A comparison of synthetic triclinic and hexagonal birnessites with natural birnessites

FLORENCE T. LING[1*], JEFFREY E. POST[2],
PETER J. HEANEY[1], EUGENE S. ILTON[3],
CARA M. SANTELLI[2], WILLIAM D. BURGOS[1] AND
ARTHUR W. ROSE[1]

[1]Penn State University, University Park, PA 16802, USA (*correspondence: ftl102@psu.edu)
[2]Department of Mineral Sciences, NHB 119, Smithsonian Institute, Washington, DC 20013-7012, USA
[3]Pacific Northwest National Laboratory, P.O. Box 999, MSIN K8-96, Richland, WA 99352, USA

Layered Mn oxides of the birnessite family are commonly found as fine-grained coatings and nodules in natural environments. They have been studied for their high cation exchange capacity and redox properties, with potential applications in environmental remediation and batteries. Synthetic triclinic and hexagonal birnessites are commonly used as analogues for natural layered Mn oxides. We have studied and compared a variety of natural and synthetic birnessite-like phases, using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). Synthetic birnessites studied include triclinic Na-, Ca-, K-, and Ba-birnessites. Synthetic hexagonal H-birnessites studied were made from triclinic birnessites placed in a pH 7 HEPES-buffered solution, or pH 2 and 3 solutions. Natural samples included Mn oxides from a Tennessee stream and several acid mine drainage sites in Pennsylvania.

All natural samples were identified as birnessites/buserites using XRD. EDS showed that all natural Mn samples were associated with Ca. Despite being indistinguishable with XRD, the XPS showed differences in ratios of Mn^{2+}, Mn^{3+}, and Mn^{4+} among natural samples. More important, the XPS results indicate that most samples analyzed contain Mn in +2, +3, and +4 oxidation states, providing new insights beyond the typically reported average Mn oxidation states measured through titrations. Among samples of synthetic hexagonal H-birnessites formed at different solution pH's, we found that as pH decreased, the amount of Mn^{3+} also decreased, while Mn^{4+} increased. For synthetic triclinic birnessites, the disproportionation of Mn varied with the interlayer cation despite all samples yielding similar XRD patterns. Our research suggests that multiple techniques may be necessary to properly characterize Mn oxides.