridgmanite would decrease in Al-rich bridgmanite in this system (Fig. 4b).

In the En-Sp system, the staring material C (En₉₅Sp₅) crystallized into a single phase of bridgmanite, indicating that this amount of MgAl₂O₄ component could completely dissolve into bridgmanite. Since the component of MgAl₂O₄ is intermediate between OV and CC, the reaction can be expressed by:

$$2\text{MgAl}_2\text{O}_4(\text{Brg}) = 2\text{MgAl}_2\text{O}_4(\text{OV}) + \text{AlAlO}_3(\text{CC})$$  \hspace{1cm} (4)

This kind bridgmanite thus contains both OV and CC components. For the D starting material (En₅₀Sp₅₀), bridgmanite coexisted with the CF phase and corundum (Figs. 2 and 3), which can be ex-
plained by the following reaction:

\[ \text{MgAl}_2\text{O}_4 (\text{CF}) + \text{MgSiO}_3 (\text{Brg}) = \text{Mg}_2\text{SiO}_4 (\text{CF}) + \text{Al}_2\text{O}_3 (\text{Brg}) \]  \( \text{(5)} \)

It would thus result a wide solid solution for the CF phase between the endmembers of MgAl$_2$O$_4$ and Mg$_2$SiO$_4$.

For the case of the En-Cor system, the starting material E (En$_{95}$Cor$_5$) crystallized into a single phase of bridgmanite, whereas F (En$_{50}$Cor$_50$) gave rise to bridgmanite with 11.7 mol% corundum, which is in agreement with previous studies (Irifune et al., 1996; Kubo and Akaogi, 2000; Liu et al., 2016, 2017b). In the En-Ky system, the starting materials G (En$_{95}$Ky$_5$) and H (En$_{50}$Ky$_50$) crystallized to bridgmanite plus stishovite both without and with corundum (Fig. 2 and 3), respectively.

Noted that a single-phase region of bridgmanite was formed towards the MgO-rich region in the ternary phase relations (Fig. 6a). From the magnified ternary phase diagram in Fig. 6b, it can be seen that the compositions of bridgmanite with a low Al content (Al pfu of 0.1) synthesized in the En-Brm system (Mg/Si > 1) are close to the ideal line of a complete oxygen vacancy substitution (OVS), while those obtained in the En-Cor and En-Ky
systems (Mg/Si ≤ 1) lie on the line of the charge-coupled substitution (CCS). This fact further supports the result obtained in Fig. 4a which demonstrates the excess MgO favors the OV component in bridgmanite, while the excess SiO2 minimizes this component and favors the CC component.

Although Navrotsky et al. (2003) attempted to characterize the relations of the OV and CC content with bulk composition, they were not able to find any clear correlation. One possible reason is that in the mentioned study, the LH-DAC was the technique used for the majority of the high-pressure-temperature bridgmanite synthesis. However, to constrain the effect of the bulk composition on the Al substitution mechanism in bridgmanite, very reproducible pressure and temperature conditions, as well as high-quality chemical analysis by means of EPMA are required. These are very difficult conditions to obtain in LH-DAC experiments, though. Another reason may be that the majority of bridgmanite synthesized by means of multi-anvil runs in the mentioned study of Navrotsky et al. (2003) did not coexist with any excess phase and only a few of them coexisted with only one phase. Since the

Table 2
Chemical compositions of the synthesized bridgmanite.

| Lett. | Phases | MgO | Al₂O₃ | SiO₂ | Total | Mg | Al | Si | O | Mg/Si | OV | CC |
|-------|--------|-----|-------|------|-------|----|----|----|---|-------|----|----|
| A     | Brg (n = 18) | 39.17 (43) | 5.12 (33) | 55.47 (77) | 99.77 (76) | 0.974 (7) | 0.100 (7) | 0.926 (6) | 2.976 (4) | 1.05 (2) | 4.9 (13) | 2.6 (3) |
| B     | Brg (n = 15) | 37.34 (51) | 8.09 (36) | 54.68 (46) | 99.90 (88) | 0.930 (8) | 0.159 (6) | 0.910 (7) | 2.988 (5) | 1.02 (2) | 2.5 (15) | 6.9 (8) |
| C     | Brg (n = 16) | 36.53 (44) | 10.95 (42) | 53.83 (61) | 101.18 (89) | 0.899 (6) | 0.213 (8) | 0.889 (7) | 2.995 (4) | 1.01 (1) | 1.0 (10) | 10.1 (5) |
| D     | Brg (n = 23) | 37.00 (46) | 10.52 (31) | 54.39 (49) | 101.92 (69) | 0.904 (7) | 0.203 (6) | 0.891 (4) | 2.992 (5) | 1.02 (2) | 1.3 (8) | 9.5 (6) |
| E     | Brg (n = 30) | 38.43 (55) | 5.09 (18) | 57.87 (55) | 101.39 (66) | 0.945 (10) | 0.099 (4) | 0.955 (6) | 3.005 (6) | 0.99 (2) | −1.0 (15) | 5.5 (8) |
| F     | Brg (n = 30) | 38.43 (55) | 5.09 (18) | 57.87 (55) | 101.39 (66) | 0.945 (10) | 0.099 (4) | 0.955 (6) | 3.005 (6) | 0.99 (2) | −1.0 (15) | 5.5 (8) |
| G     | Brg (n = 23) | 37.00 (46) | 10.52 (31) | 54.39 (49) | 101.92 (69) | 0.904 (7) | 0.203 (6) | 0.891 (4) | 2.992 (5) | 1.02 (2) | 1.3 (8) | 9.5 (6) |
| H     | Brg (n = 16) | 36.53 (44) | 10.95 (42) | 53.83 (61) | 101.18 (89) | 0.899 (6) | 0.213 (8) | 0.889 (7) | 2.995 (4) | 1.01 (1) | 1.0 (10) | 10.1 (5) |

Oxide analyses are reported in wt.%: n: number of analysis points. The total cation number is normalized to two. Number in parentheses represents the standard deviation for the last digit (s). Abbreviations: Brg, bridgmanite; OV, MgAlO2.5; CC, AlAlO3.

Fig. 4. Plots of the OV and CC components in bridgmanite with (a) Al pfu = 0.1 and (b) Al pfu > 0.1 as a function of their Mg/Si ratio. Red and blue dashed lines represent the variation of the OV and CC component, respectively. The red dotted line represents zero value of the OV content.

Fig. 5. (a) Molar volume of bridgmanite with Al pfu of 0.1 versus Mg/Si ratios. (b) Molar volume of bridgmanite versus the MgAlO2.5 (OV)/ AlAlO3 (CC) content. Red and blue lines in (b), respectively, represent the linear fitting of the data in the systems MgSiO3–MgAlO2.5 and MgSiO3–Al2O3 in the present study. Black symbols are from Liu et al. (2017b). The red and blue digital data in (b), respectively, are the slope of molar volume versus the OV and CC component and the number in parentheses represents the error for the last digit.
Fig. 6. (a) Ternary phase relations in the system MgO–AlO1.5–SiO2 (mol%) at 27 GPa and 2000 K. (b) The magnified ternary phase relations from (a) marked by the dashed lines. Open symbols represent the starting compositions of B, D, F, and H, while solid circles are the compositions of the corresponding phases. Square solid symbols are the single bridgmanite phase synthesized from A, C, E, and G starting compositions. Abbreviations: Brg, bridgmanite; Cor, corundum; Per, periclase; CF, calcium ferrite-type structure of MgAl2O4; Sti, stishovite; CCS: charge-coupled substitution; OVS: oxygen vacancy substitution.

The present chemical system consists of three components, i.e. MgO, Al2O3, and SiO2, two excess phases are necessary to fix the composition of bridgmanite. In our study, we conducted experiments both with and without excess phases for four different secondary components. This strategy allowed us to constrain the OV and CC contents as a function of the Mg/Si ratio.

Our result may explain the large variation of the bulk moduli found in aluminous bridgmanite from various starting materials and different Mg/Si ratios by Andrault et al. (2007). They found that bridgmanite from MgO-excess starting material possesses a relatively lower bulk modulus (243 GPa) than that from SiO2-excess starting material (272 GPa) under almost the same pressure range. This can be understood from the fact that OV-bearing bridgmanite becomes more compressible due to a higher molar volume of the OV component than the CC component (Fig. 5).
4.2. Implications for geochemical circulation

Here, we investigated which Al substitution mechanism dominates in the lower-mantle rocks. We simplified the bulk composition of pyrolite and MORB by assuming that Fe$^{2+}$, Ca$^{2+}$ and Mn$^{2+}$ behave in the same way as Mg$^{2+}$, denoted as X$^{2+}$ hereafter, and that Fe$^{3+}$ and Cr$^{3+}$ behave in the same way as Al$^{3+}$, denoted as Y$^{3+}$. There are some debates about the Fe$^{3+}$/fraction of the total iron (Fe$^{3+}$/ΣFe) in the lower mantle (Frost and McCammon, 2008) and the Fe$^{3+}$/ sites in bridgmanite depending on the trivalent cation content and pressure (Frost and Langenhorst, 2002; Fujino et al., 2012). We considered two extreme cases. The first case (case 1) is that Fe$^{3+}$/ΣFe in the lower mantle is identical to that (3%) in the upper mantle (Frost and McCammon, 2008). The second case (case 2) is that the Fe$^{3+}$/ΣFe ratio of bridgmanite in equilibrium with metallic Fe is more than 50% for a typical mantle Al$_2$O$_3$ content (e.g., McCammon, 1997; Frost et al., 2004; Frost and McCammon, 2008) and Fe$^{3+}$/ prefers Mg sites due to the similar cation size in the uppermost lower mantle (Fujino et al., 2012). In the case 1, the bulk X:Y:Si ratios of pyrolite and MORB are 0.57:0.05:0.38 and 0.34:0.18:0.48, respectively. In the case 2, the bulk X:Y:Si ratios of pyrolite and MORB are 0.54:0.08:0.38 and 0.31:0.21:0.48, respectively. As shown in Fig. 7, the pyrolite compositions for the case 1 and 2 are located in the region of bridgmanite + periclase and that of bridgmanite + CF phase + periclase, respectively. Therefore, the OV component will be the major component of Al incorporation. We estimated that the bridgmanite from the pyrolite bulk composition will contain 9 and 4 mol% of the OV (XYO$_2$) components in the case 1 and 2, respectively. In contrast, the bulk compositions of the MORB for both case 1 and 2 are located in the region of bridgmanite + stishovite + corundum, and bridgmanite cannot contain the OV component (Fig. 7). In more realistic estimations, the phases coexisting with bridgmanite in the MORB compositions will not be stishovite + corundum but stishovite + NAL-phase. Nevertheless, bridgmanite in the MORB compositions will virtually contain no OV component.

The OV component in bridgmanite may transport some volatiles such as water (Navrotsky, 1999; Murakami et al., 2002) and noble gases (Shcheka and Keppler, 2012) into the lower mantle. If this assumption is correct, the present OV content in a pyrolite composition leads to a maximum water content of 1 wt% and significant noble gases such as argon and krypton above 1 wt% in bridgmanite in the ambient mantle. This is enough to explain the current experimental results of 1000 to 2000 ppm of water incorporation in Al-bearing bridgmanite in a peridotite composition (Murakami et al., 2002; Litasov et al., 2003). However, Bolfan-Casanova et al. (2000 and 2003), Litasov et al. (2003), and Panero et al. (2015) reported that Al-Fe-bearing bridgmanite could contain very limited amounts of water (10–400 ppm). These observations could be explained by the fact that Al and Fe$^{3+}$ form the FeAlO$_3$ component in bridgmanite, which may diminish the OV component. Bridgmanite in the MORB composition does not incorporate water as evidenced by Litasov et al. (2003) and volatiles because of no OV component. Thus, subducted MORB slabs will transport water and noble gases into the deep lower mantle by other hydrous phase such as aluminous stishovite (e.g., Pawley et al., 1993; Panero et al., 2003) and phase D (Pamato et al., 2015). The effects of iron on the substitution mechanisms of trivalent cation in bridgmanite must be studied in detail to understand the geochemical circulation between the surface and the deep mantle.

4.3. Implications for slab stagnation in the lower mantle

Seismic tomography studies have observed some stagnant slabs at 600–1000 km depths in the lower mantle (e.g., Fukao and Obayashi, 2013). Since bridgmanite is the major mineral in this
Acknowledgements

The authors thank D. Kraußè and D. Wiesner for their technical supports in microprobe analyses, and E. Posner, H. Schulze, R. Njl, H. Fischer and S. Ólafsdóttir for their assistance with the cell assembly preparation. We also thank for the editor Bruce Buffett for processing our manuscript and anonymous reviewers for constructive comments. This project was financially supported by the Bayerisches Geoinstitut Visitor’s Program and the Fundamental Research Funds for the Central Universities of Ministry of Education of China (Grant No. 45119031C037) for Z.L. This study is also supported by research grants to T.K. (BMBF: 05K13W2, 05K16W2; DFG: KA3434/3-1, KA3434/7-1, KA3434/8-1, KA3434/9-1). This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Proposal No. 787527).

Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2019.06.037.

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Z. Liu et al. / Earth and Planetary Science Letters 523 (2019) 115697

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