

Effects of pH and Ca exchange on the structure and redox state of synthetic Na-birnessite

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ABSTRACT

Birnessite-like minerals are among the most common Mn oxides in surficial soils and sediments, and they mediate important environmental processes (e.g., biogeochemical cycles, heavy metal confinement) and have novel technological applications (e.g., water oxidation catalysis). Ca is the dominant interlayer cation in both biotic and abiotic birnessites, especially when they form in association with carbonates. The current study investigated the structures of a series of synthetic Ca-birnessite analogs prepared by cation-exchange with synthetic Na-birnessite at pH values from 2 to 7.5. The resulting Ca-exchanged birnessite phases were characterized using powder X-ray diffraction and Rietveld refinement, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning and transmission electron microscopy. All samples synthesized at pH values greater than 3 exhibited a similar triclinic structure with nearly identical unit-cell parameters. The samples exchanged at pH 2 and 3 yielded hexagonal structures, or mixtures of hexagonal and triclinic phases. Rietveld structure refinement and X-ray photoelectron spectroscopy showed that exchange of Na by Ca triggered reduction of some Mn³⁺, generating interlayer Mn²⁺ and vacancies in the octahedral layers. The triclinic and hexagonal Ca-birnessite structures described in this study were distinct from Na- and H-birnessite, respectively. Therefore, modeling X-ray absorption spectra of natural Ca-rich birnessites through mixing of Na- and H-birnessite end-members will not yield an accurate representation of the true structure.

Keywords: Na-birnessite, Ca-exchange, pH, crystal structure, redox state