High-*PT* neutron diffraction experiments on guyanaite: Pressure-temperature dependence of hydrogen bonding in hydrous minerals

*Chikara Shito[1], Hiroyuki Kagi[1], Asami Sano-Furukawa[2], Sho Kakizawa[1], Kazuki Komatsu[1], Katsutoshi Aoki[1], Riko Iizuka-Oku[1], Shinichi Machida[3], Noboru Furukawa[4], Akio Suzuki[5]

1. Geochemical Research Center, Graduate School of Science, The University of Tokyo, 2. Japan Atomic Energy Agency, 3. Comprehensive Research Organization for Science and Society, 4. Graduate School of Science, Chiba University, 5. Graduate School of Science, Tohoku University

Water is transported to the deep mantle by hydrous minerals in a subduction zone. Hydrogen bonding in hydrous minerals greatly affects their elastic properties such as compressibility, seismic velocity, and so on [e.g., 1,2]; it is important for us to clarify the effects of water into the properties of deep-mantle minerals. Under high-pressure conditions, a lot of hydrous minerals have a distorted rutile-type structure such as δ-AlOOH and ε-FeOOH. Recently, pressure-induced hydrogen bond (H-bond) symmetrization was experimentally observed in δ-AlOOH at ~18 GPa and room temperature [3]. However, the behavior of hydrogen in distorted rutile-type hydrous minerals at high temperature has not been clarified. Guyanaite (β-CrOOH) has also a distorted rutile-type structure and its H-bonds are significantly shorter than that of δ-AlOOH and other distorted rutile-type hydrous phases at ambient condition [e.g., 3,4]. Thus, H-bond symmetrization in guyanaite is expected to occur at relatively low pressure. Guyanaite can serve as an analogue material for predicting H-bond symmetrization in distorted rutile-type hydrous minerals. In this study, we conducted high-*PT* neutron diffraction measurements on guyanaite and investigated *P*-*T* dependence of hydrogen bonding in guyanaite.

Deuterated guyanaite (β-CrOOD) was used as a sample to reduce incoherent scattering from hydrogen. The sample was hydrothermally synthesized from the mixture of CrO_2, D_2O and a reducing agent $(COOD)_2 \cdot 2D_2O$. Formation of the deuterated sample was confirmed from infrared absorption spectra and powder XRD. Neutron diffraction measurements at high-*PT* conditions up to 11 GPa and 1000 K were performed using a six-axis multi-anvil press installed at BL11, MLF, J-PARC. The structure of β-CrOOD was refined by every *P*-*T* condition using Rietveld method. High-*PT* XRD measurements up to 7.6 GPa and 900 K were also performed at NE7A, PF-AR, KEK. *P*-*V*-*T* data were fitted to high-temperature Birch–Murnaghan equation of state.

Thermoelastic parameters of β-CrOOD were determined to be K_{300} = 204(4) GPa (K_p = 4), dK/dT = −0.033(9) GPa/K, and α = 3.05(17) $\times 10^{-5}$ /K, where α is expressed as $V_T = V_{300} \times \exp\{\alpha \times (T-300)\}$. These values were comparable to those of β-CrOOH [5]. At 300 K, the axal ratio a/b increased with pressure up to ~4 GPa, but it became constant above ~4 GPa. This behavior was found in the process of H-bond symmetrization in δ-AlOOH [3]. At higher temperature, the change in the gradient of a/b shifted to higher pressure. The O···O and D···O distances elongated with increasing temperature, whereas the O-D bond distance shortened with increasing temperature. It means that the D···D distance gets longer with increasing temperature. This result suggests that the pressure of H-bond symmetrization under mantle conditions would be higher than that under high-*P* and room-*T* conditions. When we consider the effect of the H-bond symmetrization on seismic observation, we would need to carefully take the temperature dependence into account.

[1] J. Tsuchiya, T. Tsuchiya, S. Tsuneyuki, and T. Yamanaka (2002) *Geophys. Res. Lett.*, **29**, 1909.
[2] A. Sano-Furukawa, T. Yagi, T. Okada, H. Gotou, and T. Kikegawa (2012) *Phys. Chem. Minerals*, **39**,

375–383.
[3] A. Sano-Furukawa, T. Hattori, K. Komatsu, H. Kagi, T. Nagai, J.J. Molaison, A.M. dos Santos, and C.A. Tulk (2018) *Sci. Rep.*, **8**, 15520.
[4] T. Fujihara, M. Ichikawa, T. Gustafsson, I. Olovsson, and T. Tsuchida (2002) *J. Phys. Chem. Solids*, **63**, 309–315.
[5] C. Shito, K. Okamoto, Y. Sato, R. Watanabe, T. Ohashi, K. Fuchizaki, T. Kuribayashi, and A. Suzuki (2019) *High Press. Res.*, **39**, 499–508.

Keywords: guyanaite, neutron diffraction, high-pressure, hydrogen bond

