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Molecular models of birnessite and related hydrated layered minerals

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Abstract

Birnessite and other charged layered manganese oxide minerals exhibit interlayers with variable cation-water behavior that controls many environmentally important cation exchange, adsorption, and redox processes. The occurrence of birnessite phases as fine-grained materials with corresponding high-surface areas makes them effective in controlling soil sediment and groundwater compositions, but difficult to structurally characterize using conventional analytical methods. Molecular simulations provide an alternative approach in which many details of bulk and interlayer structure can be ascertained to supplement and interpret the experimental findings. Classical and electronic structure methods are used to evaluate Na-, K-, and Ba-birnessite phases. Computational results compare favorably with structures obtained by synchrotron X-ray diffraction and difference electron Fourier mapping of the interlayer region. Based on the analysis of the 1 ns atomic trajectories, dynamics of water molecules is enhanced in the interlayer of K-birnessite relative to the limited motion of water molecules and cations in the other birnessite phases. Molecular dynamics simulations of ranciéite, a complex layered manganese oxide having octahedral vacancies, indicate multiple sites for Ca^{2+} in the interlayer. In addition to manganese layer charge and layer structure, the hydration enthalpy for the interlayer cation affects the structure and dynamics of the interlayer in birnessite minerals.

Keywords: Birnessite, ranciéite, manganese, interlayer, water, hydration, molecular dynamics, DFT