Time-resolved structural analysis of K- and Ba-exchange reactions with synthetic Na-birnessite using synchrotron X-ray diffraction

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ABSTRACT

Time-resolved Rietveld refinements using synchrotron X-ray diffraction (XRD) have documented real-time changes in unit-cell parameters in response to cation substitution in synthetic Na-birnessite. Potassium- and Ba-birnessite, like Na-birnessite, were found to have triclinic symmetry. Rietveld analyses of the XRD patterns for K- and Ba-exchanged birnessite revealed decreases in the α, c, and β unit-cell parameters, with a decrease of 1.7 and 0.5%, respectively, in unit-cell volume relative to Na-birnessite. Fourier electron difference syntheses revealed that the changes in the configuration of the interlayer species, and the charge, size, and hydration of the substituting cations, serve as the primary controls on changes in unit-cell parameters. Split electron density maxima with centers at (0 0 0.5) were present for Na, K, and Ba end-members; however, with increased substitution of K+ for Na+, the axis connecting the split-site maxima rotated from an orientation parallel to the b-axis to along the a-axis. Substitution of Ba2+ for Na+ did not result in rotation, but splitting of the interlayer site was more pronounced.

Keywords: Birnessite, cation exchange, synchrotron, X-ray diffraction, Mn-oxide

INTRODUCTION

Birnessite is one of the most common Mn oxides found in nature. Manganese oxides having the birnessite-type layer structure occur as fine-grained aggregates, veins, marine and freshwater nodules and concretions, crusts, dendrites, and coatings on other mineral particles and rock surfaces (Burns and Burns 1976; Dixon et al. 1986; Cornell and Giovanoli 1988; Post 1992, 1999). As a result of their fine grain sizes, birnessite phases have large surface areas for cation-exchange and redox reactions; therefore, even small amounts can significantly influence the chemical compositions of sediments and aqueous systems with which they are in contact (Paterson et al. 1986; Golden et al. 1986, 1987; Banerjee and Nesbitt 1999). The unusually high adsorption capacities and scavenging capabilities of Mn oxide/hydroxide minerals make their presence in soils a primary control on heavy metal and trace-element mobility; these characteristics make them useful geochemical exploration tools and water purification agents (Post 1999). Synthetic birnessite-like phases are extensively studied for use as catalysts, cation-exchange agents, octahedral sieves, and battery materials (Shen et al. 1993; Luo et al. 1998; Feng et al. 1999; Leroux et al. 2001). However, the same fine-grained texture that makes birnessite so reactive also makes its crystal structure difficult to study since crystals are generally unsuitable for single-crystal diffraction.

Birnessite is a layered Mn oxide consisting of edge-sharing Mn-O octahedra with an ~7 Å basal spacing (Fig. 1). The interlayer region of natural birnessites is occupied by hydrated cations, such as Na+, Ca2+, and K+. Since birnessite readily exchanges these interlayer cations, a variety of birnessite-type structures can be synthesized with different cations in the interlayer. Despite the plethora of synthesis methods for birnessite (McKenzie 1971; Golden et al. 1986; Shen et al. 1993; Luo and Suib 1997; Feng et al. 1999; Ma et al. 1999; Luo et al. 2000), details concerning the changes in atomic structure associated with cation exchange are not well documented. Because of the poorly crystalline nature of natural birnessite, structure refinement by powder diffraction is difficult, and synthetic birnessite typically is studied as an analog to the natural material (Kuma et al. 1994).

Recent studies have reported refinements of the structure of Na-birnessite using synchrotron powder XRD coupled with Rietveld analysis. This work has revealed that Na-birnessite is triclinic (Post et al. 2002; Lanson et al. 2002), not monoclinic, as was previously believed (Post and Veblen 1990). In the present study, we used synchrotron radiation, imaging plate technology, and a flow-through capillary cell (Parise et al. 2000; Lee et al. 1998, 2000) to monitor in real-time structural changes as dissolved K+ and Ba2+ exchanged for Na+ in the interlayer of birnessite. The crystal structures of the K- and Ba-birnessite end-members, as well as the intermediate, partially exchanged phases, were determined using Rietveld analysis with the same methods described by Post et al. (2002). The purpose of our study was to provide a more complete understanding of the way in which birnessite incorporates metal cations into its crystal structure. Insights into this exchange process will assist in the development of birnessite-type phases as catalysts and cation-exchange agents, and they will provide...