

Investigation of cation ordering in triclinic sodium birnessite via ^{23}Na MAS NMR spectroscopy

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ABSTRACT

Birnessite is a widespread, naturally occurring layered manganese oxide that exerts significant influence over the geochemical cycling of environmentally relevant cations due to its high-interlayer adsorption capacity. Triclinic sodium birnessite was used as a synthetic analog to gain a better understanding of the nature of cation adsorption in this important phyllosulfate. Drawing from previous work correlating observed ^{23}Na NMR shifts in manganese oxides with local environment and Mn oxidation state, the ^{23}Na NMR spectra of metastable busserite and two birnessite samples, NaBi-H-I and NaBi-II, were analyzed to determine the nature of the bound interlayer sodium ions in these materials. The small ^{23}Na chemical shift of busserite shows that its interlayer sodium is fully hydrated. X-ray diffraction indicates that NaBi-H-I is a disordered birnessite while NaBi-II is highly crystalline. High-field (14.1 T) fast MAS NMR spectra of NaBi-H-I and NaBi-II supports these observations, resolving multiple sodium environments for NaBi-H-I and only two sodium environments for NaBi-II. The observed hyperfine shifts were less than expected for sodium environments with manganate layers composed of 2/3 Mn^{4+} and 1/3 Mn^{3+} ions, and the ^{23}Na line shapes indicated that the Na^+ ions are in distorted environments. Both these factors suggest that the sodium ions are offset in the interlayers toward a single oxide layer and located near Mn^{3+} -rich environments within the layer.

Keywords: Manganese oxides, birnessite, NMR, paramagnetic