

## **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  $\sim 7.2$ ,  $\sim 2.4$ , and  $\sim 1.4$  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 Mn<sup>3+</sup> concentrations relative to Mn<sup>2+</sup> and Mn<sup>4+</sup> are correlated to increased proportions of triclinic birnessite.

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