

## Decomposition of hydrous phase D by the formation of Fe-bearing aluminous bridgmanite

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It has been considered that a certain amount of water is transported as hydrous minerals into the mantle through subduction of slab. Recent discovery of hydrous ringwoodite inclusion in a diamond suggests that the mantle transition zone is hydrous at least locally (Pearson et al. 2014). Next open question is whether the lower mantle can accommodate water or not. Although the major constituent minerals can host significant amounts of water in the upper mantle, most of the lower mantle minerals (e.g. bridgmanite (Brm) and ferropericlavite (fPc)) can incorporate only a limited amounts of water. Therefore, if water is transported into the lower mantle, water must be hosted by dense hydrous minerals (DHMs) such as hydrous phase D. However, it is not clear whether DHMs can exist in the lower mantle because temperature of slab subducted into the lower mantle is not constrained well. Brm contains significant amounts of Fe<sup>3+</sup> (Fe<sup>3+</sup>/ΣFe > 0.1) even in coexistence with metallic iron (Frost et al. 2004). The amounts of Fe<sup>3+</sup> increase with increasing Al<sub>2</sub>O<sub>3</sub> content in Brm, and the Fe<sup>3+</sup>/ΣFe ratio exceeds 0.5 in the lower-mantle Brm (Frost et al. 2004; Frost and McCammon, 2008). Since the Fe<sup>3+</sup>/ΣFe ratios are only 0.01-0.03 and 0.10-0.14 in the upper-mantle peridotite and MORB, the formation of Brm would extract oxygen from other minerals by the deposition of Fe metal. In other words, Brm should work as a reducing agent against other minerals. Therefore, we expect the breakdown of DHMs by reduction of OH to H<sub>2</sub> through the Brm formation. On the basis of this background, we conducted the following experiment using a Kawai-type multianvil press. A starting materials were used sintered Al-free and aluminous phase D pre-synthesized at 27 GPa and 1100 K, a natural olivine single crystal (Olv) and pyroxene aggregates with bulk composition of pyrolite minus fPc (Pyr-fPc) and (Mg<sub>0.9</sub>Fe<sub>0.1</sub>)(Si<sub>0.9</sub>Al<sub>0.1</sub>)O<sub>3</sub> (FeAl-En) synthesized at 1300 K in a controlled oxygen fugacity (P<sub>O<sub>2</sub></sub> ≈ IW) and ambient pressure. Pyroxene samples were packed in Mo capsule and sintered at 2 GPa and 1500 K. Sintered phase D was directly attached with Olv, sintered Pyr-fPc or FeAl-En in Au sample capsule. The samples were pressurized to 27 GPa and heated at 1100 K for 1 or 10 hours. Analyses of recovered samples were made with FE-SEM and ATEM.

No reaction between Al-free phase D and Brm + fPc aggregate formed from Olv was found in the SEM observation. The existence of 2-4 μm thick SiO<sub>2</sub>-rich fine-grained layers were discovered on the boundary between Al-free / aluminous phase D and Brm formed from Pyr-fPc or FeAl-En. TEM observation indicated amorphous phases with Brm composition in fine SiO<sub>2</sub> stishovite. These observations strongly indicate that the decomposition of phase D accompanied by the formation of Fe-bearing aluminous Brm. The present result suggests that, although water can be transported into the top of the lower mantle due to the formation of phase D through subduction of slab, phase D will decompose by reduction at the depth to 720 km. The produced H<sub>2</sub> should come back to the upper mantle. Thus, water cannot be transported through slab subduction to the majority of the lower mantle.

Keywords: hydrous phase D, lower mantle, bridgmanite, subducting slab, water transportation, ferric iron