

Super-Hydration and Reduction of Manganese Oxide Minerals at Shallow Terrestrial Depths

As major components of manganese nodules found on the ocean floor, birnessite and buserite have been known to be two distinct water-containing minerals with interlayer separation distance by ~ 7 Å and ~ 10 Å, respectively. We show that buserite is a super-hydrated birnessite formed near 5 km depth conditions. As one of the most hydrous minerals containing ca. 34.5 wt. % water, super-hydrated birnessite, i.e., buserite, remains stable up to ca. 70 km depth conditions, where it transforms into manganite by releasing ca. 24.3 wt. % water. Our work forwards an abiotic geochemical cycle of manganese minerals in subduction and/or other aqueous terrestrial environments, with implications for water storage and cycling, and the redox capacity of the region.

Manganese is the 3rd most abundant transition element in the Earth's crust and one of the most important indicators for aqueous terrestrial environments due to its redox sensitivity. Most Mn on Earth is stored in oceanic sediments in the form of oxide nodules at all depths and latitudes. Yet, the stability and phase relationship of different Mn oxide/hydroxide minerals, especially the enigmatic paragenesis and compositional-structural relationship of birnessite and buserite, the two representative phases in submarine nodules, have not yet been established since the early estimation on their association with subduction-related processes [1].

In continuation of our earlier work on super-hydrated kaolinite and its relevance for terrestrial water storage and transport [2], we establish in this work that buserite is a "super-hydrated" form of birnessite [3]. It forms at ca. 0.19 GPa in the presence of water at room tempera-

ture, which corresponds to shallow terrestrial environments near ca. 5 km depth and with a 34.5 weight-%, higher than the 30 weight-% of brucite and the 29 weight-% of super-hydrated kaolinite, it is one of the most hydrated minerals known.

Ex-situ synchrotron X-ray powder diffraction (XRD) experiments were performed at the 3D and 6D beamlines at the Pohang Accelerator Laboratory (PAL) and the BL-18C beamline at Photon Factory (PF), and in-situ experiments were done at the 13-BMC beamline at the Advanced Photon Source (APS). We have applied pressure and temperature on synthetic birnessite ($\text{Na}_{0.54}\text{Mn}_2\text{O}_4 \cdot 1.5(1)\text{H}_2\text{O}$) in a water medium to follow the subduction geotherm model W1300 of the Tonga trench [4] where Mn-abundant oceanic sediments in the Penrhyn Basin subduct; in-situ experiments were performed using resistively-heated diamond-anvil cell

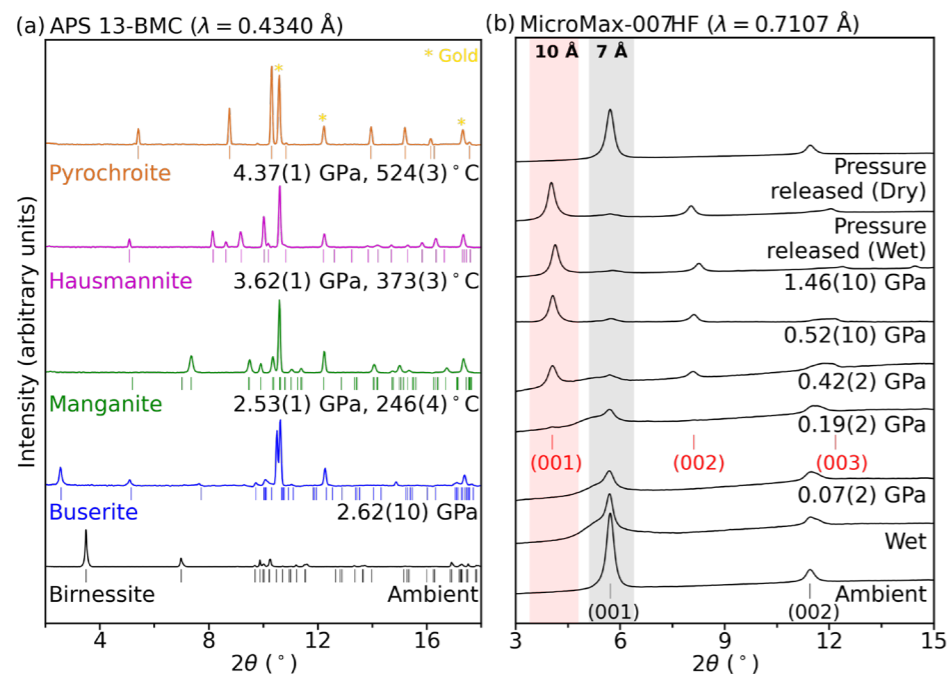


Figure 1: Synchrotron X-ray diffraction patterns showing successive transformations from birnessite. (a) In-situ synchrotron XRD patterns at selected pressures and temperatures. (b) Laboratory XRD patterns in sub-gigapascal range using fluospheres method.

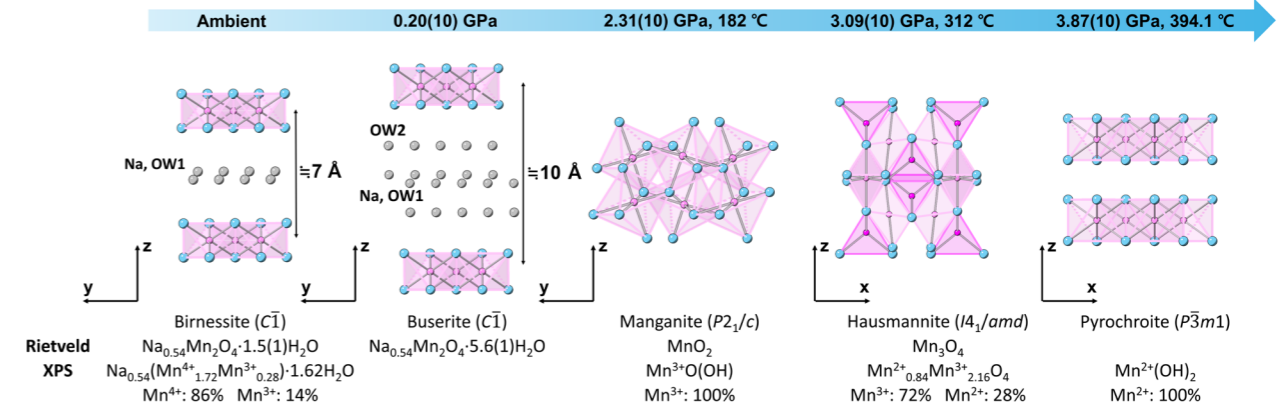


Figure 2: Successive transformations from birnessite to buserite, manganite, hausmannite, and pyrochroite along the simulated cold subduction geotherm conditions.

(RH-DAC) while ex-situ experiments were done by placing the prepared DAC in an electric furnace for 1 hour. Upon contact with water at ambient pressure, a shoulder peak appears at the low-angle side of the initial ~ 7 Å (001) X-ray diffraction peak. Upon increase of pressure from 0.07(2) to 0.19(2) GPa, a new X-ray diffraction peak near ~ 10 Å d-spacing starts to form with a concomitant decrease in the intensity of the initial ~ 7 Å d-spacing (Fig. 1). At 0.42(2) GPa, the newly formed ~ 10 Å phase becomes dominant to the initial ~ 7 Å phase and persists up to 1.46(10) GPa at room temperature. The ~ 10 Å phase is recovered after pressure release when immersed in water. It transforms back to the initial ~ 7 Å phase, i.e., in a low humidity environment (Fig. 1). The XRD pattern of the newly formed ~ 10 Å phase is indexed as a birnessite-related phase with the c-axis expanded by ca. 41.9%, resulting in a volume expansion by ca. 42.9% (Fig. 2 in the reference [3]). The structural model of the expanded phase was refined using the Rietveld method to reveal two crystallographically-distinct interlayer sites to lead to the refined chemical formula of the expanded birnessite to be $\text{Na}_{0.54}\text{Mn}_2\text{O}_4 \cdot 5.6(1)\text{H}_2\text{O}$ (Fig. 2), a super-hydrated phase that is about 3.7 times more hydrated than the original birnessite, placing it among the most hydrated known minerals with a water wt. % of 34.5. Based on the structural and compositional characteristics, we consider the super-hydrated birnessite to be buserite and have thus established its paragenetic relationship to natural birnessite. Above ca. 2.3 GPa after heating to 190 °C, conditions equivalent to depths near 70 km in a cold subduction slab, transformation of buserite to manganite occurs concomitant with the reduction of Mn^{4+} to Mn^{3+} and release of water (Figs. 1 and 2). Subsequent transformations to hausmannite and pyrochroite occur near 100 km and 120 km depths, respectively, con-

comitant with a progressive reduction of Mn^{4+} to Mn^{2+} (Figs. 1 and 2).

Our results provide a new paradigm how different manganese oxide and hydroxide minerals are generated along a subduction slab and related regions while cycling water and metals which impacts the chemistry of the ocean and its sediments. Furthermore, the depth range where successive hydration and dehydration of manganese minerals takes place is within the fore arc region where earthquake generation mechanism has not yet been linked to mineral transformations. The fact that super-hydration of layered Mn oxides occurs and facilitates water storage and transport at near surface conditions along terrestrial subduction zones and/or other aqueous environments is particularly intriguing in light of recent discoveries of Mn(II) in Martian rocks and sediments.

REFERENCES

- [1] M. Thonis and R. G. Burns, *Nature* **253**, 614 (1975).
- [2] H. Hwang, D. Seoung, Y. Lee, Z. Liu, H. -P. Liermann, H. Cynn, T. V., C. -C. Kao and H. -K. Mao, *Nat. Geosci.* **10**, 947 (2017).
- [3] S. Yun, H. Hwang, G. Hwang, Y. Kim, D. Blom, T. Vogt, J. E. Post, T. -Y. Jeon, T. J. Shin, D. -Z. Zhang, H. Kagi and Y. Lee, *Nat. Commun.* **13**, 1942 (2022).
- [4] E. M. Syracuse, P. E. van Keken and G. A. Abers, *Phys. Earth Planet. Inter.* **183**, 73 (2010).

BEAMLINE

BL-18C

S. Yun¹, H. Hwang¹, G. Hwang¹, Y. Kim², D. Blom³, T. Vogt⁴, J. E. Post⁵, T. -Y. Jeon⁶, T. J. Shin⁷, D. -Z. Zhang⁸, H. Kagi⁹, Y. Lee¹ (¹Yonsei Univ, ²Kyungpook National Univ., ³Univ. of South Carolina, ⁴Univ. of South Carolina, ⁵Smithsonian Institution, ⁶Pohang Accelerator Lab., ⁷UNIST, ⁸Univ. of Hawaii at Manoa, ⁹The Univ. of Tokyo)