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Structure of synthetic monoclinic Na-rich birnessite and hexagonal birnessite: II. Results from chemical studies and EXAFS spectroscopy

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ABSTRACT

Solution chemical techniques were used to study the conversion of synthetic Na-rich buserite (NaBu) to hexagonal (H^+-exchanged) birnessite (HBi) at low pH. The low-pH reaction is broadly characterized by the exchange of structural Na^+ with solution H^+ and the partial loss of Mn^{2+} to the aqueous phase. The desorption of Na^+ in two temporally distinct steps indicates the existence of two types of binding sites for this cation. Mn^{2+} appears to originate from a partial disproportionation of Mn^{3+} in the NaBu layers, according to the sequence

$$Mn^{3+}_{layer} + Mn^{3+}_{layer} \rightarrow Mn^{4+}_{layer} + Mn^{2+}_{layer} \rightarrow Mn^{4+}_{layer} + \text{Vacancy} + Mn^{2+}_{aq}.$$

EXAFS measurements on Na-rich birnessite (NaBi) show that this mineral is primarily a layered structure formed by edge-sharing MnO_6 octahedra, with no evidence for triple-corner (TC) sharing Mn. HBi is significantly different with strong evidence for TC-sharing Mn and therefore layer vacancies. The relative numbers of edge (E)-sharing and TC-sharing neighbors determined from EXAFS measurements on HBi is consistent with SAED results (Drits et al. 1997), which suggest that the layer vacancies are restricted to every third row of Mn cations, with 50% of the Mn sites along these rows vacant. The density of vacancies in the entire layer is therefore one in six of layer Mn sites. Polarized EXAFS measurements on orientated films of NaBi and HBi confirm the absence of TC-sharing Mn in NaBi and indicate that Mn adsorbed at layer vacancy sites in HBi at pH 4 is dominantly Mn^{3+}. The intensity of the TC-sharing contribution to the Mn EXAFS spectra of HBi samples increases with increasing pH from pH 2 to 5, and supports a mechanism of formation involving both the direct migration of layer Mn^{3+} to interlayer TC-sharing positions and re-adsorption of Mn^{2+} from solution onto layer vacancy sites. The migration of Mn^{3+} cations into the interlayer releases the steric strain associated with the Jahn-Teller distortion of these octahedra. This model of the NaBu-to-HBi conversion explains the transformation from orthogonal to hexagonal layer symmetry, respectively, as reported by Drits et al. (1997).

Analysis of the Zn EXAFS spectrum of Zn^{2+}-exchanged birnessite shows that Zn^{2+} also occupies TC-sharing positions at layer vacancy sites. The results of this study strongly suggest that lattice cation vacancies are of critical importance in adsorption and electron transfer processes occurring at the surface of this mineral.