Phase transition of manganese oxide minerals under moderate hydrostatic pressures and temperatures

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Manganese oxide minerals are important indicators of planetary surface environments as they are redox sensitive and capable of water storage. Amongst them, birnessite and buserite are the two major components in manganese nodules on the ocean floor, composed of edge-shared MnO_6 octahedral sheets separated by ~7 Å and ~10 Å, respectively. The arrangement and stability of cations-water assembly in-between the layers of buserite, however, has not been established yet. In this study, we show that buserite is a super-hydrated form of birnessite with ca. 17 wt.% more water. We compressed birnessite in a diamond anvil cell (DAC) using water as a pressure transmitting medium. At 0.25(10) GPa we found that the ~7 Å layer spacing of birnessite expands to ~10 Å. A structural model of buserite derived from Rietveld refinement revealed that the central layer of disordered Na^+ cations and water molecules is sandwiched by additional water layers. Further transformation of buserite to manganite is induced above 1.8(1) GPa after heating at 150℃ and then to hausmannite above 2.0(1) GPa after heating at 200℃. While buserite can be recovered as long as maintained in water medium, the latter transformations are irreversible, and the recovered samples reveal distinctive morphologies compared to birnessite. Further structural details have been derived from crystal structure searching based on first principle calculations to show the evolution of hydrogen-bonded cation-water assembly from birnessite to buserite. We thus demonstrate that super-hydration occurs at the sub-surface conditions of the Earth and other planets and could be a novel means to store and transport water.