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Melting phase relation of Fe-bearing Phase D up to the uppermost lower mantle

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Abstract

Dense hydrous magnesium silicates (DHMSs) are considered important water carriers in the deep Earth. Due to the significant effect of Fe on the stability of DHMSs, Fe-bearing Phase D (PhD) deserves much attention. However, few experiments have been conducted to determine the stability of PhD in different bulk compositions. In this study, we provide experimental constraints for the stability of PhD in the AlOOH-FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ system between 18 and 25 GPa at 1000-1600 °C, corresponding to the P-T conditions of the mantle transition zone and uppermost lower mantle.

Fe$^{3+}$-bearing PhD was synthesized from the FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ binary system with two different Fe$^{3+}$ contents. The resultant Al, Fe$^{3+}$-bearing compositions are close to analog specimens of the fully oxidized mid-ocean ridge basalt (MORB) and pyrolite in the AlOOH-FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ ternary system. The substitution mechanism of Fe is shown to be dependent on pressure, and Fe$^{3+}$ occupies both Mg and Si sites in PhD at pressures below 21 GPa. In contrast, Fe$^{3+}$ only occupies Si site at pressures exceeding 21 GPa. The presence of Fe$^{3+}$ results in a slight reduction in the thermal stability field of PhD in the FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ system in comparison to Mg-bearing, Fe-free PhD. In contrast, Al, Fe$^{3+}$-bearing PhD is more stable than Mg-bearing PhD in both MORB and pyrolite compositions. In this regard, Al, Fe$^{3+}$-bearing PhD could act as a long-term water reservoir during subduction processes to the deep mantle.

1. Introduction

Water is one of the most important volatiles, and so it plays a crucial role in the
geochemical and geophysical evolution of the Earth. Even a small amount of water may significantly change the physical and chemical properties of the Earth’s interior. For example, the presence of water decreases the melting temperature of minerals and changes seismic wave velocity and rheological behavior, thereby influencing the thermodynamic processes of the mantle (Kavner, 2003; Komabayashi and Omori, 2006; Xu et al., 2020). It has previously been found that a series of dense hydrous magnesium silicates (DHMSs), such as Phase A (PhA), Phase E (PhE), Superhydrous phase B (SUB), Phase D (PhD), and Phase H (PhH) are promising water hosts within the context of subduction in the deep Earth (Kawamoto et al., 1996; Ohtani et al., 2001a; Litasov and Ohtani, 2003; Komabayashi et al., 2005; Nishi et al., 2014). The stability of these phases is, therefore, key to unraveling water recycling throughout the planet over geological time scales.

PhD was identified by Liu (1987) as a new DHMS resulting from the breakdown of serpentine under high $P$-$T$ conditions. The ideal chemical formula of PhD is $\text{MgSi}_2\text{H}_2\text{O}_6$, however, PhD exhibits non-stoichiometry with regards to the Mg/Si ratio, which varies from 0.55 to 0.71, and the H content, which varies from 2 to 3.4 per formula unit (Frost and Fei, 1999). PhD also exists as a solid solution via $\text{Mg} \rightarrow \text{Fe}$, $\text{Mg}+\text{Si} \rightarrow 2\text{Al}$, and $\text{Mg}+\text{Si} \rightarrow 2\text{Fe}^{3+}$ substitution mechanisms. It has trigonal symmetry ($P\overline{3}1m$) with SiO$_6$ and MgO$_6$ octahedra alternately stacked along the c-axis (Kudoh et al., 1997; Yang et al., 1997). PhD is potentially a stable phase in hydrous peridotite among DHMSs at the upper part of the lower mantle, allowing it to play a key role in the transportation of water, subsequently transforming to Phase H (PhH) at 50 GPa (Nishi et al., 2014). Earlier experimental results suggest that additional $\text{Al}_2\text{O}_3$ may increase the region of thermal stability of PhD (Ghosh...
and Schmidt, 2014; Xu and Inoue, 2019a), and Al-rich PhD could remain stable up to 2000 ºC at 25 GPa (Pamato et al., 2015). However, there is no clear consensus in the literature regarding the effect of Fe substitution on the stability of PhD. Ghosh and Schmidt (2014) suggested that the maximum stability limit of PhD is between 1350 ºC and 1400 ºC at 22-24 GPa in both the FeO-MgO-Al₂O₃-SiO₂-H₂O (FMASH) and MSH systems, i.e., 200 ºC lower than that of the MASH system. However, compared with the MSH system between 18-23 GPa, Ganskow and Langenhorst (2014) argued that the presence of Fe²⁺ would increase the stability of PhD in the FMASH system up until 1450 ºC at 20.5 GPa. Beyond these studies, there is a paucity of research on the effect of Fe on the stability of DHMSs. Fe is an abundant and important element in both pyrolite and mid-ocean ridge basalts (MORB), and the presence of Fe may significantly change the stability of PhD and its water solubility. Additionally, the stability of PhD containing Fe and Al simultaneously, which is closer in composition to pyrolite or MORB, is unknown.

The oxide hydroxides AlOOH and FeOOH are common minerals in sediments (Otte et al., 2009; Panero and Stixrude, 2004). At low pressures, AlOOH has two polymorphic structures; diaspora (α-AlOOH, space group Pbnm) and boehmite (γ-AlOOH, Amam), which transform to δ-AlOOH (P21nm) at around 17 GPa and 1000 ºC (Ohtani et al., 2001b), and subsequently to pyrite-type structures at 170 GPa (Pa-3) (Tsuchiya and Tsuchiya, 2011). At lower pressures, FeOOH has three polymorphic structures, i.e., goethite (α-FeOOH iso-structure with α-AlOOH), akaganeite (β-FeOOH, I4/m), and lepidocrocite (γ-FeOOH, Cmcm). Goethite transforms to ε-FeOOH (isostructural with δ-AlOOH) at pressures above 5 GPa at 200 ºC (Gleason et al., 2008), which then transforms into pyrite-type FeOOH at
pressures between 60–90 GPa and temperatures exceeding 1227 ºC (Nishi et al., 2017). Experimental results show that δ-AlOOH, ε-FeOOH, and PhH (MgSiH$_2$O$_4$) may form solid solutions in the Earth’s deep lower mantle (Sano et al., 2008; Ohira et al., 2014; Ohtani et al., 2014; Nishi et al., 2017; Xu et al., 2019a). However, the stability of δ-AlOOH and ε-FeOOH in the Mg, Si-bearing systems under transition zone conditions has not been as well investigated.

In this study, we determined the effect of Fe$^{3+}$ on the stability of PhD in the FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ system at pressures between 18 and 25 GPa and temperatures between 1000 and 1600 ºC. Additionally, we determined the stability of PhD with intermediate Al and Fe$^{3+}$ content in the AlOOH-FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ system whose composition is similar to pyrolite and MORB in the natural system. We simultaneously clarified the effect of Mg and Si on the stability of AlOOH-FeOOH phases for transition zone conditions, as Mg and Si change the symmetry of δ-AlOOH (Komatsu et al., 2011), which might influence the stability of the phase.

2. Experiment

To prepare PhD with a homogeneous composition close to Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$, we used a mixture of Mg(OH)$_2$ + SiO$_2$ in appropriate stoichiometry. To study the effect of Fe$^{3+}$ content on the stability of PhD, 15.0 wt% and 8.0 wt% of α-FeOOH + Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ respectively, were adopted. Furthermore, 5.7 wt% of AlOOH (Al$_2$O$_3$ + Al(OH)$_3$ in appropriate stoichiometry) + 9.4 wt% of α-FeOOH (4.0 wt% A$_2$O$_3$, 8.4 wt% Fe$_2$O$_3$) +
Mg$_{1.11}$Si$_{1.89}$O$_{6}$H$_{2.22}$ and 16.0 wt\% of AlOOH + 8.8 wt\% of α-FeOOH (13.6 wt\% A$_2$O$_3$, 7.9 wt\% Fe$_2$O$_3$) + Mg$_{1.11}$Si$_{1.89}$O$_{6}$H$_{2.22}$ were utilized, respectively, whose Al and Fe composition were close to pyrolite (4.3 wt\% A$_2$O$_3$, 8.0 wt\% Fe$_2$O$_3$) and MORB (15.3 wt\% A$_2$O$_3$, 10.4 wt\% Fe$_2$O$_3$) (Ringwood, 1975; Hofmann, 1988).

The experiments were conducted at pressures of 18–25 GPa and temperatures from 1000 ºC to 1600 ºC using a MA-8 type apparatus (ORANGE-1000) at the Geodynamics Research Center (GRC) of Ehime University, Japan. The pressure was calibrated at room temperature through the diagnostic changes in the electrical resistances of ZnTe (9.6 and 12.0 GPa), ZnS (15.5 GPa), GaAs (18.3 GPa), and GaP (23.0 GPa), induced by the semiconductor-metal phase transitions at high pressures. Tungsten carbide cubes with a truncation edge length (TEL) of 4 mm were combined with Cr-doped MgO-octahedra with an edge length of 10 mm (10/4 assemblage). Preformed pyrophyllite gaskets were used between the anvils, and lanthanum chromate (LaCrO$_3$) was used as the heater. The sample was sealed by welding it in a gold capsule to prevent water loss during the experiment. The temperature was monitored by a W$_{97}$Re$_3$-W$_{75}$Re$_{25}$ thermocouple, and the thermocouple emf was not corrected for the effect of pressure. The samples were recovered when the pressure was released slowly over 720 minutes.

The recovered products of each experimental run were mounted in epoxy resin and polished to undergo phase identification and composition analysis. The phase assemblages were identified by a micro-focus X-ray diffractometer (Rigaku MicroMax-007HF) using Cu Kα radiation. For electron microscopic measurements, the samples were coated with carbon. The micro-textures and composition were obtained using a field emission scanning...
electron microscope (FESEM, JEOL JSM7000F) combined with an energy dispersive X-ray spectrometer (EDS, Oxford Instruments X-MaxN) with the working parameters of 15 kV, 1 nA, and collection times of 30–50 s. Olivine and alumina were employed as the standards for Mg, Al, Si, and Fe. The Aztec software (version 2.4, Oxford Instruments Nanotechnology Tools Ltd) was used to determine the composition by EDS. For more detailed experimental information, please refer to Text S1.

3. Results

3.1 Phase relations

Figure 1 shows the back-scattered electron (BSE) images of typical experimental run products, and a summary of the quenched phase assemblages is given in Table 1. The phase assemblages are simple and include PhD, Fe$_2$O$_3$, bridgmanite, garnet, stishovite, and melt. A trace amount of ringwoodite was also observed.

At 25 GPa and 1200 °C, the BSE image (shown in Figure 1a) shows the presence of PhD and Fe$_2$O$_3$ in bright and dark colors, respectively, with higher Fe$^{3+}$ content in the FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ system. The same phase assemblage was observed under equivalent $P$-$T$ conditions with lower Fe$^{3+}$ content in the FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$, system as shown in Figure 1b. This suggests that the solubility of Fe$^{3+}$ in PhD was quite low. At elevated temperatures, phase assemblages with both higher and lower Fe$^{3+}$ content look the same, except that excess Fe$_2$O$_3$ was identified in the system with higher Fe$^{3+}$ content, as shown in Figures. 1c and 1d. In the AlOOH-FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ ternary
system, garnet, stishovite, and melt were found with both MORB and pyrolite-type compositions at 21 GPa. Additionally, phase Egg was also observed in the MORB-type composition.

3.1.1 The FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ system

A new PhD phase diagram is shown in Figure 2. At 18 GPa and 1000 °C, the phase assemblages look similar to each other within both starting compositions. PhD was observed with both higher and lower Fe content, and a trace amount of ringwoodite was identified in the quenched samples. At 20 GPa and 1100 °C, ringwoodite disappeared with higher iron content. Furthermore, Fe$_2$O$_3$ instead of ε-FeOOH formed in some of the quenched samples at pressures of 18 GPa to 25 GPa. Although ε-FeOOH has the same CaCl$_2$-type crystal structure as δ-AlOOH (Ohtani et al., 2001b; Suzuki, 2010), our data indicates that the Fe-rich ε-phase decomposed into Fe$_2$O$_3$ + H$_2$O at all P-T conditions in this study. We observe that dehydration of δ-AlOOH occurs at 20 GPa and 1200 °C, suggesting that the dehydration temperature of ε-FeOOH is lower than that of both δ-AlOOH and Fe$^{3+}$-bearing PhD, or that the activity of H$_2$O was too low, or the activity of SiO$_2$ was too high to stabilize ε-FeOOH.

PhD was observed at 21 GPa and 1100 °C in both starting compositions, but disappeared at 1300 °C. At 25 GPa and 1200 °C, PhD coexisted with Fe$_2$O$_3$ in both compositions. When the temperature was increased to 1400 °C, both phase assemblages transformed into bridgmanite (brg) + stishovite (st) + melt (shown in Figures 1c and 1d).
This reaction is the same as the thermodynamic calculation \( \text{PhD} = \text{Brg} + \text{St} + \text{H}_2\text{O} \) reported by Komabayashi and Omori (2006).

The highest thermal stability of PhD at 18 GPa, 20 GPa, 21 GPa, and 25 GPa is around 1100 °C, 1150 °C, 1200 °C, and 1350 °C, respectively, indicating that our results are consistent with a positive Clapeyron slope in a Fe\(^{3+}\)-bearing system. Such a positive slope had been previously determined by Frost and Fei (1998) in the Fe-free system, and by Ghosh and Schmidt (2014) in the Al, Fe\(^{2+}\)-bearing system, however, our results are different from the Fe\(^{2+}\)-bearing and Al, Fe\(^{2+}\)-bearing systems suggested by Ganskow and Langenhorst (2014).

### 3.1.2 The AlOOH-FeOOH-Mg\(_{1.11}\)Si\(_{1.89}\)O\(_6\)H\(_{2.22}\) system

The phase relation is shown in Figure 2. At 21 GPa and 1300 °C, Fe-bearing PhD was observed in the starting compositions. Nevertheless, a small amount of Fe\(_2\)O\(_3\) appeared in the pyrolite-type composition as shown in Figures 1e and 1f. Our results indicate that Al\(_2\)O\(_3\) enhances the solubility of Fe\(^{3+}\) in PhD. In addition, the added Al\(_2\)O\(_3\) in the starting composition has a great impact on the stability field of PhD at 21 GPa, causing the stability boundary to shift to around 1400 °C. At 1500 °C, PhD decomposed to Gt + St + melt, whereas hydrous phase Egg was observed in the MORB-type starting composition at high temperatures (Figures 1g and 1h). The stability condition of phase Egg in this study is consistent with that of previous reports (Sano et al., 2004; Fukuyama et al., 2017), implying that phase Egg is a potential hydrous phase at high temperatures around the mantle.
transition zone.

3.2. Mineral compositions

3.2.1. Mineral chemistry

Representative mineral compositions are summarized in Table S1. In the FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_{6}$H$_{2.22}$ binary system, the content range of MgO and SiO$_2$ in PhD is very narrow, i.e., from 20.44 to 22.91 wt% and 58.83 to 62.26 wt%, respectively, in the high Fe$^{3+}$ content system, and 20.27 to 21.79 wt% MgO and 60.59 to 63.58 wt% SiO$_2$ in the low Fe$^{3+}$ content system between 18-25 GPa. The H$_2$O content in the PhD was calculated from the deficit of the total weight percent in the EDS analysis for an average of 12.19 wt% and 12.02 wt%, respectively. The relationship between the pressure and Fe$_2$O$_3$ content in PhD is shown in Figure 3, which clearly shows that, with increasing pressure, Fe content decreases below 21 GPa, and then slightly increases up to 25 GPa. This trend was consistent with the previous result obtained by Ganskow and Langenhorst (2014), as shown in Figure 3, although the starting composition in that study showed very high FeO content (37.9 wt%). Compared with pressure, temperature seems to have little effect on the solubility of Fe$^{3+}$ in PhD. In the AlOOH-FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_{6}$H$_{2.22}$ ternary system, both MgO and SiO$_2$ decreased in PhD with increasing pressure. By contrast, the Fe$^{3+}$ content increased in both the pyrolite and MORB-type compositions compared with the FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_{6}$H$_{2.22}$ binary system, as shown in Figure 3.

At higher temperatures, garnet is able to stabilize in the FeOOH-Mg$_{0.5}$Si$_{0.5}$OOH
binary system. A large amount of garnet was found at 21 GPa and 1500 °C, which contains 22.07 and 21.59 wt% of Al₂O₃ in the MORB- and pyrolite-type starting compositions, respectively. The calculated Mg/Si ratio of the ringwoodite that appeared in the FeOOH-Mg₁.₁₁Si₁.₈₉O₆H₂.₂₂ binary system is less than 2, implying the incorporation of H₂O via the substitution mechanism Mg²⁺ = 2H⁺. The H₂O content in ringwoodite estimated by EDS total deficit is 1.5 wt% at 21 GPa and 1300 °C in MORB-type compositions, and 1.3 wt% at 20 GPa and 1100 °C in pyrolite-type compositions. Based on previous experiments, the H₂O solubility in ringwoodite was as high as 3.1 wt%, meaning that the mantle transition zone may be water-saturated (Inoue et al., 1995; Fei et al., 2017), indicating that ringwoodite is a potential water reservoir within the mantle transition zone.

3.2.2. Lattice parameters

The relationship between unit cell volume of PhD in the FeOOH-Mg₁.₁₁Si₁.₈₉O₆H₂.₂₂ binary system and Mg/Si is shown in Figure 4, where there are distinctly different relationships between Mg/Si and unit cell volumes between 18 and 20 GPa compared to 25 GPa. The unit cell volume slightly decreased with increased pressure from 18 to 20 GPa, and almost the same Mg/Si ratios were obtained within this pressure range. The volume change is consistent with the Fe₂O₃ content in PhD below 21 GPa, as shown in Figure 3. The decreased Fe₂O₃ content may lead to a decrease in volume due to the larger ion size of Fe³⁺ compared with Mg and Si. However, the unit cell volume increases even with low Fe₂O₃ content at 25 GPa, and the Mg/Si ratio also increased at the same pressure. This phenomenon is probably related to different substitution mechanisms of Fe³⁺ in PhD. The crystal structure of PhD is rather simple, as all the Mg and Si occupy octahedral sites.
When the pressure is below 21 GPa, Tschemark-type substitution (Mg$^{2+}$+Si$^{4+}$=2Fe$^{3+}$) occurs in both Mg and Si sites. That is, the decrease of Fe$^{3+}$ content would lead to a decrease in volume. By contrast, Fe$^{3+}$ only occupied Si sites at elevated pressures (Si$^{4+}$=Fe$^{3+}$+H$^+$), leading to an increase of volume even with low Fe$_2$O$_3$ content. For more information, please refer to Figure S1. Of course, there may exist another possibility that the coexisting phases with PhD will influence both the Mg/Si ratios and the substitution mechanism. Further studies will be required to clarify this issue.

4. Discussion

4.1 The stability of Fe-bearing PhD in the mantle

The stability of PhD was analyzed in the MgO-SiO$_2$-H$_2$O (MSH) system for pressure ranging from 16 to 25 GPa and temperature from 900 to 1400 ºC by Frost and Fei (1998). It can be seen from the results that PhD has a wide stability region ranging from 1000 ºC at 17 GPa to 1400 ºC at 26 GPa. PhD was also investigated in the MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O (MASH) system by Ghosh and Schmidt (2014), whose results showed that the addition of Al$_2$O$_3$ increased the stability field of PhD until 1600 ºC at 24 GPa. It has also been reported that Al-rich PhD could remain stable at temperatures up to 2000°C at 26 GPa (Pamato et al., 2015).

However, there remains significant regarding the effect of Fe on DHMSs, which is important considering that Fe is an abundant element on the Earth. Ghosh and Schmidt (2014) reported that Fe$^{2+}$ decreased the stability of PhD by 200 ºC when adding 4.3 wt% of
FeO into reduced FMASH composition compared with the MASH system at pressures between 22 and 24 GPa. By contrast, Ganskow and Langenhorst (2014) observed that Fe$^{2+}$ was available to maintain the stability of PhD of both reduced FMSH and FMASH compositions with a FeO content of 37.9 wt% and 17.9 wt%, respectively. It can be seen that the highest thermal stability is up to 1450 ºC at 20.5 GPa, which is higher compared to the reported thermal stability of Mg-PhD at 1400 ºC and 25 GPa (Frost and Fei, 1998). According to our results, Fe$^{3+}$ slightly destabilizes the thermal stability of PhD when considering PhD with both low (7.2 wt%) and high Fe$_2$O$_3$ (13.5 wt%) contents. For example, in the MSH system, PhD was observed at 21.7 GPa and 1300 ºC (Frost and Fei, 1998), whereas Fe$^{3+}$-bearing PhD has already disappeared under the same $P$-$T$ conditions in our experiments.

Oxygen fugacity plays an important role in the determination of the physical and chemical properties of mantle materials. By controlling the Fe$^{3+}$ or Fe$^{2+}$ content in a mineral, the transport properties can be influenced, including element partitioning, electrical conductivity, and creep (Ryerson et al., 1989; Frost et al., 2001). The minimum Fe$^{3+}$/ΣFe of the bulk rock ratio is estimated to be 3% under mid-transition zone conditions (Frost and McCammon, 2008), indicating that the oxidation state of the mantle is reduced. However, in the current experiment, we describe extremely oxidized bulk starting compositions, but were unable to determine if oxygen fugacity influences the stability limit of PhD. Previous research has illustrated that even when Fe$^{2+}$ was used in the starting compositions under very reducing redox conditions, a certain amount of Fe$^{3+}$ is still found in the resultant synthesized products (Frost et al., 2004; Saikia et al., 2009). For example, electron
energy-loss spectroscopy by Ganskow and Langenhorst (2014) found \( \text{Fe}^{3+}/\Sigma\text{Fe} = 74\% \) in Fe and Al, \( \text{Fe}^{2+} \)-bearing PhD, even though they used FeO in their starting material. Additionally, earlier studies have shown that \( \text{Fe}^{2+} \) tends to partition into ringwoodite rather than PhD under transition zone conditions (Frost et al., 2004; Saikia et al., 2009; Ganskow and Langenhorst, 2014). This means that the gap between the \( \text{Fe}^{3+} \) contents of the PhD in our experiment and those of previous studies may be negligible under subduction zone conditions. Further experiments have to be conducted to investigate whether oxygen fugacity has an impact on the thermal stability of \( \text{Fe}^{3+} \)-bearing PhD.

Although \( \text{Fe}^{3+} \)-bearing PhD decomposes at 21 GPa and below 1300 °C, Al, \( \text{Fe}^{3+} \)-bearing PhD remains stable above 1300 °C in both hydrous pyrolite and MORB-type compositions, as shown in Figure 2. Meanwhile, previous studies have suggested that Al preferentially partitions into PhD rather than coexisting wadsleyite, ringwoodite, bridgmanite, and phase H (Bolfan-Casanova et al., 2003; Litasov et al., 2005; Ghosh and Schmidt, 2014; Ohira et al., 2014; Bindi et al., 2015; Pamato et al., 2015). The main factor for this stabilization was attributed to the effect of Al on the stability of PhD. It can be seen from our results that Al could offset the negative effect of \( \text{Fe}^{3+} \) on the stability of PhD and stabilize it at higher temperatures. Consequently, considering the stabilizing effect of Al, the stability region of Al, \( \text{Fe}^{3+} \)-bearing PhD should increase.

5. Implications

5.1 Long water reservoir
The stability region of DHMSs has been intensively reported upon by many researchers for simple MSH or MAS systems (Kanzaki, 1991; Kawamoto et al., 1996; Frost and Fei, 1998; Ulmer and Trommsdorff, 1999; Ohtani et al., 2001, 2004; Litasov and Ohtani, 2002; Komabayashi et al., 2005; Komabayashi and Omori, 2006; Ghosh and Schmidt, 2014; Nishi et al., 2014; Pamato et al., 2015; Xu and Inoue, 2019b), where these studies agree that Al drastically increases the thermal stability region of DHMSs. Among the DHMSs, PhD represents an important water carrier from the transition zone to the upper parts of the lower mantle. With the increase in pressure, PhD transforms into a high-pressure polymorph, phase H, at around 48 GPa, which is equivalent to a depth of 1,500 km (Nishi et al., 2014). Recent experimental research has shown that Phase H could form a solid solution with δ-AlOOH, and coexist with bridgmanite along slab geotherms, which means that water may be transported to the base of the lower mantle (Ohira et al., 2014).

Through the combination of the current experiments and previous results, PhD may be expected to remain stable along the hot subduction zone in both hydrous pyrolite and MORB-type materials, and the increased Fe content may help PhD to sink into deeper regions. Furthermore, if subducting slabs stagnate at the mantle transition zone, Al-rich PhD may transform into phase Egg under P-T conditions, approximating the mantle geotherm. As subduction continues, some PhD may decompose to bridgmanite, stishovite, and H₂O when present in the uppermost lower mantle. The released water from the breakdown of PhD may cause partial melting and contribute to the observed low-velocity zones at the uppermost lower part of the Japanese subduction zone (Liu et al., 2016).
Additionally, a previous study has suggested that Al-bearing stishovite enhanced (<2.3 wt % Al₂O₃) the substitution of water in stishovite via the mechanism \( Al^{3+} + H^+ = Si^{4+} \) (Pawley et al., 1993). The recovered stishovite, with a Al₂O₃ content of 2.89 wt% and a total weight percent of 98.97 at 21 GPa and 1500°C indicates that water could be held in stishovite even under normal mantle geotherm conditions. Therefore, Al-bearing stishovite is expected to be carried to the lower mantle along the subduction zone in Al-rich bulk compositions (Lin et al., 2020; Nisr et al., 2020) and may transport water with it. Based on these new findings, this study helps to broaden our understanding of the deep-water cycle within the Earth.

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**Table 1.** Experimental run conditions and observed phase assemblages in the $\alpha$-FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ and AlOOH-$\alpha$-FeOOH-Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ systems.

<table>
<thead>
<tr>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>Results</th>
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<tr>
<td>25</td>
<td>1600</td>
<td>St+Melt</td>
<td>St+Melt</td>
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<tr>
<td>25</td>
<td>1400</td>
<td>Brg+$\alpha$-Fe$_3$O$_2$+St+Melt</td>
<td>Brg+St+Melt</td>
</tr>
<tr>
<td>25</td>
<td>1200</td>
<td>PhD+$\alpha$-Fe$_3$O$_2$</td>
<td>PhD+$\alpha$-Fe$_3$O$_2$</td>
</tr>
<tr>
<td>21*</td>
<td>1500*</td>
<td>Gt+Egg+St+Melt</td>
<td>Gt+St+Melt</td>
</tr>
<tr>
<td>21*</td>
<td>1300*</td>
<td>PhD+Melt (T)</td>
<td>PhD+$\alpha$-Fe$_3$O$_2$+Melt (T)</td>
</tr>
<tr>
<td>21</td>
<td>1300</td>
<td>rw+St+Melt</td>
<td>rw+St+Melt</td>
</tr>
<tr>
<td>21</td>
<td>1100</td>
<td>PhD+$\alpha$-Fe$_3$O$_2$+Melt</td>
<td>rw+PhD+St+Melt</td>
</tr>
<tr>
<td>20</td>
<td>1100</td>
<td>PhD+$\alpha$-Fe$_3$O$_2$+Melt</td>
<td>rw+PhD+St+Melt</td>
</tr>
<tr>
<td>18</td>
<td>1000</td>
<td>rw (T)+PhD+$\alpha$-Fe$_3$O$_2$+Melt</td>
<td>rw (T)+PhD+Melt</td>
</tr>
</tbody>
</table>

*Starting compositions are MORB and pyrolite-type.

PhD-phase D, St-stishovite, Brg-bridgmanite, Egg-phase Egg, Gt-garnet, rw-ringwoodite, T-trace amounts.

The duration times of heating at 1100-1400 °C and 1500-1600 °C are 60 and 20 minutes, respectively.
Figure 1. BSE images of representative run products (PhD-phase D, St-stishovite, Brg-bridgmanite, Egg-phase Egg, M-melt, Gt, garnet) for samples synthesized at 25 GPa and 1200 °C with 15.0 wt% (a) and 8.0% wt% (b) of α-FeOOH + Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$; 25 GPa and 1400 °C with 15.0 wt% (c) and 8.0% wt% (d) of α-FeOOH + Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$; 21 GPa and 1300 °C in pyrolite (e) and MORB-type (f) composition; and 21 GPa and 1500 °C in pyrolite (g) and MORB-type (h) composition.
Figure 2. Phase diagram of PhD. MASH, MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O. FMSH, MgO-FeO/Fe$_2$O$_3$-SiO$_2$-H$_2$O. FMASH, MgO-Al$_2$O$_3$-FeO/Fe$_2$O$_3$-SiO$_2$-H$_2$O. The numbers 1 and 2 refer to high and low Al$_2$O$_3$ and FeO/Fe$_2$O$_3$ contents, respectively. The numbers in parentheses represent the FeO/Fe$_2$O$_3$ content in a given starting composition. The stability limit of Fe$^{3+}$-bearing PhD with both high and low Fe$^{3+}$ contents is illustrated by the black solid line, which is slightly lower than that of Mg-PhD (pink solid line) (Frost and Fei, 1998), and much lower than that for the Fe$^{2+}$-rich starting composition (yellow solid line) (Ganskow and Langenhorst, 2014). The stability limit of Al, Fe$^{3+}$-bearing PhD in both pyrolite and MORB-type composition is illustrated by the black dash line, which is much higher than that of Fe$^{3+}$-bearing PhD. The trend of black dash line at high pressure is possibly between the blue dash line in MASH and the blue solid line in FMASH (Ghosh and Schmidt, 1998). However, Ganskow and Langenhorst (2014) observed different behaviors of PhD in FMASH (yellow dash line). Hot slab geotherm from Kirby et al. (1996) is plotted as a reference, e.g. 1200 °C at 660 km and 1300 °C at 820 km.
Figure 3. Variation of the Fe$_2$O$_3$ content in PhD as a function of pressure. Error bars are 2-sigma. The Fe$_2$O$_3$ content displays a decreasing trend with increasing pressure from 18 to 21 GPa; afterwards, it slightly increases to 25 GPa if ignore the uncertainties due to its small crystalline size. This trend is consistent with that obtained by Ganskow and Langenhorst (2014).
Figure 4. Relationship between the unit-cell volume and Mg/Si ratio of PhD at different pressures. Error bars are 2-sigma. Solid and open symbols refer to 15.0 wt% α-FeOOH + Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$ and 8.0 wt% αFeOOH + Mg$_{1.11}$Si$_{1.89}$O$_6$H$_{2.22}$, respectively. Obviously, different volume-Mg/Si relations exist at pressures of 18 - 20 GPa and 25 GPa. This is probably caused by different substitution mechanisms of Fe$^{3+}$ in PhD. Between 18 and 20 GPa, the Tschermak-type substitution occurs in both Mg and Si sites (Mg$^{2+} + $Si$^{4+} = 2$Fe$^{3+}$). Thus, the decrease of Fe$^{3+}$ content leads to a decrease in volume. By contrast, Fe$^{3+}$ only occupies the Si site at elevated pressures (Si$^{4+} = $Fe$^{3+} + $H$^+$), thereby leading to an increase in volume even with a low Fe$_2$O$_3$ content.