

The pyrite-type high-pressure form of FeOOH

Hydrogen (H) is the most abundant element in the universe and it has played an important role in the structure, dynamics, and evolution of the Earth. About 70% of the Earth's surface is covered with water (H₂O) and a huge amount of water is also estimated to be maintained in the Earth's interior. However, the actual amount, distribution, and origin of the water deep in the Earth's interior are unclear. Although liquid water is generally present on the surface of the Earth, hydrous phases (which contain hydrogen in their crystal structure) can retain water in the deep mantle. Therefore, a significant amount of water has been transported into the Earth's interior via the subduction of hydrous phases in the cold oceanic lithosphere since the initiation of plate tectonics in the Archaean. Our research group previously contributed to understanding of the stability of hydrous phases at high pressures [1]. Several recent studies have suggested that δ -AlOOH - phase H (MgSiO₄H₂) solid solution can retain water without dehydration even at high pressures and temperatures corresponding to the base of the mantle [2]. Thus, the surface water may be transported as far as the core–mantle boundary (2,900 km depth) [1,2]. However, the strong dependence of the stability of hydrous minerals on the chemical composition may prevent the passage of water to such a great depth. For example, one of the possible hydrogen carriers, iron hydroxide ϵ -FeOOH, was recently reported to decompose at 80 GPa (corresponding to 1,900 km depth) to form FeO₂, releasing H₂ [3]. This reaction suggests that the separation of hydrogen and oxygen is cyclic and that water cannot reach the deeper regions of the lower mantle. In this study [4], we further examined the high-pressure behavior of iron hydroxide FeOOH and obtained data showing the formation of a new hydrous phase under the conditions of the deep lower mantle.

First, we conducted first-principles calculations to determine the stability of FeOOH phases at high pressures. The calculated relative enthalpies indicated that the pyrite - type structure may be stabilized at above \sim 70 GPa (Fig. 1), although the previous study suggested that FeOOH decomposes into FeO and H₂ under such conditions.

On the basis of these first-principles predictions, we performed *in situ* XRD measurements using a laser-heated diamond anvil cell (DAC) system at SPing-8 BL10XU. We used symmetric diamond anvil cells with 90 μ m and 200 μ m culet diamond anvils

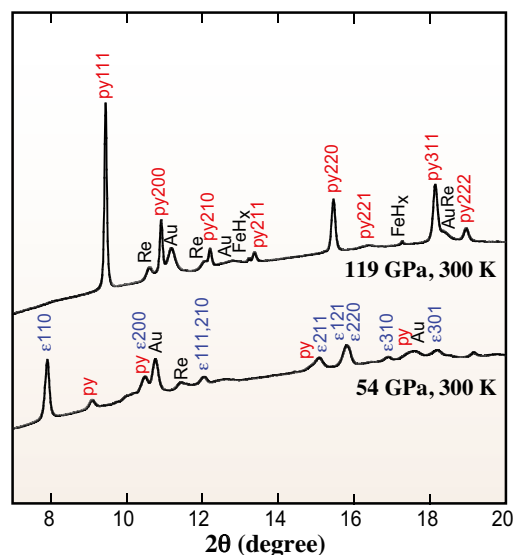


Fig. 1. Typical XRD patterns obtained by *in situ* observations at high pressure after heating at 1,500 K. ϵ , ϵ -FeOOH; py, pyrite-type FeOOH; FeH_x, dhcp-FeH_x; Au, gold; Re, rhenium.

to generate high pressures. Pellets of α -FeOOH with thickness 10–15 μ m were used as the starting material. Each sample was coated with sputtered gold (Au) films on both sides, which acted as an internal pressure standard and a laser absorber. The sample was loaded into a sample chamber in a pre-indenting rhenium gasket with insulation provided by layers of fine-grained SiO₂ glass. We used two 100 W single-mode fiber lasers and heated the sample from both sides. The temperatures were maintained for 3–30 min and measured using spectroradiometry. Angle-dispersive *in situ* XRD patterns were obtained at high pressures and temperatures with an imaging plate (Rigaku) and an X-ray flat panel detector (PerkinElmer) with typical exposure times of 30 s and 1 s, respectively. The wavelengths of the monochromatic incident X-ray beam were 0.415–0.416 Å. Pressures were calculated from the various equations of state for gold.

XRD patterns obtained at \sim 120 GPa at room temperature only showed diffraction peaks for sputtered gold owing to the amorphization of goethite during the compression process. After the heating of the sample to \sim 1500 K, the *in situ* XRD pattern showed clear diffraction peaks that can be accounted for by a simple cubic symmetry (Fig. 2), which

matches that predicted by theoretical calculation for the pyrite-type framework of FeO_6 octahedra. In order to determine the stability fields of this phase, we reheated this sample after decompression. The peaks corresponding to the pyrite-type FeOOH remained as the stable phase in the pressure range between 90 GPa and 129 GPa. Upon heating after further decompression to ~ 60 GPa, we observed the transition of pyrite-type FeOOH to ϵ - FeOOH , which is known as the polymorph in FeOOH . Thus, the phase boundary between ϵ - FeOOH and pyrite-type FeOOH is located between 60 GPa and 90 GPa at 1,500 K. XRD patterns of the pyrite-type FeOOH were also obtained in additional *in situ* experiments up to 2,400 K using the same starting material at ~ 96 GPa with weak peaks corresponding to double hexagonal-close-packed (dhcp) FeH_x . When the sample was heated to temperatures of above 2,400 K, the pyrite-type FeOOH dehydrated into an assemblage containing an Fe_2O_3 post-perovskite phase.

Although anhydrous FeO_2 with a pyrite-type structure was recently reported to be stable above 80 GPa [3], the cell volume of pyrite-type FeOOH is approximately 8% greater than that of FeO_2 synthesized by a reaction between Fe_2O_3 and O_2 at about 80 GPa (Fig. 3). Moreover, our first-principles calculations clearly indicate that pyrite-type FeOOH is a thermodynamically stable phase since the enthalpy of the mixture of FeO_2 plus H_2 is much higher than that of pyrite-type FeOOH . Thus, pyrite-type FeOOH or the recently proposed FeOOH_x (a partially solid solution between FeO_2 and FeOOH) [5] may deliver water to the deep lower mantle. The deep-seated

pyrite-type FeOOH may release the free water by dehydration to form Fe_2O_3 when the slabs warm up during a long period of stagnation at the core-mantle boundary, as we observed. This dehydration process at the bottom of the lower mantle may cause partial melting at this depth. Further studies are required to test this hypothesis.

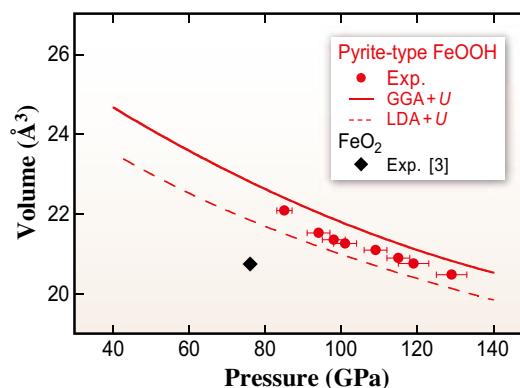


Fig. 3. Volume of pyrite-type FeOOH as a function of pressure. The experimental data at 300 K derived from XRD patterns after annealing at 1500–2400 K shows a larger volume of pyrite-type FeOOH than that of anhydrous FeO_2 [3]. Calculated volume compression curves of pyrite-type FeOOH at 0 K obtained using GGA+ U and LDA+ U (solid and dashed lines, respectively) are shown for comparison.

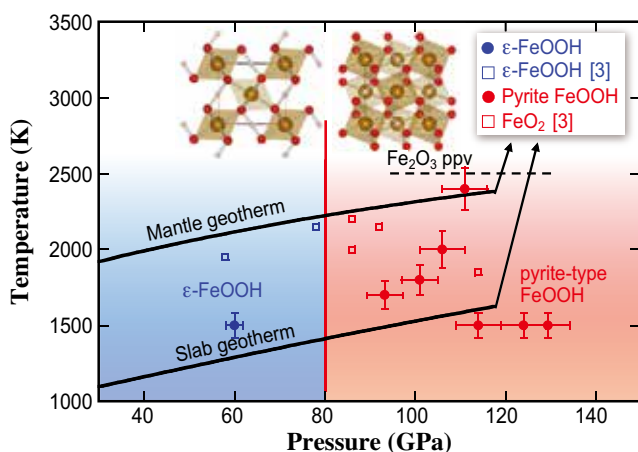


Fig. 2. Crystal structures and stability fields of ϵ - FeOOH and pyrite-type FeOOH . The appearance of Fe_2O_3 post-perovskite (ppv) associated with the dehydration process was observed above 2,400 K. Geotherms for cold subducted slabs and the mantle are shown by thick solid curves.

Masayuki Nishi

Geodynamics Research Center, Ehime University

Email: nishi@sci.ehime-u.ac.jp

References

- [1] M. Nishi *et al.*: Nat. Geosci. **7** (2014) 224.
- [2] I. Ohira *et al.*: Earth Planet. Sci. Lett. **401** (2014) 12.
- [3] Q. Hu *et al.*: Nature **534** (2016) 241.
- [4] M. Nishi, Y. Kuwayama, J. Tsuchiya, T. Tsuchiya: Nature **547** (2017) 205.
- [5] J. Liu *et al.*: Nature **551** (2017) 494.