American Mineralogist, Volume 105, pages 833–847, 2020

A multi-method characterization of natural terrestrial birnessites

Florence T. Ling[1,2,*], Jeffrey E. Post[3], Peter J. Heaney[1], Cara M. Santelli[4,†], Eugene S. Ilton[5], William D. Burgos[6], and Arthur W. Rose[1]

[1]Department of Geosciences, Penn State University, University Park, Pennsylvania 16802, U.S.A.
[2]Department of Biology, Environmental Science Program, La Salle University, Philadelphia, Pennsylvania 19141, U.S.A.
[3]Department of Mineral Sciences, NHB 119, Smithsonian Institute, Washington, DC 20013-7012, U.S.A.
[4]Department of Earth and Environmental Sciences, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.
[5]Pacific Northwest Laboratory, 902 Battelle Boulevard, Richland, Washington 99352, U.S.A.
[6]Department of Civil and Environmental Engineering, Penn State University, University Park, Pennsylvania 16802, U.S.A.

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 Mn^{3+} concentrations relative to Mn^{2+} and Mn^{4+} are correlated to increased proportions of triclinic birnessite.

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