A multi-method characterization of natural terrestrial birnessites

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ABSTRACT

With a focus on a large set of natural birnessites collected from terrestrial, freshwater systems, we applied and compared the capabilities of X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) to characterize crystal structure and chemistry. Using XRD, we successfully identified 3 of the 11 natural birnessite samples as hexagonal ranciéite-like phases, but the remaining samples yielded less interpretable “3-line” diffraction patterns with broad, asymmetrical peaks at d-spacings of ~7.2, ~2.4, and ~1.4 Å. EXAFS analysis suggested that many of these samples had characteristics of both triclinic and hexagonal birnessite. However, application of EXAFS to the ranciéite-like phases yielded unreasonably high concentrations of triclinic birnessite as an intergrowth, calling into question the use of synthetic hexagonal H-birnessite as an appropriate standard in the linear combination fitting of EXAFS data for natural birnessites. FTIR spectroscopy of the “3-line” birnessite samples successfully distinguished triclinic and hexagonal constituents, and analyses of peak positions suggested that natural birnessites occur as a full spectrum of triclinic and hexagonal intergrowths. XPS analysis of these samples revealed that higher Mn3+ concentrations relative to Mn2+ and Mn4+ are correlated to increased proportions of triclinic birnessite.

Keywords: Manganese oxide, birnessite, FTIR, EXAFS, XPS, XRD

INTRODUCTION

Manganese oxides occur in a wide variety of surficial environments, for example, as fine-grained sediments in soils, as nodules in lakes and oceans, and as coatings on rock surfaces (Post 1999). Their fine grain sizes and high surface areas result in their high reactivity, and Mn oxides consequently play a vital role in heavy metal cycling and redox reactions occurring in the environment (Paterson et al. 1986; Lopano et al. 2007, 2009, 2011; Fleeger et al. 2013). For instance, Mn oxides can sorb Zn, Sn, and Ni (Chao and Theobald 1976; Usui and Mita 1994), and they can oxidize Se4+ to Se6+, Cr3+ to Cr6+, and Co2+ to Co3+, just a few of the redox reactions in which Mn oxides are involved (Bartlett and James 1979; Murray and Dillard 1979; Oscarson et al. 1981; Scott and Morgan 1996; Kay et al. 2001; Fandeur et al. 2009; Lafferty et al. 2011; Peacock and Moon 2012; Kazakis et al. 2015; Kong et al. 2019). Due to their high reactivity with organic carbon, they also play a role in carbon cycling, making Mn oxides an important mineral for modeling the role of mineral-carbon reactions in climate change (Remucal and Ginder-Vogel 2014; Johnson et al. 2015; Allard et al. 2017; Stuckey et al. 2018).

The layered Mn oxide minerals in the birnessite family are widely studied for their natural occurrence in a range of terrestrial settings and for their chemical reactivity (Potter and Rossman 1979; Post 1999; McKeown and Post 2001; Manceau et al. 2002, 2007; Weaver and Hochella 2003). Birnessites exist as two symmetries, triclinic and hexagonal (Fig. 1). According to Post and Veblen (1990) and Post et al. (2002), synthetic triclinic Na-birnessite [Na0.45(Mn3+0.42Mn2+0.58)O4·1.5H2O] consists of layered Mn octahedral sheets with ~71% Mn4+ and ~29% Mn3+, along with hydrated Na+ cations in the interlayer sites. In contrast, Silvester et al. (1997) describe synthetic hexagonal H-birnessite [H5.33Mn3+1.11Mn2+0.72(Mn2+0.053Mn3+0.047)2O3·0.167] as having Mn octahedral sheets consisting of ~72% Mn4+ cations, ~11% Mn3+ cations, and ~17% vacancies, along with Mn2+, Mn3+, and H+ cations that occupy the interlayer near the octahedral vacancy sites. As the Mn oxidation states and the vacancy concentrations are different for triclinic and hexagonal birnessite, they can behave differently in similar geochemical environments. The vacancies in hexagonal birnessite, for example, act as sites for the sorption of Pb and Zn (Toner et al. 2006; Kwon et al. 2010). In contrast, the absence of octahedral vacancies in triclinic birnessite diminishes the capacity for transition metal uptake (Wang et al. 2012). Moreover, Mn3+, which exists in higher concentrations in triclinic birnessite, plays a role in the oxidation of Cr3+ to Cr6+.