Phase transition of aluminium hydroxide at extremely high pressure

Hydrogen is the most abundant element in the universe. In the Earth, hydrogen is transported into deep mantle regions as a hydrous mineral via the subduction of oceanic plates. To better understand the global hydrogen circulation in the Earth's mantle, a number of high-pressure experiments were conducted on the stability of hydrous phases under lower mantle conditions. The results of recent experimental and theoretical studies indicated that hydrous phases may deliver a certain amount of water to the bottom of the Earth's mantle (~130 GPa) [1,2]. Despite its ubiquity and the profound effects of hydrogen on our Earth, there have been few studies on the stabilities of hydrous minerals on other planets. We consider that there is a possibility that water is present in hydrous phases in such planetary interiors, because a mixture of anhydrous minerals and H_2O phases has been used to discuss the interior structure of icy planets. There have also been reports of the existence of extrasolar planets having a few times the Earth's mass, where hydrous phases may play important roles as hosts of water in the deep interior of those planets.

An *ab initio* calculation predicted that a new high-pressure form of AlOOH, which has a pyrite-type structure, would be stabilized at pressures >170 GPa [3]. Furthermore, in a recent theoretical study, it was proposed that the transformation of δ-AlOOH to a new orthorhombic phase at ~160 GPa would occur prior to the transformation to pyrite-type AlOOH [4]. Thus, mineralogy based on theoretical calculations implies the potential stability of hydrous phases under extreme conditions. In this study, we conduct high pressure–temperature (P–T) experiments on the stability of pure AlOOH and its solid solutions with FeOOH using laser-heated diamond anvil cell (DAC) techniques and first-principles density-functional calculations for a range of pressures up to 270 GPa [5].

In situ X-ray diffraction (XRD) measurements were performed at SPring-8 **BL10XU**. High P–T conditions were achieved using a laser-heated DAC technique and the instrument was equipped with beveled anvils with 50 and 90 μm culets. We used $CaCl_2$-type hydroxide powders with compositions of AlOOH and $(Fe_{0.75}Al_{0.25})OOH$ as starting materials. They were synthesized at ~20 GPa and 1,000 K in a multianvil apparatus prior to DAC experiments. Samples were coated with a sputtered gold (Au) film on both sides to serve as an internal pressure standard and laser absorber. AlOOH and $(Fe_{0.75}Al_{0.25})OOH$ were loaded into ~20 μm holes in a pre-indented rhenium gasket, together with insulation layers of AlOOH and SiO_2 glass powders, respectively. Heating was performed from both sides of the samples using two 100 W single-mode fiber lasers. Angle-dispersive XRD patterns at high P–T were collected with an imaging plate (IP, Rigaku) and an X-ray flat-panel (FP) detector

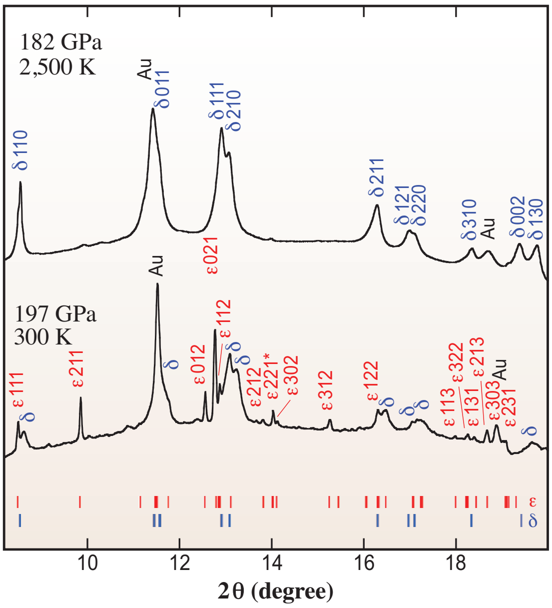

Fig. 1. *In situ* XRD patterns of ε-AlOOH formed from δ-AlOOH under various P–T conditions. The XRD pattern at 195 GPa and 300 K, after heating at 204 GPa and 2,500 K, shows the formation of ε-AlOOH. δ, δ-AlOOH; ε, ε-AlOOH; Au, gold.

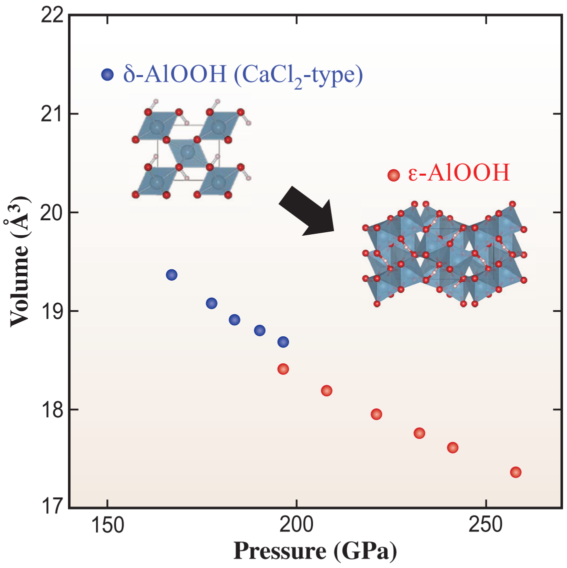

Fig. 2. Cell volumes (V/Z) of hydroxides as a function of pressure. Pressure and volume errors are smaller than the symbol size.

(Perkin Elmer) with typical exposure times of 30 s and 1 s, respectively.

We observed that XRD patterns of δ-AlOOH changed at 190 GPa and ~2500 K, where additional diffraction peaks corresponding to the new high-pressure form (hereafter, ε-AlOOH) appeared (Fig. 1). All of these new peaks were reasonably indexed with an orthorhombic symmetry phase, as predicted by a recent theoretical study [4]. Furthermore, the observed cell parameters ($a = 8.311(8)$, $b = 4.145(2)$, $c = 4.275(2)$ Å, and $V = 18.43(5)$ Å^3/AlOOH at 197 GPa and 300 K; Table 1) were close to those of the theoretically predicted orthorhombic phase of AlOOH ($a = 8.354$ Å, $b = 4.191$, $c = 4.314$ Å, and $V = 18.88$ Å^3/AlOOH at 180 GPa and 0 K). Formation of ε-AlOOH was reproduced in an additional experiment using AlOOH boehmite powder up to 271 GPa and 2,500 K. Experimentally determined cell volumes of δ-AlOOH and ε-AlOOH up to 258 GPa are shown in Fig. 2. Our experimental results show a density reduction of ~1.8% during the δ-AlOOH to ε-AlOOH transition at 197 GPa, in good agreement with the *ab initio* calculation.

In the structural and compositional models of ice giants such as Uranus and Neptune, H_2O is a dominant component stored mainly as mantle water or ice overlying the central rocky core. Our experimental results show that the high-pressure forms of hydroxides have wide stability fields, up to at least ~270 GPa, far beyond the pressures found in the Earth's mantle. If hydrous phases are stable even in other major chemical compositions at extreme high pressures, hydrous phases may be present in the rocky cores of some icy planets with sizes smaller than Neptune.

Terrestrial exoplanets that are a few times Earth's mass (super-Earths), have been discovered in extra-solar systems. Deep water transport via the hydrous phase, as suggested in the Earth's interior, may be applicable to those super-Earths that feature plate tectonics (Fig. 3). Although further studies on the dehydration temperatures of ε-AlOOH, pyrite-type hydroxides and their potential high-pressure forms are required, we conclude that water may be stored in hydroxides in the deep interior of some terrestrial super-Earths and the rocky cores of ice giants.

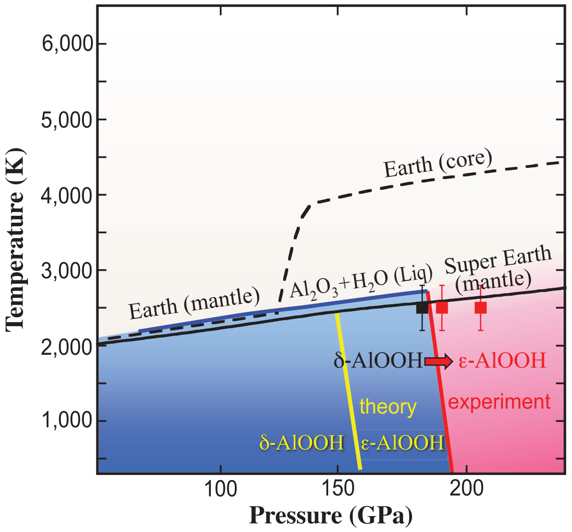

Fig. 3. High P–T phase diagram of AlOOH. The thick red solid line indicates the phase boundary estimated by combining the transition pressure of the present experiment with the previous ab initio calculation of the Clapeyron slope [3,4]. The thick blue line indicates the dehydration melting temperature of δ-AlOOH. Colored areas represent the regions where water is retained in AlOOH. The P–T conditions of Earth and super-Earth having a mass several times that of Earth are shown as black solid and dashed lines, respectively. Note that the dehydration temperatures of the ε-AlOOH phases were not clarified.

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References

[1] M. Nishi *et al.*: Nat. Geosci. **7** (2014) 224.
[2] M. Nishi *et al.*: Nature **547** (2017) 205.
[3] J. Tsuchiya and T. Tsuchiya: Phys. Rev. B **83** (2011) 054115.
[4] A.K. Verma *et al.*: Am. Miner. **103** (2018) 1906.
[5] *M. Nishi, Y. Kuwayama, J. Tuchiya: Icarus* ***338*** *(2020) 113539.*