Transportation of water into the deep lower mantle by new type of dense hydrous magnesium silicate

Water is a key component in the Earth's evolution and dynamics because it strongly influences many chemical and physical properties of the mantle materials. In a descending slab, a certain amount of water is transported into the Earth's interior via dense hydrous magnesium silicate (DHMS). Phase D, which is one form of DHMS, is known to have large stability fields and be stable in the upper part of the lower mantle conditions. According to the previous experimental study, the transportation of water by DHMS would be terminated in the middle of the lower mantle (~1250 km depth) due to the dissociation of phase D into assemblages of $MgSiO_3$ bridgmanite plus water. On the other hand, a new type of DHMS has been theoretically predicted to be stable at pressures above ~45 GPa [1]. A multianvil apparatus using sintered diamond anvils in conjunction with a synchrotron X-ray diffraction technique allows this theoretical prediction to be confirmed. We are the first to experimentally show that phase D transforms to an assemblage with a new DHMS, named phase H, at pressures above ~48 GPa [2].

In situ X-ray diffraction measurements were performed using a multi-anvil apparatus (SPEED-Mk.II) at beamline **BL04B1**. White X-rays from synchrotron radiation were used as the incident beam. Sintered diamond anvils with a truncated edge length of 1.5 mm were used as the second-stage anvils to generate pressures up to 50 GPa. The chemical compositions of the starting materials were $MgSiO_4H_2$ and $MgSi_{1.5}H_2O_5$, which were prepared by mixing $Mg(OH)_2$ brucite and SiO_2 silica. The diffracted beam was measured using the energy-dispersive method with a fixed angle of 6.0° and a Ge solid-stage detector. A small amount of Au powder mixed into the samples was used to determine the pressure.

At 400°C, 37.3 GPa and a starting composition of $MgSiO_4H_2$, broad diffraction peaks of $Mg(OH)_2$ brucite and the Au pressure marker were observed (Fig. 1(a)). At 900°C and 37.3 GPa, peaks corresponding to phase H appeared and remained at least up to 42.0 GPa and 1,000°C (Fig. 1(b)). BSE images of the recovered sample show an almost single phase of phase H (Fig. 2(a)). Additional quenching experiments indicated the formation of phase H at least up to 50 GPa and 1000°C. Using a starting composition of $MgSi_{1.5}H_2O_5$, phase D transformed to phase H plus stishovite around 48 GPa (Fig. 2(b)). These reactions and transition boundaries are consistent with those predicted by the theoretical calculation [1]. The diffraction peaks of phase H were indexed with an orthorhombic symmetry identical to a high-pressure hydrous phase δ-AlOOH, yielding $a = 4.478$ Å, $b = 4.091$ Å and $c = 2.700$ Å at 42 GPa and 1,000°C. This structure slightly differs from the
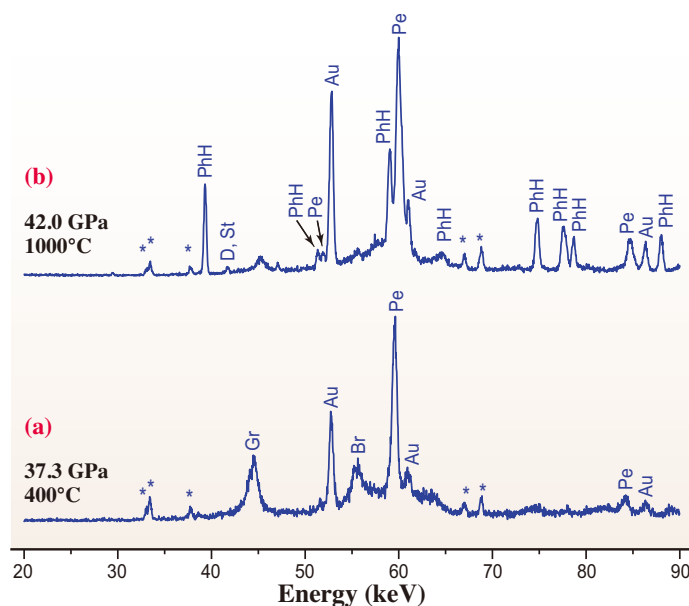

Fig. 1. X-ray diffraction patterns of *in situ* observations at BL04B1.
PhH, phase H; St, stishovite; Br, brucite; Pe, periclase; Gr, graphite; D, phase D; *, characteristic lines of Au (gold) and La (lanthanum).
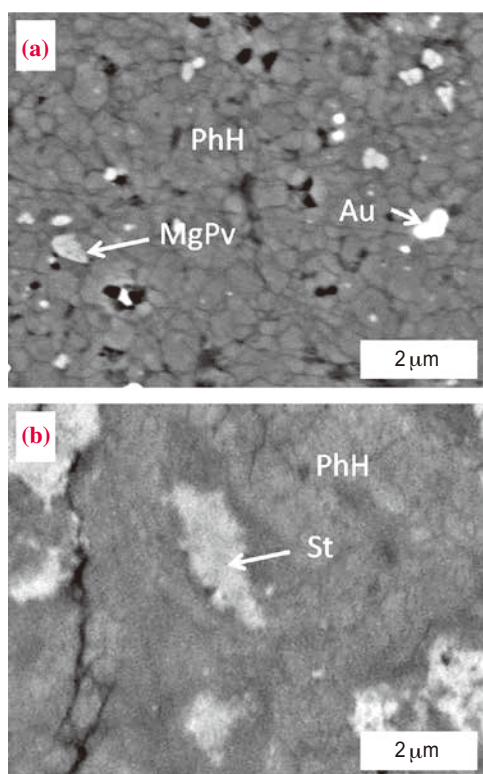
expanded towards a higher pressure and temperature since aluminium is a common element in Earth.

Recent experimental results using a diamond anvil cell (DAC) at beamline **BL10XU** also support a largely stable phase H. Phase H - δAlOOH solid solution (aluminous phase H) is stable up to the conditions of the base in the lower mantle and coexists with $MgSiO_3$ bridgmanite and post-perovskite [5]. Thus, aluminous phase H may be stable at pressures and temperatures corresponding to the conditions of whole lower mantle and should be capable of delivering a certain amount of water into the deepest regions of the lower mantle.
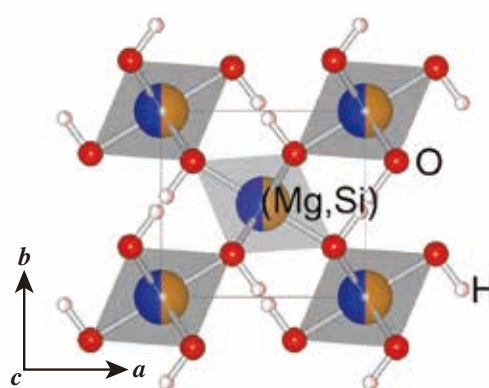

Fig. 2. Back-scattered electron images of the run products. **(a)** 42 GPa and 1000°C with the composition of $MgSiH_2O_4$ phase H (PhH). **(b)** 50 GPa and 950°C with the composition of $MgSi_{1.5}H_2O_5$ phase D. St: stishovite, MgPv: bridgmanite, Br: brucite, Au: gold.

Fig. 3. Crystal structure of $MgSiH_2O_4$ phase H determined by the single crystal X-ray diffraction method [3]. Large bi-colored spheres indicate the atomic positions where Mg and Si atoms are disordered. Medium spheres are oxygen atoms. Small bi-colored spheres indicate hydrogen atoms with half-occupations to avoid forming adjacent H-H bonding.

theoretical prediction, which possesses a monoclinic symmetry. On the other hand, white X-ray diffraction measurements did not provide detailed structural data at ambient conditions due to the rapid amorphization of the sample during observation. Therefore, we also tried to investigate the structure of phase H at ambient conditions by single-crystal X-ray diffraction; the structure is orthorhombic in space group $Pnnm$ ($CaCl_2$-type structure, Fig. 3) with lattice parameters $a = 4.733$, $b = 4.3250$, $c = 2.8420$ Å, V = 58.18 Å^3 [3].

In additional experiments, we confirmed that phase H forms a solid solution with δ-AlOOH by substitution of $Mg^{2+} + Si^{4+} \Leftrightarrow Al^{3+}$ because of their similar crystal structures. Moreover, alumina is strongly partitioned into phase H relative to coexisting $MgSiO_3$ bridgmanite. Our experimental results and the theoretical calculation indicate that the stability field of end-member $MgSiO_4H_2$ phase H is limited up to ~55 GPa and 1000°C, which correspond to the conditions of the middle lower mantle in a cold subducting plate. On the other hand, it is known that δ-AlOOH has an extremely large stability field over the entire range of conditions in the lower mantle [4]. Therefore, the stability field of phase H in the actual mantle should be

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