**Fourier-transform infrared spectroscopy (FTIR) analysis of triclinic and hexagonal
birnessites**

Florence T. Ling ^{*a}, Jeffrey E. Post ^b, Peter J. Heaney ^a, James D. Kubicki ^c, Cara M. Santelli ^d

^aDepartment of Geosciences, Penn State University, University Park, PA 16802, USA,

[*ftling@princeton.edu](mailto:ftling@princeton.edu)

**^bDepartment of Mineral Sciences, NHB 119, Smithsonian Institute, Washington, DC 20013-
7012, USA**

**^cDepartment of Geological Sciences, University of Texas at El Paso, El Paso, TX 79968,
USA**

^dDepartment of Earth Sciences, University of Minnesota, Minneapolis, MN 55455

ABSTRACT

The characterization of birnessite structures is particularly challenging for poorly crystalline materials of biogenic origin, and a determination of the relative concentrations of triclinic and hexagonal birnessite in a mixed assemblage has typically required synchrotron-based spectroscopy and diffraction approaches. In this study, Fourier-transform infrared spectroscopy (FTIR) is demonstrated to be capable of differentiating synthetic triclinic Na-birnessite and synthetic hexagonal H-birnessite. Furthermore, IR spectral deconvolution of peaks resulting from Mn-O lattice vibrations between 400 and 750 cm^{-1} yield results comparable to those obtained by linear combination fitting of synchrotron X-ray absorption fine structure (EXAFS) data when applied to known mixtures of triclinic and hexagonal birnessites. Density functional theory (DFT) calculations suggest that an infrared absorbance peak at $\sim 1628 \text{ cm}^{-1}$ may be related to OH vibrations near vacancy sites. The integrated intensity of this peak may show sensitivity to vacancy concentrations in the Mn octahedral sheet for different birnessites.

KEYWORDS: birnessite; manganese oxide; FTIR; EXAFS; density functional theory

1. INTRODUCTION

Manganese (Mn) oxides form in a wide variety of natural environments, sometimes as nodules in fresh-water lakes and oceans and also as coatings on soil and sediment particles (Post 1999). Within the Critical Zone, Mn oxides are involved in the cycling of heavy metals. The metals Pb, Ni, and Zn, for example, commonly sorb to surfaces or intercalate within the interlayers and tunnels of naturally occurring manganates (Chao and Theobald 1976; Usui and Mita 1994). Mn oxides also promote redox reactions, and have been implicated in the oxidation of Cr^{3+} to Cr^{6+} , As^{3+} to As^{5+} , and Tl^{1+} to Tl^{3+} , among other redox active metals in natural environments (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).

Although a wide variety of Mn oxide phases have been described in natural environments, the layered Mn oxides in the birnessite family have been the target of numerous studies for several reasons. Birnessite-like phases are among the most commonly occurring and chemically active natural Mn oxides (Post 1999; Weaver and Hochella 2003) and exist as two varieties, triclinic and hexagonal birnessite, both of which are layer structures. Post and Veblen (1990) and Post et al. (2002) describe a synthetic triclinic Na-birnessite, with formula $\text{Na}_{0.58}(\text{Mn}^{4+}_{1.42}\text{Mn}^{3+}_{0.58})\text{O}_4 \cdot 1.5\text{H}_2\text{O}$, whose octahedral sheets are completely filled with Mn^{3+} and Mn^{4+} cations. Their Rietveld refinements suggest that Mn^{3+} occupies ~29% of the octahedral sites and Mn^{4+} the remaining ~71%. Hydrated Na^+ cations partially occupy sites in the interlayer (Fig. 1a). In contrast, Silvester et al. (1997) characterized synthetic hexagonal H-birnessite, with proposed formula $\text{H}_{0.33}\text{Mn}^{3+}_{0.111}\text{Mn}^{2+}_{0.055}(\text{Mn}^{4+}_{0.722}\text{Mn}^{3+}_{0.111}\square_{0.167})\text{O}_2$, and they argue that the octahedral sheets contain ~72% Mn^{4+} cations, ~11% Mn^{3+} cations, and ~17% vacancies. Mn^{2+} ,

Mn³⁺, and H⁺ cations are located in the interlayer over vacancy sites (Fig. 1b). These differences in Mn valence states and vacancy concentrations are integral in establishing their stability with respect to pH and in predicting their chemical reactivity in natural environments (Ling et al. 2015).

The characterization of birnessite-like phases, however, is complicated by poor crystallinity and/or small particle size. The most common method of material identification, X-ray diffraction (XRD), is especially challenged by the absence of long-range order in many Mn oxide samples, requiring complementary techniques such as transmission electron microscopy, electron microprobe analysis, and IR spectroscopy for proper identification (Post 1999). X-ray absorption spectroscopy (XAS) has instead become a standard method for differentiating triclinic and hexagonal birnessite. Analysis of the EXAFS region has been used extensively for phase identification along with the determination of short-range structure (Jürgensen et al. 2004; Webb et al. 2005; Villalobos et al. 2006; Bargar et al. 2009; Saratovsky et al. 2009; Learman et al. 2011; Santelli et al. 2011). EXAFS also has been applied to quantify mixtures of triclinic and hexagonal birnessite through linear combination fitting (LCF) of the EXAFS region using end-member standards of triclinic and hexagonal birnessite (Zhu et al. 2010; Learman et al. 2011, 2013; Santelli et al. 2011; Zhao et al. 2016). Because this approach requires a synchrotron source, data collection can be logistically difficult. Also, the significance of the quantization is strongly dependent upon the choice and quality of the characterization of the end-member phases.

Clearly, it is desirable to utilize relatively simple, laboratory-based techniques that can be applied in parallel with synchrotron-based spectroscopy and diffraction in the structural characterization of Mn oxide minerals. Fourier-transform infrared spectroscopy (FTIR) has long

been used to identify Mn oxides (Potter and Rossman 1979; Krishnamurti and Huang 1988; Parikh and Chorover 2005; White et al. 2009; Palchik et al. 2014). A few scientists have attempted to quantify chemical properties of birnessite using FTIR, making efforts to attribute specific IR bands to certain vibrations, such as OH, H₂O, and Mn-O vibrations (Tsyganenko 1975; Potter and Rossman 1979; Yang and Wang 2001; Julien et al. 2004). Other FTIR investigations have examined differences in IR spectra before and after Pb sorption reactions with birnessite (Zhao et al. 2012), acid treatments (Kang et al. 2007), crystallization reactions (Luo et al. 1998), cation-exchange (Golden et al. 1987), and birnessite transformations to the tunnel-structured todorokite (Atkins et al. 2014; Zhao et al. 2015). To the best of our knowledge, no studies have focused on understanding and applying differences in IR spectra for triclinic and hexagonal birnessites.

In this study, we employed FTIR to differentiate between analogues for natural birnessites, examining a triclinic and a hexagonal birnessite synthesized and characterized by Rietveld analysis of X-ray diffraction patterns. The data obtained from these samples were used to determine the relative concentrations of triclinic and hexagonal birnessites in known mixtures. The results of FTIR analyses were compared with those from EXAFS and XRD analyses to explore the consistency of these techniques for quantification of the birnessite mixtures. By examining synthetic birnessite-like phases, we hope to lay the groundwork for identifying natural triclinic and hexagonal birnessites with FTIR. Finally, we explored the usefulness of density functional theory (DFT) to calculate, and help interpret, infrared absorbance behavior for the model structures, and for hexagonal birnessite, with and without the vacancies that populate the octahedral sheets.

2. METHODS

2.1. Materials synthesis

Synthesis of standard triclinic birnessite.

Triclinic Na-birnessite was synthesized according to the procedure described in Golden et al. (1986). A 200 ml solution of 0.5 M MnCl_2 (Mallinckrodt Baker) was mixed with 250 ml of 5.5 M NaOH (J.T. Baker). The mixture was oxygenated through a glass frit for ~5 hrs at a rate of 1.5 L/min. The precipitate was divided evenly and centrifuged in 14 centrifuge tubes. The solution was decanted and replaced with pH 6.49 deionized (DI) water to rinse, measured using a pH meter prior to rinsing. The resistivity of the DI water was ~17.6 megohms, and we observed that slight variations in the pH did not affect the quality of the Na-birnessite produced. The rinse cycle was repeated five times. The precipitated Na-birnessite was stored in ~350 ml DI water until experimental use. For experiments, aliquots of Na-birnessite were filtered with a 0.05 μm Nuclepore Track-Etched polycarbonate membrane filter (Whatman), rinsed three times with 100 ml DI water, and left to air-dry at room temperature to effect a transformation to Na-birnessite. The Mn oxidation state ratios of this triclinic Na-birnessite sample were previously determined in Ilton et al. (2016) using X-ray photoelectron spectroscopy (XPS) as 60% Mn^{4+} , 38% Mn^{3+} , and 2% Mn^{2+} through fitting of the $\text{Mn}3p$ peak. The Mn^{4+} content is lower by 11% and the Mn^{3+} is higher by 9% than the values published in Post and Veblen (1990) and Post et al. (2002), in part because they assumed that no Mn^{2+} was present in the structure, and calculated oxidation state ratios were based on Mn-O bond lengths. Additionally, XPS is sensitive to oxidation states at mineral surfaces rather than in the bulk structure, which may lead to higher Mn^{2+} and Mn^{3+} values on the surfaces than on the bulk material.

Synthesis of standard hexagonal birnessite.

Our hexagonal birnessite standard was synthesized by reacting ~100 mg of dried triclinic Na-birnessite in 100 ml of 0.01 M HCl for 24 hrs as described in Giovanoli et al. (1970). The H-birnessite then was filtered with a 0.05 μm Nuclepore Track-Etched polycarbonate membrane filter (Whatman), rinsed three times with 100 ml DI water, and left to air-dry. X-ray diffraction with a Rigaku D/MAX-RAPID microdiffractometer (Smithsonian Institute, Mineral Sciences Department) using a Mo tube source ($\lambda_{\alpha 1\alpha 2} = 0.71069 \text{ \AA}$) confirmed the synthesis of both triclinic and hexagonal birnessite. The Mn oxidation state ratios for this hexagonal birnessite were reported in Ilton et al. (2016) to contain 68% Mn^{4+} , 22% Mn^{3+} , and 10% Mn^{2+} using XPS fitting of the $\text{Mn}3p$ peak. The Mn^{4+} content is 4% lower, and the Mn^{2+} content is 4% higher, than the values reported in Silvester et al. (1997), once again suggesting slight discrepancies between bulk and surface analyses, with higher Mn^{2+} content for surface analyses.

Known mixtures of standard triclinic and hexagonal birnessite.

To test the effectiveness of linear spectral unmixing for quantitative analysis of birnessite mixtures, we combined the triclinic Na-birnessite and the pH 2 hexagonal birnessite standards to prepare samples with weighted ratios of 25:75, 50:50, and 75:25. All mixtures were lightly ground under acetone in a mortar and pestle to disaggregate and blend the samples. Two sets of mixtures were created. The first suite of mixtures was analyzed by FTIR, XRD, and EXAFS. The second suite was analyzed by FTIR only.

2.2 X-ray diffraction (XRD) and structure refinements

The structures of the triclinic and hexagonal birnessites were refined using powder X-ray diffraction (XRD) and the Rietveld method. All samples were ground in an agate mortar under

acetone to disaggregate clumps. For XRD analysis, ~2 mg of sample were mounted on glass fibers using superglue, which in turn were loaded into a Rigaku D/MAX-RAPID microdiffractometer with an imaging plate detector and a Mo tube. Samples were rotated 360° around the *phi* axis at 1° s⁻¹ during data collection with a 10 min exposure time.

Rietveld refinements (Rietveld, 1969) were completed for all birnessite samples using the General Structure Analysis System-II (GSAS-II) software (Toby and Von Dreele 2013). The starting atom positions for the triclinic Na-birnessite refinements were drawn from Post et al. (2002), and those for the H-birnessite refinements were taken from Fischer (2011). Peak profile parameters that described instrumental broadening were determined by Rietveld analysis of a diffraction pattern generated by a LaB₆ standard (NIST SRM 660a) as collected using the same sample holder as was used for birnessite. The background parameters, scale factor, unit-cell parameters, and peak profile coefficients were allowed to vary. The background intensities were fitted with a Chebyshev function using 6 terms. Diffraction peak profiles were fitted with a pseudo-Voigt function as parameterized by Thompson et al. (1987), with asymmetry correction by Finger et al. (1994), and microstrain anisotropic broadening terms by Stephens (1999). Final refinements for the pure phases only allowed the atomic positions, occupancies, and temperature factors to vary. For all refinements, the (0 0 1) peak was omitted due to its high relative intensity and problems with integrating the diffraction images near the direct beam.

Because of the similarity of the structures of triclinic and hexagonal birnessite, and consequent strong correlation among certain structural parameters, it can be challenging for Rietveld analysis to extract accurate phase concentrations from X-ray diffraction patterns of mixtures of triclinic and hexagonal birnessite. Therefore, we developed a structure refinement strategy that yielded good results for the 50:50 mixture that was then applied to the 75:25 and

25:75 triclinic and hexagonal birnessite mixtures to test its robustness for other compositions. The approach was similar to that used for single-phase birnessite with the following exceptions. Phase fractions rather than single scale factors were refined. Atomic positions, occupancies, and temperature factors were held constant. Instead of the general anisotropic microstrain broadening model, an isotropic microstrain term initially was varied, and then a uniaxial model was introduced. The equatorial and axial microstrain parameters were then refined separately for each phase and held constant. The Lorentzian Y peak profile parameter was varied after the microstrain terms had been refined, due to initial instability.

2.3. X-ray absorption spectroscopy/extended X-ray absorption fine structure (XAS/EXAFS)

For X-ray absorption spectroscopy, samples were ground under acetone in a mortar and pestle, and sieved with a 425 or 500 mesh sieve into a thin layer onto kapton tape. The kapton tape was then folded over to seal the sample. Manganese *K*-edge XAS spectra were collected using a synchrotron source at Beamline 12-BM of the Advanced Photon Source (APS), Argonne National Laboratory, using a Si(111) double-crystal, fixed exit monochromator and a double mirror system (flat plus torroidal) with an energy cutoff of 23 keV. The pre-edge peak of a Mn foil was used for energy calibration (6539 eV). Fluorescence data were collected with a 13-element Ge detector and Cr(III) foil in front of the Ge detector to eliminate scatter. Three to six scans were collected per sample at room temperature from -200 eV to about +800 eV around the Mn *K*-edge (6539 keV). During data collection, the peak positions and line forms in the near-edge region (XANES) were examined to check for photochemical reduction with successive scans, and no changes were observed. Care was also taken to avoid self-absorption, and samples were re-prepared if dampening of EXAFS oscillations was observed.

Analyses of spectra were conducted using the ATHENA software (Ravel & Newville 2005). XAS spectra were calibrated using a Mn foil, averaged, background-subtracted, and normalized. If 1 or 2 outlier points were present, deglitching was used to remove those points. Analysis of the Mn *K*-edge EXAFS region was used for the structural identification and quantification of phase fractions for samples (Webb et al. 2005; Villalobos et al. 2006; Saratovsky et al. 2009; Feng et al. 2010). The $\chi(k)$ spectra were converted to k ($\text{\AA}^{-1}$) (Sayers & Bunkers, 1988). The resulting $\chi(k)$ data were k^2 -weighted and analyzed using the k -range from 2.3 to 11.3 $\text{\AA}^{-1}$. Principal component analysis (PCA) was used to determine the number of components representing the entire data set (Manceau et al. 2002). The linear combination fitting (LCF) of $\chi(k)$ spectra collected from synthetic birnessites yielded phase fractions of triclinic and hexagonal birnessite (Webb et al. 2005; Villalobos et al. 2006; Saratovsky et al. 2009; Feng et al. 2010). All weights were set between 0 and 1, and all combinations were fit with at most 2 standards. Weights of standards were not forced to sum to 1. The synthetic triclinic Na-birnessite and synthetic pH 2 hexagonal birnessite were used as standards to fit the EXAFS data.

2.4. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra data collection and processing. Samples were ground under acetone in a mortar and pestle and sieved through a 325 mesh sieve, so particle sizes were less than 44 μm , but individual crystal diameters were ~ 300 nm based on SEM observations. Then, 0.5 to 1 mg of Mn oxide sample was milled with ~ 250 mg KBr using a SPECAC ball mixing mill for 1-2 min, and pressed into a pellet. Up to six pellets of each sample were prepared to test reproducibility of the analyses. Vibrational spectra were collected on a Nicolet 6700 Analytical FTIR

Spectrometer from 400 to 4000 cm^{-1} . The resolution was set at 3.86 cm^{-1} and 64 scans were co-added for each spectrum. The Omnic 8 software (Nicolet) was used to view data during data collection. In order to ensure similar data collection conditions, FTIR spectra of pure triclinic Na-birnessite and hexagonal H-birnessite standards were collected within ~1 hr of data collection for the other samples. Background spectra for samples showed no significant shift within that time.

In order to quantify the amount of hexagonal and triclinic birnessite in a sample, FTIR spectra were normalized by setting the intensities of the highest peaks in the 400 to 750 cm^{-1} region to 1, and then linear backgrounds were subtracted from the spectra using MATLAB R2015a (Mathworks). For the pure triclinic and hexagonal birnessite samples, the spectra were re-scaled after background subtraction with the maximum intensities reset to 1 to adjust for any decreases in the maximum intensity that may have occurred during background subtraction. The 50:50 mixture of triclinic and hexagonal birnessite was also used to develop FTIR reference intensity ratios (RIRs) for triclinic and hexagonal birnessite, since the intensity of the strongest peak in the hexagonal birnessite spectrum was 90% of that for the triclinic birnessite spectrum. Because of the small relative difference, however, application of this correction factor did not result in significant changes to the fits.

Linear spectral unmixing of normalized, background-subtracted FTIR spectra was performed using the Least Squares Fitting algorithm with SIXpack (Webb 2005). We used the observed spectra in the range of 400 to 750 cm^{-1} for spectral decomposition of birnessite mixtures, fitting the spectra with components obtained from our pure triclinic birnessite and hexagonal birnessite standards (Thomson and Salisbury 1993; Ramsey and Christensen 1998). Components were not summed to 1 to allow slight adjustments to scaling from not re-

normalizing sample spectra after background subtraction, which was performed only for the pure standards. Peak deconvolution was also performed for peaks in the 1300 to 1800 cm^{-1} range using OPUS 7.0 spectroscopy software (Bruker). The peaks were deconvoluted with the Levenberg-Marquardt algorithm using a combination of Gaussian and Lorentzian peak shapes. Results of phase fractions from spectral unmixing are reported as volume fractions. The known weight fractions of the mixtures measured during sample preparation were also converted to volume fractions for comparison by using the densities determined for triclinic and hexagonal birnessite from Rietveld analyses.

DFT Computations of IR spectra. Using Materials Studio (Accelrys Inc., San Diego, CA), three models (Fig. 2) of birnessite nanoparticles were created as clusters to represent a triclinic birnessite nanoparticle, a hexagonal birnessite nanoparticle free of defects, and a hexagonal birnessite with a vacancy site, similar to the procedure in Zhu et al. (2009) and Cygan et al. (2012). The triclinic birnessite nanocluster was built with 7 Mn atoms bonded together with 12 O atoms and terminated with 12 H_2O groups. The nanocluster represented 5 Mn^{4+} and 2 Mn^{3+} atoms to yield a mean charge of +3.71 for Mn, similar to that of triclinic Na-birnessite (Post and Veblen 1990) and producing a final formula of $\text{Mn}_7\text{O}_{24}\text{H}_{22}$ (Fig. 2a). The defect-free hexagonal birnessite nanocluster consisted of 7 Mn atoms, including 4 Mn^{4+} and 3 Mn^{3+} , bonded together with 12 O atoms and terminated with 11 H_2O and 1 OH group, giving a final formula of $\text{Mn}_7\text{O}_{24}\text{H}_{23}$ (Fig. 2b). This cluster produced a mean charge of +3.57 to approximate the total average valence (+3.66) in hexagonal H-birnessite according to Silvester et al. (1997). The hexagonal birnessite nanocluster with a vacancy had 7 Mn atoms and 11 O atoms with a mean charge of +3.71 to represent 6 Mn^{4+} atoms and 1 Mn^{2+} adsorbed near a vacancy site (Fig. 2c,d). Its chemical formula upon addition of terminating H_2O and OH groups was $\text{Mn}_7\text{O}_{26}\text{H}_{26}$. To test

the effects of protonation state and configuration, models of $\text{Mn}_7\text{O}_{26}\text{H}_{24}$ (-2 charge), $\text{Mn}_7\text{O}_{26}\text{H}_{25}$ (-1 charge) and $\text{Mn}_7\text{O}_{26}\text{H}_{26}$ with H^+ ions placed at terminal Mn-OH groups rather than bridging Mn-O-Mn linkages were also energy minimized and subjected to frequency analysis with the same methods.

Energy minimizations for the birnessite nanoclusters were performed with Gaussian 09 (Frisch et al. 2010). Mn atoms were initially frozen and then permitted to relax after minimization of the O and H atomic positions. The B3LYP exchange-correlation functional (Lee et al. 1988; Becke 1993) was used along with the 6-31G(d,p) basis set (Rassolov et al. 2001). After energy minimizations were completed, frequency calculations were performed. Model harmonic frequencies were scaled by 0.96 for comparison with experimental data to account for basis set effects, anharmonicity, and approximations in electron correlation based on the approximate scale factor of 0.9614 from Scott and Radom (1996) for B3LYP/6-31G(d). Normal modes were visualized using the program Molden (Schaftenaar and Noordik, 2000).

3. RESULTS & DISCUSSION

3. 1. Distinguishing triclinic and hexagonal birnessite with XRD and FTIR

We present here the detailed structure refinement results for the triclinic and hexagonal birnessites used in this study to fully characterize their structures. Rietveld analyses of triclinic Na- and hexagonal H-birnessite confirmed the differences in crystal structure previously established for these phases (Silvester et al., 1997; Post et al., 2002). The refined fit parameters for these analyses are included in Tables 1 and 2, and the excellent fits between the observed and calculated XRD patterns are illustrated in Figure 3. Birnessites prepared using different methods

or having different compositions may not have identical structures, making comparisons among studies sometimes confusing, or impossible.

We also present FTIR spectra for triclinic and hexagonal birnessite in Figure 4, and for the first time, we demonstrate differences in IR spectra for these two varieties of birnessite. Most strikingly, triclinic Na-birnessite displays three prominent absorbances at 418, 478, and 511 cm^{-1} , and a low-intensity peak at 639 cm^{-1} , whereas hexagonal H-birnessite shows two broad, high-intensity peaks at 440 and 494 cm^{-1} , and a low-intensity peak at 659 cm^{-1} (Fig. 4c, Table 3). FTIR absorbances in the 400 to 650 cm^{-1} region represent contributions from Mn-O bond vibrations (Julien et al. 2004). More subtle distinctions are also visible for peaks in the regions of ~ 2950 to ~ 3670 cm^{-1} and ~ 1330 to ~ 1725 cm^{-1} (Fig. 4) that represent bending and stretching of H_2O and OH bonds, although it is important to note that absorbed water also contributes to these regions (Potter & Rossman 1979). Interestingly, in the region from ~ 2950 to ~ 3670 cm^{-1} , the peaks in the FTIR spectrum for triclinic Na-birnessite are sharper than for hexagonal H-birnessite, suggesting that water is relatively well-ordered in Na-birnessite, as is consistent with the neutron and modeling studies of Post et al. (2011) and Cygan et al. (2012).

3.2 Quantitative analysis of known triclinic-hexagonal birnessite mixtures: FTIR, EXAFS, and XRD

Quantitative analyses for known mechanical mixtures of end-member birnessite standards were performed to compare the relative abilities of FTIR, XRD, and EXAFS to reproduce the known phase fractions. FTIR spectral analyses yielded generally good results, with a maximum average error factor of 0.0021 (Table 4). The calculated ratios of triclinic-to-

hexagonal birnessite were within 13 vol% of the known value for the first 25:75 triclinic-to-hexagonal birnessite mixture, and within 3 vol% for all other mixtures.

The quality of the quantitative analysis obtained by FTIR was slightly worse than the results obtained by Rietveld analysis of XRD data for birnessite mixtures (Table 4). Our XRD protocol for quantitative analysis yielded phase fractions within 3 wt% of the known values (or 4 vol% for better comparison to FTIR and EXAFS results). Refinement results for the three triclinic-to-hexagonal birnessite mixtures are shown in Fig. 6; a strong 1:1 correlation exists between the FTIR and XRD results (Fig. 7a).

Because many studies employ EXAFS to quantify the relative concentrations of hexagonal and triclinic (or “pseudo-orthogonal”) birnessite in their samples (Learman et al. 2011, 2013; Santelli et al. 2011; Zhao et al. 2016), we applied linear combination fitting (LCF) of the EXAFS region using end-member standards to our mechanical mixtures of birnessite (Table 4). Results from LCF gave errors within 7 vol% for the known physical mixtures when weights of standards were forced to 1, and errors within 10 vol% when weights of standards were not forced to 1 (Table 4 and SI). When comparing the results from EXAFS with the FTIR and XRD results, we found that strong 1:1 correlations exist among the various methods (Fig. 7b, 7c). In general, Rietveld refinements gave the most accurate results, although spectral fitting of FTIR and LCF of EXAFS still yielded reasonable values.

3.3. Comparison of observed FTIR spectra to DFT calculations

DFT calculations of birnessite-like clusters were performed to gain insights into the disparities between the observed FTIR patterns of triclinic and hexagonal birnessite. An unavoidable discrepancy between our modeled IR spectra and the observed patterns involved a

shift in frequencies (Cramer 2004). The harmonic oscillator approximation used in our calculation of vibrational frequencies has an infinite number of vibrational levels that are all equally spaced. In contrast, the variable energy changes during transitions to other vibrational levels in real bonds are finite. Consequently, we considered both absorption frequencies and relative IR intensities when correlating calculated and observed peaks. In the comparison between average Mn-O and Mn-Mn bond distances calculated from the DFT models and from Rietveld analysis of triclinic and hexagonal birnessites, the average bond distances are within 0.1 Å of each other (Table 5). The similarities in bond distances support our use of DFT calculated frequencies in interpreting the FTIR data of triclinic and hexagonal birnessite. However, the DFT calculations have a wider range of values for their bond distances because they are not constrained by crystal symmetry, whereas Rietveld analysis is.

Mn-O vibrations. Over the spectral range representing Mn-O bond vibrations, relative peak positions for the calculated FTIR patterns were shifted to higher values by $\sim 135\text{ cm}^{-1}$ for the vacancy-free nanoclusters relative to the corresponding peaks observed for triclinic birnessite (Fig. 8). Correlative peaks between the spectrum for the nanocluster with a vacancy site and that displayed by hexagonal birnessite were shifted upward by $\sim 160\text{ cm}^{-1}$. Specifically, the three calculated high-intensity peaks at 559, 611, and 642 cm^{-1} (Table 6) of the triclinic birnessite-like nanocluster ($\text{Mn}_7\text{O}_{24}\text{H}_{22}$), labeled T1, T2, and T3, correlated to observed peaks at 418, 478, and 511 cm^{-1} in actual triclinic Na-birnessite (Table 3, Fig. 8c). Similar to the FTIR spectrum for actual hexagonal birnessite, the hexagonal birnessite nanoclusters exhibited two rather than three high-intensity peaks over the range of Mn-O vibrations labeled H2 and H3. The calculated pattern revealed peaks at 578 and 636 cm^{-1} for the hexagonal birnessite-like cluster with no vacancy ($\text{Mn}_7\text{O}_{24}\text{H}_{23}$), and at 612 and 650 cm^{-1} for the hexagonal birnessite-like cluster with a

vacancy ($\text{Mn}_7\text{O}_{26}\text{H}_{26}$) (Fig. 8c). Correlative peaks for the observed hexagonal birnessite FTIR spectra occurred at 440 and 494 cm^{-1} (Fig. 4c). Upon re-arranging H^+ from Mn-O-Mn linkages to terminal Mn-OH groups, the changes in the vibrational frequencies of the central Mn atom were minor, suggesting that the Mn-O lattice vibrations were not significantly affected by the protonation state of the nanocluster. The model frequencies in the Mn-O lattice vibration range changed by 1 to 26 cm^{-1} , so Peak H1 could increase from 462 cm^{-1} to 488 cm^{-1} but it is still far from the 559 cm^{-1} Peak T1 (Table 6e). A calculated peak at 463 cm^{-1} in both hexagonal birnessite nanoclusters (labeled H1 in Fig. 8) was not seen in the observed data, most likely due to the energy cutoff of the FTIR spectrometer at 400 cm^{-1} (when the $\sim 160 \text{ cm}^{-1}$ peak shift is factored into the expected peak position). For the H2 and H3 peaks, the observed hexagonal birnessite had peak ratios similar to those of the calculated hexagonal birnessite with a vacancy site.

The calculated Mn-O vibrations associated with bonds not immediately attached to the central Mn atom in the birnessite nanoclusters fell within the range of 761 to 908 cm^{-1} (Table 6b). These peaks were the result of Mn-O vibrations moving in conjunction with OH vibrations on the edges of the nanoclusters (Fig. 9b), in contrast to the vibrations associated with the interior Mn-O bonds, which were calculated to lie within the 384 to 758 cm^{-1} range (Fig. 9a). The number of peaks calculated over the higher range exceeded the number of peaks observed in the range of ~ 550 to $\sim 900 \text{ cm}^{-1}$ for actual triclinic and hexagonal birnessite. We attribute this discrepancy to the fact that the nanocluster models included disproportionately more water molecules and OH bonds relative to Mn-O bonds than the synthetic birnessites analyzed (Fig. 2).

Our calculations suggest two possibilities for the observation of three prominent peaks over the Mn-O vibrational range in triclinic birnessite and only two in hexagonal birnessite. One

possibility attributes the differences to Jahn-Teller distortions in the octahedral sheets of triclinic Na-birnessite, in which the symmetry-breaking associated with the distortions may account for the additional peak in triclinic birnessite (Drits et al. 1997). Although calculated Mn-O bond lengths in all three nanoclusters range from 1.88 to 2.23 Å (Fig. 2), the presence of Jahn-Teller distortions is not immediately obvious based on the relative locations of short and long bond lengths. Bond lengths in the triclinic birnessite nanocluster point to the possibility of distortions, with the 2.11 and 2.16 Å bond lengths located on opposite sides of the central Mn atoms and the short bond lengths doing the same. However, the hexagonal birnessite without a vacancy and the hexagonal birnessite with a vacancy site exhibit equally wide ranges of Mn-O bond lengths from 1.88 to 2.23 Å surrounding their central Mn atom. The uncertainty in whether Jahn-Teller distortions exist in the DFT models does not rule out whether distortions contribute to the differences between the observed FTIR spectra in the Mn-O range.

A second explanation for the difference in the FTIR spectra lies in the possibility that structural disorder in birnessite could lead to band broadening and peak overlap. The DFT peaks in the synthetic spectra for the triclinic birnessite nanocluster $\text{Mn}_7\text{O}_{24}\text{H}_{22}$ are combinations of 5 modes: 492-507 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, 531-537 Mn-O_{br} symm, 559-571 Mn-O_{br} asymm, 588-630 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, and 642-646 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$. For $\text{Mn}_7\text{O}_{24}\text{H}_{23}$, the hexagonal birnessite nanocluster without a vacancy, the modes consist of combinations of 530-544 Mn-O_{br} symm, 557-566 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, 577-622 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, 630-637 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, and 649-664 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$. In the hexagonal birnessite nanocluster with a vacancy, $\text{Mn}_7\text{O}_{26}\text{H}_{26}$, the modes include combinations of 551-560 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, 580-597 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, 612-641 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, 663-680 $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, and 763 on the defect site. Exemplary depictions of each vibrational mode can be found in Supplementary Information (SI). Each individual

mode listed often contained multiple vibration types, such as in the case of $\text{Mn-O}_{\text{br}} + \text{Mn}_3\text{-O}_{\text{br}}$, complicating the distinctions between modes. Furthermore, most modes are separated by a range of 8 to 22 cm^{-1} , suggesting that significant peak overlap and peak broadening could prevent proper identification of peaks in the observed spectra.

H₂O and OH vibrations. The region from 1534 to 3732 cm^{-1} in the calculated spectra reflects vibrations related to H₂O and OH movement (Table 6c, 6d), and the high ratio of OH bonds to Mn-O bonds in the clusters also accounted for additional peaks in the calculated relative to the observed spectra. Specifically, the hexagonal birnessite cluster with a vacancy site exhibited additional peaks at $\sim 2152 \text{ cm}^{-1}$ and at $\sim 2720 \text{ cm}^{-1}$, and these peaks have no correlations in the observed spectra. These vibrations were all related to OH vibrations surrounding the vacancy site, but were likely not present in high enough concentrations throughout the actual birnessite sample to be observed in the FTIR spectra.

In the observed spectra, the region from ~ 1330 to $\sim 1725 \text{ cm}^{-1}$ represents vibrations from H₂O bending (Potter and Rossman 1979). In the corresponding region in the simulated IR spectra, 4 distinguishable peaks were calculated over the ~ 1498 to $\sim 1661 \text{ cm}^{-1}$ range when a vacancy site was present as opposed to only 2 peaks when all octahedral sites were occupied (Fig. 8b). The 2 peaks calculated for these vacancy-free nanoclusters were associated with H₂O bending motions on the edge of the nanocluster similar to that depicted in Fig. 9c. In the hexagonal birnessite with a vacancy, the motions related to each of the 4 peaks in the calculated spectra are depicted in Fig. 10. As seen in Figure 10a, the peak at 1653 cm^{-1} was related to H₂O bending around the vacancy site. The observed peaks in the FTIR spectra in the region from ~ 1300 to $\sim 1800 \text{ cm}^{-1}$ may correspond to the calculated peaks from H₂O bending, although the broadness of the peaks prevents clear identification of the quantity and positions of peaks (Fig.

8b). More important, the peak splitting seen in the hexagonal birnessite nanocluster with a vacancy site may provide information for future studies concerning vacancy concentrations in samples.

Because the absorbance, or more accurately, the integrated measurement of the peak area, is linearly related with concentration and sample thickness according to the Beer-Lambert law (Libowitzky and Beran 2004), the integrated area of the peak at 1653 cm^{-1} in the DFT calculations could be directly proportional to the number of OH vibrations surrounding a vacancy site in a specific birnessite structure. If the peak(s) in the observed spectra at $\sim 1628\text{ cm}^{-1}$ is correlated with the 1653 DFT peak, then perhaps the intensity of that peak may be related to the vacancy-related OH vibrations, and we may be able to use the peak area in the observed birnessite samples to compare relative concentrations of this vacancy-related OH vibration.

Although this study did not have a sufficiently large sample set of birnessites with varying vacancy concentrations to test this relationship, it is noteworthy that the peak area at $\sim 1628\text{ cm}^{-1}$ for triclinic Na-birnessite was $1.36\text{ absorbance units} \cdot \text{cm}^{-1}$, whereas the corresponding peak area for hexagonal H-birnessite was $5.41\text{ absorbance units} \cdot \text{cm}^{-1}$ as determined from peak-fitting (Fig. 11). The larger peak area observed experimentally for hexagonal H-birnessite than triclinic Na-birnessite (Lanson et al. 2000) suggested that the $\sim 1628\text{ cm}^{-1}$ peak(s) may be sensitive to vacancy concentration, especially because Rietveld analyses indicated that the Mn octahedral sheets in hexagonal H-birnessite have an occupancy of only ~ 0.80 , whereas the octahedral sites in triclinic Na-birnessite are fully occupied. At the same time, the broadness of the observed peak could potentially be fit by several smaller peaks, and no clear conclusions concerning the correspondence of the 1628 cm^{-1} peak(s) can be made with the

calculated 1653 cm^{-1} peak in the hexagonal birnessite nanocluster with a vacancy site until additional samples are analyzed.

Peaks in the ~ 1300 to $\sim 1800\text{ cm}^{-1}$ region for both triclinic Na-birnessite and hexagonal H-birnessite had similar peak positions and shapes (Fig. 11), although at lower intensities for triclinic Na-birnessite. This observation implies the presence of a small number of vacancy-related vibrations in both materials, as seen in the peaks calculated for the birnessite model with a vacancy site. Rietveld analysis of XRD data, however, revealed no vacancies for triclinic Na-birnessite, suggesting that perhaps FTIR is a more sensitive method for determining the concentration of vacancies in a sample.

4. CONCLUSIONS

FTIR serves as a relatively simple, in-house technique for differentiating between synthetic triclinic and hexagonal birnessite samples. Linear spectral unmixing can be used to calculate fractions of two birnessite end-members with a degree of accuracy that is comparable to EXAFS. Rietveld analyses of X-ray diffraction data remains the most accurate means of quantifying mixtures of triclinic and hexagonal birnessite, but this technique is only applicable to reasonably well crystalline samples. Because the two phases differ in their Mn oxidation state ratios and vacancy concentrations, determining their relative proportions in a sample can help predict sorption and redox reactions. However, it is important to bear in mind that the FTIR spectra of physical mixtures of endmember triclinic and hexagonal birnessite may differ from birnessite that represents a partial transformation of one phase to the other. Moreover, the effects that different metal cations within the interlayer will exert on the FTIR spectra will require further investigation.

Nevertheless, because FTIR is sensitive to short-range order, it may succeed in characterizing very poorly crystalline, natural birnessite samples whose triclinicity or hexagonality cannot be easily quantified using XRD. FTIR even may provide insight into the concentration and distribution of vacancies in the structures of natural birnessites. In summary, this work suggests that FTIR may serve as a convenient method for comparing synthetic and natural birnessites, and for analyzing the evolution of birnessite-like phases.

5. ACKNOWLEDGEMENTS

Funding for this work was provided by NSF Grant EAR-1147728 and EAR-1552211 and the Committee on Institutional Cooperation (CIC) and Smithsonian Institution Fellowship. This research also utilized samples from the Smithsonian Mineral Research Collection at the Museum of Natural History. The FTIR laboratory at the Smithsonian Institution was established with generous support from Stephen Turner. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Portions of this research were conducted with Advanced CyberInfrastructure computational resources provided by The Institute for CyberScience at The Pennsylvania State University (<http://ics.psu.edu>). Special thanks to Alexandre Fowler for her contribution to data collection.

6. REFERENCES

- Atkins, A., Shaw, S., & Peacock, C. (2014). Nucleation and growth of todorokite from birnessite: Implications for trace-metal cycling in marine sediments. *Geochimica et Cosmochimica Acta*, 144, 109–125. <http://doi.org/10.1017/CBO9781107415324.004>
- Bargar, J. R., Fuller, C. C., Marcus, M. A., Brearley, A. J., Perez De la Rosa, M., Webb, S. M., & Caldwell, W. A. (2009). Structural characterization of terrestrial microbial Mn oxides from Pinal Creek, AZ. *Geochimica et Cosmochimica Acta*, 73, 889–910. <http://doi.org/10.1016/j.gca.2008.10.036>
- Bartlett, R. J., & James, B. (1979). Behavior of Chromium in Soils: III. Oxidation. *Journal of Environment Quality*, 8(1), 31–35. <http://doi.org/10.2134/jeq1976.00472425000500040010x>
- Becke, A. D. (1993). Density-functional thermochemistry.III. The role of exact exchange. *The Journal of Chemical Physics*, 98, 5648–5652. <http://doi.org/10.1063/1.464913>
- Chao, T. T., & Theobald, P. K. (1976). The significance of secondary iron and manganese oxides in geochemical exploration. *Economic Geology*, 71, 1560–1569. <http://doi.org/10.2113/gsecongeo.71.8.1560>
- Cramer, C. J. (2004). *Essentials of Computational Chemistry Theories and Models. Essentials of Computational Chemistry*. <http://doi.org/10.1021/ci010445m>
- Cygan, R. T., Post, J. E., Heaney, P. J., & Kubicki, J. D. (2012). Molecular models of birnessite and related hydrated layered minerals. *American Mineralogist*, 97(8-9), 1505–1514. <http://doi.org/10.2138/am.2012.3957>
- Drits, V. A., Silvester, E., Gorshkov, A. I., & Manceau, A. (1997). Structure of synthetic monoclinic Na-rich birnessite and hexagonal birnessite: II. Results from chemical studies and EXAFS spectroscopy. *American Mineralogist*, 82(9-10), 962–978.
- Fandeur, D., Juillot, F., Morin, G., Olivi, L., Cognigni, A., Webb, S. M., ... Brown, G. E. (2009). XANES evidence for oxidation of Cr(III) to Cr(VI) by Mn-oxides in a lateritic regolith developed on serpentized ultramafic rocks of New Caledonia. *Environmental Science & Technology*, 43, 7384–7390. Retrieved from <http://www.ncbi.nlm.nih.gov/pubmed/19848150>
- Feng, X. H., Zhu, M., Ginder-Vogel, M., Ni, C., Parikh, S. J., & Sparks, D. L. (2010). Formation of nano-crystalline todorokite from biogenic Mn oxides. *Geochimica et Cosmochimica Acta*, 74, 3232–3245. <http://doi.org/10.1016/j.gca.2010.03.005>
- Finger, L. W., Cox, D. E., & Jephcoat, A. P. (1994). A Correction for Powder Diffraction Peak Asymmetry Due to Axial Divergence. *Journal of Applied Crystallography*, 27, 892–900. <http://doi.org/10.1107/S0021889894004218>
- Fischer, T. B. (2011). *Structural transformations of birnessite (δ -MnO₂) during biological and abiological reduction*.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., ... Pople, J. A. (2004). Gaussian 03.
- Giovanoli, R., Stähli, E., & Feitknecht, W. (1970). Über Oxidhydroxide des vierwertigen Mangans mit Schichtengitter. 1. Mitteilung: Natrium-mangan(II,III)manganat(IV). *Helvetica Chimica Acta*, 53, 454 – 464.
- Golden, D. C., Chen, C. C., & Dixon, J. B. (1986). Synthesis of todorokite. *Science (New York, N.Y.)*, 231(4739), 717–719. <http://doi.org/10.1126/science.231.4739.717>

- Golden, D. C., Chen, C. C., & Dixon, J. B. (1987). Transformation of birnessite to buserite, todorokite, and manganite under mild hydrothermal treatment. *Clays and Clay Minerals*, 35(4), 271–280.
- Ilton, E. S., Post, J. E., Heaney, P. J., Ling, F. T., & Kerisit, S. N. (2016). XPS determination of Mn oxidation states in Mn (hydr)oxides. *Applied Surface Science*, 366, 475–485. <http://doi.org/10.1016/j.apsusc.2015.12.159>
- Julien, C. M., Massot, M., & Poinson, C. (2004). Lattice vibrations of manganese oxides: Part I. Periodic structures. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 60, 689–700. [http://doi.org/10.1016/S1386-1425\(03\)00279-8](http://doi.org/10.1016/S1386-1425(03)00279-8)
- Jürgensen, A., Widmeyer, J. R., Gordon, R. A., Bendell-Young, L. I., Moore, M. M., & Crozier, E. D. (2004). The structure of manganese oxide on the seath of the bacterium *Leptothrix discophora*: An XAFS study. *American Mineralogist*, 89, 1110–1118.
- Kang, L., Zhang, M., Liu, Z. H., & Ooi, K. (2007). IR spectra of manganese oxides with either layered or tunnel structures. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 67, 864–869. <http://doi.org/10.1016/j.saa.2006.09.001>
- Kay, J. T., Conklin, M. H., Fuller, C. C., & O'Day, P. A. (2001). Processes of nickel and cobalt uptake by a manganese oxide forming sediment in Pinal Creek, Globe mining district, Arizona. *Environmental Science & Technology*, 35(24), 4719–4725. Retrieved from <http://www.ncbi.nlm.nih.gov/pubmed/11775144>
- Kazakis, N., Kantiranis, N., Voudouris, K. S., Mitrakas, M., Kaprara, E., & Pavlou, a. (2015). Geogenic Cr oxidation on the surface of mafic minerals and the hydrogeological conditions influencing hexavalent chromium concentrations in groundwater. *Science of The Total Environment*, 514, 224–238. <http://doi.org/10.1016/j.scitotenv.2015.01.080>
- Krishnamurti, G. S. ., & Huang, P. M. (1988). Influence of manganese oxide minerals on the formation of iron oxides. *Clays and Clay Minerals*, 36(5), 467–475.
- Lafferty, B. J., Ginder-Vogel, M., & Sparks, D. L. (2011). Arsenite Oxidation by a Poorly-Crystalline Manganese Oxide. 3. Arsenic and Manganese Desorption. *Environmental Science & Technology*, 45, 9218–9223. <http://doi.org/10.1021/es201281u>
- Lanson, B., Drits, V. A., Silvester, E., & Manceau, A. (2000). Structure of H-exchanged hexagonal birnessite and its mechanism of formation from Na-rich monoclinic buserite at low pH. *American Mineralogist*, 85, 826–838.
- Learman, D. R., Voelker, B. M., Madden, A. S., & Hansel, C. M. (2013). Constraints on superoxide mediated formation of manganese oxides. *Frontiers in Microbiology*, 4, 1–11. <http://doi.org/10.3389/fmicb.2013.00262>
- Learman, D. R., Wankel, S. D., Webb, S. M., Martinez, N., Madden, A. S., & Hansel, C. M. (2011). Coupled biotic–abiotic Mn(II) oxidation pathway mediates the formation and structural evolution of biogenic Mn oxides. *Geochimica et Cosmochimica Acta*, 75, 6048–6063. <http://doi.org/10.1016/j.gca.2011.07.026>
- Lee, C., Yang, W., & Parr, R. G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37(2), 785–789.
- Libowitzky, E., & Beran, A. (2004). IR spectroscopic characterization of hydrous species in minerals. In *EMU Notes in Mineralogy: Spectroscopic Methods in Mineralogy* (pp. 227 – 279).
- Ling, F. T., Heaney, P. J., Post, J. E., & Gao, X. (2015). Transformations from triclinic to hexagonal birnessite at circumneutral pH induced through pH control by common biological buffers. *Chemical Geology*, 416, 1–10.

- <http://doi.org/10.1016/j.chemgeo.2015.10.007>
- Luo, J., Huang, A., Park, S. H., Suib, S. L., & Young, C. O. (1998). Crystallization of Sodium - Birnessite and Accompanied Phase Transformation. *Chemistry of Materials*, 10, 1561–1568.
- Manceau, A., Marcus, M. A., & Tamura, N. (2002). Quantitative Speciation of Heavy Metals in Soils and Sediments by Synchrotron X-ray Techniques. *Applications of Synchrotron Radiation in Low-Temperature Geochemistry and Environmental Science*, 49, 341–428.
- Murray, J. W., & Dillard, J. G. (1979). The oxidation of cobalt(II) adsorbed on manganese dioxide. *Geochimica et Cosmochimica Acta*, 43, 781–787.
- Oscarson, D. W., Huang, P. M., Defosse, C., & Herbillon, A. (1981). Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature*, 291, 50–51.
- Palchik, N. A., Moroz, T. N., Grigorieva, T. N., & Miroshnichenko, L. V. (2014). Manganese Minerals from the Miassovo Freshwater Lake: Composition and Structure. *Russian Journal of Inorganic Chemistry*, 59(5), 511–518. <http://doi.org/10.1134/S0036023614050131>
- Parikh, S. J., & Chorover, J. (2005). FTIR spectroscopic Study of Biogenic Mn-Oxide Formation by *Pseudomonas putida* GB-1. *Geomicrobiology Journal*, 22, 207–218. <http://doi.org/10.1080/01490450590947724>
- Peacock, C. L., & Moon, E. M. (2012). Oxidative scavenging of thallium by birnessite: Explanation for thallium enrichment and stable isotope fractionation in marine ferromanganese precipitates. *Geochimica et Cosmochimica Acta*, 84, 297–313. <http://doi.org/10.1016/j.gca.2012.01.036>
- Post, J. E. (1999). Manganese oxide minerals: Crystal structures and economic and environmental significance. *Proceedings of the National Academy of Sciences*, 96, 3447–3454. <http://doi.org/10.1073/pnas.96.7.3447>
- Post, J. E., Heaney, P. J., and Cho, Y. (2011) Neutron diffraction study of hydrogen in birnessite structures. *American Mineralogist*, 96, 534–540.
- Post, J. E., Heaney, P. J., & Hanson, J. (2002). Rietveld refinement of a triclinic structure for synthetic Na-birnessite using synchrotron powder diffraction. *Powder Diffraction*, 17(3), 218–221.
- Post, J. E., & Veblen, D. R. (1990). Crystal structure determinations of synthetic sodium, magnesium, and postassium birnessite using TEM and the Rietveld Method. *American Mineralogist*, 75, 477–489.
- Potter, R. M., & Rossman, G. R. (1979). The tetravalent manganese oxides : identification , hydration , and structural relationships by infrared spectroscopy. *American Mineralogist*, 64, 1199–1218. Retrieved from http://www.minsocam.org/ammin/AM64/AM64_1199.pdf?ref=PandoraISP
- Ramsey, M. S., & Christensen, P. R. (1998). Mineral abundance determination: Quantitative deconvolution of thermal emission spectra. *Journal of Geophysical Research*, 103(B1), 577–596. <http://doi.org/10.1029/97JB02784>
- Rassolov, V. A., Ratner, M. A., Pople, J. A., Redfern, P. C., & Curtiss, L. A. (2001). 6-31G* Basis Set for Third-Row Atoms. *Journal of Computational Chemistry*, 22(9), 976–984. <http://doi.org/10.1002/jcc.1058>
- Ravel, B., & Newville, M. (2005). ATHENA , ARTEMIS , HEPHAESTUS : data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation*, 12, 537–541. <http://doi.org/10.1107/S0909049505012719>

- Rietveld, H. M. (1969). A profile Refinement Method for Nuclear and Magnetic Structures. *Journal of Applied Crystallography*, 2, 65–71. <http://doi.org/10.1107/S0021889869006558>
- Santelli, C. M., Webb, S. M., Dohnalkova, A. C., & Hansel, C. M. (2011). Diversity of Mn oxides produced by Mn(II)-oxidizing fungi. *Geochimica et Cosmochimica Acta*, 75, 2762–2776. <http://doi.org/10.1016/j.gca.2011.02.022>
- Saratovsky, I., Gurr, S. J., & Hayward, M. A. (2009). The Structure of manganese oxide formed by the fungus *Acremonium* sp. strain KR21-2. *Geochimica et Cosmochimica Acta*, 73, 3291–3300. <http://doi.org/10.1016/j.gca.2009.03.005>
- Sayers, D. E., & Bunkers, B. A. (1988). *X-ray Absorption Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*. New York: Wiley.
- Schaftenaar, G., & Noordik, J. H. (2000). Molden: a pre-and post-processing program for molecular and electronic structures. *Journal of Computer-Aided Molecular Design*, 14, 123–134. <http://doi.org/10.1023/A:1008193805436>
- Scott, A. P., & Radom, L. (1996). Harmonic Vibrational Frequencies: An Evaluation of Hartree - Fock, Møller - Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. *Journal of Physical Chemistry*, 100, 16502–16513.
- Scott, J. M., & Morgan, J. J. (1996). Reactions at oxide surfaces. 2. Oxidation of Se(IV) by synthetic Birnessite. *Environmental Science & Technology*, 30, 1990–1996. <http://doi.org/10.1021/es950741d>
- Silvester, E., Manceau, A., & Drits, V. A. (1997). Structure of synthetic monoclinic Na-rich birnessite and hexagonal birnessite: II. Results from chemical studies and EXAFS spectroscopy. *American Mineralogist*, 82, 962–978.
- Stephens, P. W. (1999). Phenomenological model of anisotropic peak broadening in powder diffraction. *Journal of Applied Crystallography*, 32, 281–289. <http://doi.org/10.1107/S0021889898006001>
- Thompson, P., Cox, D. E., & Hastings, J. B. (1987). Rietveld Refinement of Debye-Scherrer Synchrotron X-ray Data from A1203. *Journal of Applied Crystallography*, 20(2), 79–83. <http://doi.org/10.1107/S0021889887087090>
- Thomson, J. L., & Salisbury, J. W. (1993). The Mid-Infrared Reflectance of Mineral Mixtures (7–14 μm). *Remote Sensing of Environment*, 45, 1–13. [http://doi.org/10.1016/0034-4257\(93\)90077-B](http://doi.org/10.1016/0034-4257(93)90077-B)
- Toby, B. H., & Von Dreele, R. B. (2013). GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *Journal of Applied Crystallography*, 46(2), 544–549. <http://doi.org/10.1107/S0021889813003531>
- Tsyganenko, A. A. (1975). IR spectra and structure of the hydroxyl covering of oxides comparison with the spectra of hydroxides and silicates. *Journal of Structural Chemistry*, 16(4), 536–540.
- Usui, A., & Mita, N. (1994). IX. Mineralogy, geochemistry and internal growth structure of manganese nodules in the western part of the Penrhyn Basin, South Pacific (GH83-3 area). *Geological Survey of Japan Cruise Report*, (23), 165–185.
- Villalobos, M., Lanson, B., Manceau, A., Toner, B., & Sposito, G. (2006). Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *American Mineralogist*, 91, 489–502. <http://doi.org/10.2138/am.2006.1925>
- Weaver, R. M., & Hochella, M. F. J. (2003). The reactivity of seven Mn-oxides with $\text{Cr}^{3+} + \text{aq}$: A comparative analysis of a complex, environmentally important redox reaction. *American Mineralogist*, 88, 2016–2027.

- Webb, S. M. (2005). SIXPack : a Graphical User Interface for XAS Analysis Using IFEFFIT. *Physica Scripta*, T115, 1011–1014.
- Webb, S. M., Tebo, B. M., & Bargar, J. R. (2005). Structural characterization of biogenic Mn oxides produced in seawater by the marine bacillus sp. strain SG-1. *American Mineralogist*, 90, 1342–1357. <http://doi.org/10.2138/am.2005.1669>
- Webb, S. M., Tebo, B. M., & Bargar, J. R. (2005). Structural characterization of biogenic Mn oxides produced in seawater by the marine bacillus sp. strain SG-1. *American Mineralogist*, 90, 1342–1357. <http://doi.org/10.2138/am.2005.1669>
- White, W. B., Vito, C., & Scheetz, B. E. (2009). The mineralogy and trace element chemistry of black manganese oxide deposits from caves. *Journal of Cave and Karst Studies*, 71(2), 136–143. Retrieved from <Go to ISI>://WOS:000270607100005
- Yang, D. S., & Wang, M. K. (2001). Syntheses and Characterization of Well-Crystallized Birnessite. *Chemistry of Materials*, 13, 2589–2594.
- Zhao, H., Liang, X., Yin, H., Liu, F., Tan, W., Qiu, G., & Feng, X. (2015). Formation of todorokite from “c-disordered” H⁺-birnessites: the roles of average manganese oxidation state and interlayer cations. *Geochemical Transactions*, 16, 1–11. <http://doi.org/10.1186/s12932-015-0023-3>
- Zhao, H., Zhu, M., Li, W., Elzinga, E. J., Villalobos, M., Liu, F., ... Sparks, D. L. (2016). Redox Reactions between Mn(II) and Hexagonal Birnessite Change its Layer Symmetry. *Environmental Science & Technology*, 1–33. <http://doi.org/10.1021/acs.est.5b04436>
- Zhao, W., Liu, F., Feng, X., Tan, W., Qiu, G., & Chen, X. (2012). Fourier transform infrared spectroscopy study of acid birnessites before and after Pb²⁺ adsorption. *Clay Minerals*, 47, 191–204. <http://doi.org/10.1180/claymin.2012.047.2.04>
- Zhu, M., Ginder-Vogel, M., Parikh, S. J., Feng, X.-H., & Sparks, D. L. (2010). Cation Effects on the Layer Structure of Biogenic Mn-Oxides. *Environmental Science and Technology*, 44, 4465–4471. <http://doi.org/10.1021/es1009955>
- Zhu, M., Paul, K. W., Kubicki, J. D., & Sparks, D. L. (2009). Quantum Chemical Study of Arsenic (III , V) Adsorption on Mn-Oxides : Implications for Arsenic (III) Oxidation. *Environmental Science and Technology*, (43), 6655–6661.

7. FIGURE CAPTIONS

Fig. 1. Schematic diagrams of (a) synthetic triclinic Na-birnessite and (b) synthetic hexagonal H-birnessite after Lanson et al. (2000).

Fig. 2. Geometry optimized models of nanoclusters representing (a) triclinic birnessite $\text{Mn}_7\text{O}_{24}\text{H}_{22}$, (b) hexagonal birnessite without a vacancy, $\text{Mn}_7\text{O}_{24}\text{H}_{23}$, and (c) hexagonal birnessite with a vacancy, $\text{Mn}_7\text{O}_{26}\text{H}_{26}$, using a front and side view to depict the location of the vacancy and the Mn atom over the vacancy site. Figures were drawn in Materials Studio (Accelrys Inc., San Diego CA).

Fig. 3. Rietveld refinement fits for (a) synthetic triclinic Na-birnessite and (b) synthetic hexagonal H-birnessite.

Fig. 4. (a) Full IR spectra of synthetic triclinic Na-birnessite and synthetic hexagonal H-birnessite, (b) enlarged portion of the IR spectra over the OH-vacancy vibration range, and (c) enlarged portion of the IR spectra for the Mn-O bond vibration range.

Fig. 5. FTIR spectra of pure triclinic and hexagonal birnessite and the first set of mechanical mixtures with weighted ratios of 25:75, 50:50, and 75:25 triclinic-hexagonal birnessite.

Fig. 6. Rietveld refinement fits for (a) 25:75, (b) 50:50, and (c) 75:25 triclinic-to-hexagonal birnessite mixtures.

Fig. 7. Comparison for volume fractions of mechanical mixtures of triclinic and hexagonal birnessite from (a) FTIR compared with XRD volume fractions, (b) FTIR compared with EXAFS volume fractions, and (c) EXAFS compared with XRD volume fractions. The dashed lines represent the 1:1 correlation line.

Fig. 8. (a) Full calculated IR spectra for nanoclusters representing triclinic birnessite, hexagonal birnessite with no vacancy site, and hexagonal birnessite with a vacancy site, along with

collected FTIR spectra for endmember triclinic Na-birnessite and hexagonal H-birnessite with intensities multiplied by a scale factor of 3000 for comparison. (b) The data in the range from 1300 to 1800 cm^{-1} are enlarged to highlight differences resulting from varying vacancy concentration in the birnessite structure. (c) The data in the range of 400 to 1000 are enlarged for easier comparison of peaks related to Mn-O bonding in the DFT calculations and observed FTIR spectra.

Fig. 9. Exemplary vibrations in a birnessite nanocluster for (a) inner Mn-O lattice vibrations leading to vibrations in the 400 to 700 cm^{-1} range, (b) peripheral Mn-O vibrations leading to vibrations in the 700 to 1400 cm^{-1} range, (c) H₂O scissoring vibrations leading to peaks in the 1400 to 1800 cm^{-1} range, and (d) OH stretches leading to peaks in the 1800 to 4000 cm^{-1} range. The larger, thick arrows represent the main vibrations, while smaller arrows represent resulting motions due to the close vicinity or connectivity in the nanocluster to the main vibrations occurring simultaneously.

Fig. 10. All vibrations for a hexagonal birnessite nanocluster with a vacancy site in the 1300 to 1800 cm^{-1} range, including the OH vibrations at (a) 1653, (b) 1599, (c) 1569, and (d) 1498 cm^{-1} .

Fig. 11. Gaussian-Lorentzian peak shapes for peaks in the OH vacancy-related range from 1300 to 1800 cm^{-1} for (a) hexagonal H-birnessite and (b) triclinic Na-birnessite.

8. TABLES

Table 1. Rietveld refinement results for unit-cell parameters for end-member synthetic triclinic Na-birnessite and hexagonal H-birnessite.

	Triclinic Na-birnessite	Hexagonal H-birnessite
Space group	C -1	P -3
Unit cell		
a (Å)	5.167(6)	2.873(3)
b (Å)	2.849(1)	-
c (Å)	7.347(9)	7.432(4)
α (°)	90.1(1)	90
β (°)	103.14(6)	90
γ (°)	90.1(1)	120
vol (Å ³)	105.3(1)	53.12(7)
Density (g/cm ³)	3.573	2.917
Refinement		
No. of diffraction points	1820	1820
No. of reflections	125	43
Diffraction range (2 θ), λ = 0.71069 Å	8.00 – 44.41	8.00 - 44.41
No. of variables	24	22
R(F ²)	0.0488	0.0804
Rwp	0.0232	0.0151

Table 2. Atom positions for end-member synthetic triclinic Na-birnessite and hexagonal H-birnessite from Rietveld analysis.

	Atom	x	y	z	Site occupancy factor	Uiso
Triclinic Na- birnessite	Mn(oct)	0	0	0	1	0.00286
	O(oct)	0.379(1)	0.01(1)	0.143(1)	1	0.01871
	Na or H ₂ O(int)	0.579(2)	0.200(3)	0.489(2)	0.83(2)	0.05580
Hexagonal H- birnessite	Mn(oct)	0	0	0	0.727	0.02447
	O(oct)	0.3333	0.6667	0.099(2)	1	0.01731
	H ₂ O(int)	0.6667	0.3333	0.643(3)	0.444	0.14121
	Mn(int)	0	0	0.670(3)	0.065	0.02840

Table 3. Peak locations in the Mn-O range (400 to 750 cm^{-1}) for synthetic birnessites, and their respective peak labels to compare with Fig. 8.

Sample	Peak 1	Peak 2	Peak 3	Peak 4
Na-birnessite	418 (T1)	478 (T2)	511 (T3)	639 (T4)
Hexagonal Birnessite		440 (H2)	494 (H3)	659 (H4)

Table 4. Volume fractions of triclinic Na- and hexagonal H-birnessite in mixtures determined with FTIR, EXAFS, and XRD.

Wt. % ratio of triclinic-to-hexagonal birnessite	Vol. % ratio of triclinic-to-hexagonal birnessite	IR Spectral Unmixing		
		<i>Vol Fraction Na-birnessite</i>	<i>Vol Fraction H-birnessite</i>	<i>R-factor</i>
Mix 1 25:75	Mix 1 22:78	0.347 ± 0.002	0.653 ± 0.002	0.0009
Mix 1 50:50	Mix 1 45:55	0.482 ± 0.002	0.518 ± 0.002	0.0015
Mix 1 75:25	Mix 1 71:29*	0.700 ± 0.002	0.300 ± 0.002	0.0014
Mix 2 25:75	Mix 2 22:78*	0.232 ± 0.003	0.768 ± 0.003	0.0021
Mix 2 50:50	Mix 2 45:55*	0.468 ± 0.004	0.552 ± 0.004	0.0021
Mix 2 75:25	Mix 2 70:30	0.719 ± 0.002	0.281 ± 0.002	0.0010
Wt. % ratio of triclinic-to-hexagonal birnessite	Vol. % ratio of triclinic-to-hexagonal birnessite	EXAFS Linear Combination Fitting		
		<i>Vol Fraction Na-birnessite</i>	<i>Vol Fraction H-birnessite</i>	<i>R-factor</i>
Mix 1 25:75	Mix 1 22:78	0.180 ± 0.021	0.820 ± 0.023	0.0156
Mix 1 50:50	Mix 1 45:55	0.436 ± 0.022	0.564 ± 0.025	0.0184
Mix 1 75:25	Mix 1 71:29	0.639 ± 0.022	0.361 ± 0.024	0.0144
Wt. % ratio of triclinic-to-hexagonal birnessite	Vol. % ratio of triclinic-to-hexagonal birnessite	XRD Structure Refinements		
		<i>Vol Fraction Na-birnessite</i>	<i>Vol Fraction H-birnessite</i>	<i>Rwp</i>
Mix 1 25:75	Mix 1 22:78	0.217 ± 0.006	0.783 ± 0.010	0.0407
Mix 1 50:50	Mix 1 45:55	0.490 ± 0.004	0.510 ± 0.005	0.0204
Mix 1 75:25	Mix 1 71:29	0.702 ± 0.004	0.298 ± 0.005	0.0294

*results averaged from spectral unmixing of 2 – 4 KBr pellets

Table 5. Bond distances in DFT-calculated structures and from Rietveld analysis.

Triclinic Birnessite		
	Rietveld analysis	DFT Mn ₇ O ₂₄ H ₂₂
Mn - O	1.999(7)	1.903
	1.9836(25)	2.110
	1.972(24)	1.904
	1.936(25)	1.907
		2.162
		1.952
	AVE = 1.973	AVE = 1.990
Mn - Mn	2.849	2.900
	2.952	2.889
	2.949	2.745
		2.867
		2.883
		2.770
	AVE = 2.917	AVE = 2.842

Hexagonal Birnessite			
	Rietveld analysis	DFT Mn ₇ O ₂₄ H ₂₃ (no vacancy)	DFT Mn ₇ O ₂₆ H ₂₆ (vacancy)
Mn - O	1.814(5)	1.946	1.916
		1.972	2.233
		2.116	1.95
		1.876	1.878
		1.890	2.183
		2.175	2.004
		AVE = 1.996	AVE = 2.03
Mn - Mn	2.873	2.801	2.993
		2.832	3.002
		2.870	2.859
		2.865	2.956
		2.839	2.952
		2.928	
		AVE = 2.856	AVE = 2.9524

Table 6. Peak positions from calculated FTIR spectra of birnessite nanoclusters.

(a.)

Model	Inner Mn-O lattice vibrations		
	Peak 1	Peak 2	Peak 3
Mn ₇ O ₂₄ H ₂₂	559(T1)	611(T2)	642(T3)
Mn ₇ O ₂₄ H ₂₃	463(H1)	578(H2)	636(H3)
Mn ₇ O ₂₆ H ₂₆	463(H1)	612(H2)	650(H3)

(b.)

(c)

Model	Peripheral Mn-O vibrations								
	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9	Peak 10	Peak 11	Peak 12
Mn ₇ O ₂₄ H ₂₂	761	848				1045			
Mn ₇ O ₂₄ H ₂₃	756	803	885		957				
Mn ₇ O ₂₆ H ₂₆	763		866	907	995	1051	1122	1167	1218

(c.)

Model	H ₂ O vibrations			
	Peak 13	Peak 14	Peak 15	Peak 16
Mn ₇ O ₂₄ H ₂₂	1536(T13)	1572(T14)		
Mn ₇ O ₂₄ H ₂₃	1544(H13)	1569(H14)		
Mn ₇ O ₂₆ H ₂₆	1536(H13)	1569(H14)	1599(H15)	1653(H16)

(d.)

Model	OH vibrations					
	Peak 17	Peak 18	Peak 19	Peak 20	Peak 21	Peak 22
Mn ₇ O ₂₄ H ₂₂				2881		
Mn ₇ O ₂₄ H ₂₃				3083	3124	3237
Mn ₇ O ₂₆ H ₂₆	2152	2187	2685	2720		
Model	OH vibrations (cont.)					
	Peak 23	Peak 24	Peak 25	Peak 26	Peak 27	Peak 28
Mn ₇ O ₂₄ H ₂₂	3425	3521		3571	3690	3731
Mn ₇ O ₂₄ H ₂₃	3448	3533	3542	3575	3698	3732
Mn ₇ O ₂₆ H ₂₆		3528		3589		3733

(e.)

Protonation Effect Models	Inner Mn-O lattice vibrations		
	Peak 1	Peak 2	Peak 3
Mn ₇ O ₂₆ H ₂₄	593(T1)	637(T2)	663(T3)
Mn ₇ O ₂₆ H ₂₅	464(H1)	588(H2)	636(H3)

$\text{Mn}_7\text{O}_{26}\text{H}_{26}$	470(H1)	652(H2)	713(H3)
---	---------	---------	---------

9. FIGURES

Fig. 1

a.) $\text{Mn}_7\text{O}_{24}\text{H}_{22}$, triclinic birnessite b.) $\text{Mn}_7\text{O}_{24}\text{H}_{23}$, hexagonal birnessite without a vacancy c.) $\text{Mn}_7\text{O}_{26}\text{H}_{26}$, hexagonal birnessite with a vacancy, front and side view

Fig. 2

Fig. 3

a.)

b.)

c.)

Fig. 4

Fig. 5

Fig. 6

Fig. 7

a.)

b.)

c.)

Fig. 8

a.) 618 cm^{-1}

c.) 1550 cm^{-1}

b.) 995 cm^{-1}

d.) 3570 cm^{-1}

Fig. 9

a.) 1653 cm^{-1} c.) 1569 cm^{-1} b.) 1599 cm^{-1} d.) 1498 cm^{-1}

Fig. 10

a.) triclinic Na-birnessite

b.) hexagonal H-birnessite

Fig. 11

SUPPLEMENTARY INFORMATION

a.) Mn-O_{br} (in Mn₇O₂₄H₂₂ at 511 cm⁻¹) b.) Mn₃-O_{br} (in Mn₇O₂₄H₂₂ at 528 cm⁻¹) c.) Mn-O_{br} asymm (in Mn₇O₂₄H₂₂ at 582 cm⁻¹) d.) Mn-O_{br} symm (in Mn₇O₂₄H₂₂ at 559 cm⁻¹) e.) Defect site (in Mn₇O₂₆H₂₆ at 795 cm⁻¹)

Fig. 1. Exemplary movements for vibrational modes a.) Mn-O_{br} , b.) $\text{Mn}_3\text{-O}_{\text{br}}$, c.) Mn-O_{br} asymm, d.) Mn-O_{br} symm, and e.) defect site.

Fig. 2. EXAFS $\chi(k)$ plots of a.) hexagonal birnessite, b.) triclinic birnessite, c.) 25:75 mixture of triclinic-to-hexagonal birnessite, d.) 50:50 mixture of triclinic-to-hexagonal birnessite, and e.) 75:25 mixture of triclinic-to-hexagonal birnessite.

747

Fig. 3. Radial distribution functions (RDFs) of a.) hexagonal birnessite, b.) triclinic birnessite, c.) 25:75 mixture of triclinic-to-hexagonal birnessite, d.) 50:50 mixture of triclinic-to-hexagonal birnessite, and e.) 75:25 mixture of triclinic-to-hexagonal birnessite.