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

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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 ~1628 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.

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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 [38]. 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 [5,59]. 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 [3,9,21,22,24,33,34,37,52].

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 [38,61] and exist as two varieties, triclinic and hexagonal birnessite, both of which are layer structures. Post and Veblen [41] and Post et al. [40] describe a synthetic triclinic Na-birnessite, with formula $Na_{0.58}(Mn^{4+}_{1.42}Mn^{3+}_{0.58})O_4 \cdot 1.5H_2O$, 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. [53] characterized synthetic hexagonal H-birnessite, with proposed formula $H_{0.33}Mn^{3+}_{0.111}Mn^{2+}_{0.055}(Mn^{4+}_{0.722}Mn^{3+}_{0.111}\square_{0.167})O_2$, and they argue that the octahedral sheets contain ~72% Mn^{4+} cations, ~11% Mn^{3+} cations, and ~17% vacancies. Mn^{2+}, Mn^{3+}, 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 [30].

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 [38]. 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 [2,19,27,47,48,60,63]. 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 [26,27,47,67,69]. Because this approach requires a synchrotron source, data collection can be

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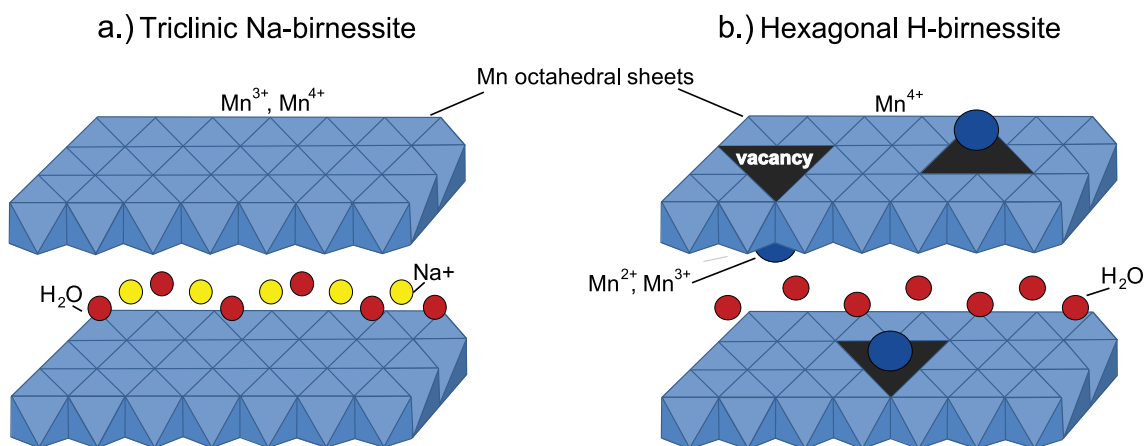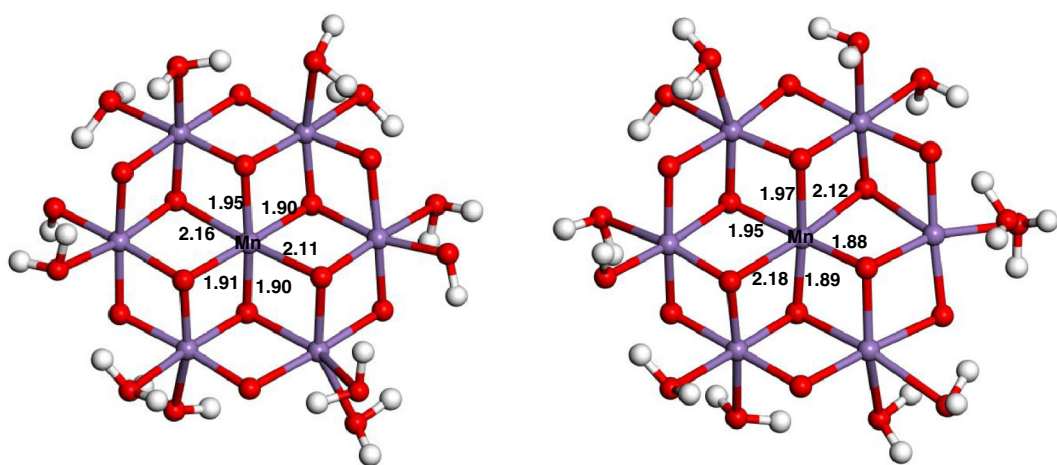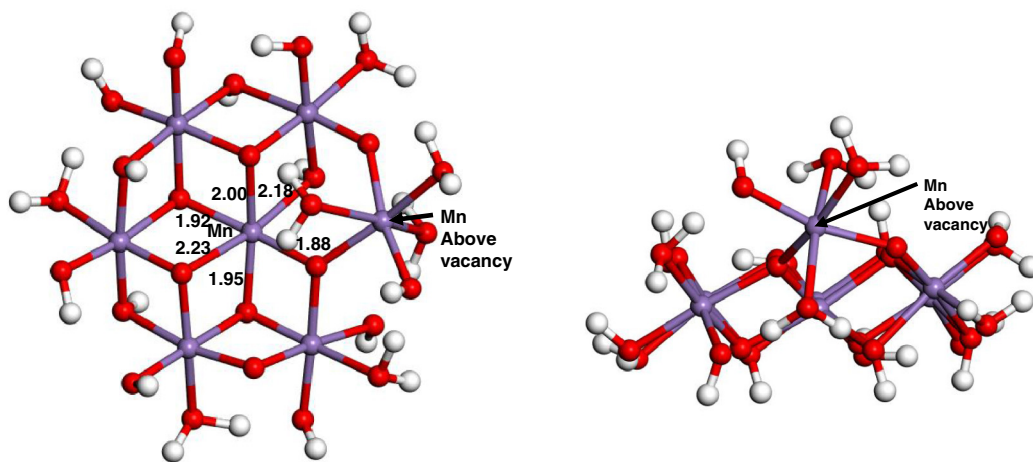*E-mail address:* ftling@princeton.edu (F.T. Ling).

a.) Triclinic Na-birnessite

b.) Hexagonal H-birnessite

Fig. 1. Schematic diagrams of (a) synthetic triclinic Na-birnessite and (b) synthetic hexagonal H-birnessite after Lanson et al. [25].

a.) $Mn_7O_{24}H_{22}$, triclinic birnessite

b.) $Mn_7O_{24}H_{23}$, hexagonal birnessite without a vacancy

c.) $Mn_7O_{26}H_{26}$, hexagonal birnessite with a vacancy, front and side view

Fig. 2. Geometry optimized models of nanoclusters representing (a) triclinic birnessite $Mn_7O_{24}H_{22}$, (b) hexagonal birnessite without a vacancy, $Mn_7O_{24}H_{23}$, and (c) hexagonal birnessite with a vacancy, $Mn_7O_{26}H_{26}$, 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).