High Co-doping promotes the transition of birnessite layer symmetry from orthogonal to hexagonal

Hui Yin [a], Yu Liu [a], Luuk K. Koopal [b], Xionghan Feng [a], Shengqi Chu [c], Mengqiang Zhu [d], Fan Liu [a,*]

[a] Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River) Ministry of Agriculture, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China
[b] Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands
[c] Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China
[d] Department of Ecosystem Science and Management, University of Wyoming, 1000 E. University Ave., Laramie, WY 82071, USA

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ABSTRACT

Despite its presence in limited amounts, birnessite has a wide spread distribution and is often highly enriched in trace metals such as Co in diverse geological environments. This study investigated the effects of Co doping on the layer structure and properties of birnessites synthesized through the oxidation of Mn^{2+} by O_2 under alkaline conditions, by using powder X-ray diffraction (XRD) and X-ray absorption spectroscopy (both XANES and EXAFS). The Co doped, high-pH birnessites are composed of platy crystals, and have lower crystallinity, larger specific surface areas (SSAs) and higher Mn average oxidation states (AOSs) than pure birnessite. Cobalt K-edge EXAFS analysis reveals that no CoOOH is formed, and ~76% of the total Co is located in the layers of the Co-doped birnessites. Careful examination of these Co-doped samples by XRD and EXAFS analyses demonstrates that the presence of Co during the synthesis of high-pH birnessite promotes the structural transition of the birnessite layer symmetry from orthogonal to hexagonal. This is due to the decrease in Mn(III) in the layers of the doped solids, leading to the attenuation of Jahn–Teller effect. The decrease in Mn(III) in the layers might be attributed to the substitution of Mn(III) by Co(III) in the layers. The competitive adsorption of $Co^{2+/3+}$ with Mn^{2+} might also decrease the oxidation of Mn^{2+} to Mn(III) and the subsequent migration of Mn(III) into the birnessite layers. The results provide new insights into the interaction mechanisms between transition metals and birnessite-like minerals, and improve our understanding of the abiotic oxidation of Mn^{2+} as well as the prevalence of birnessites with hexagonal symmetry in natural environments.

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1. Introduction

Birnessite is a phyllomanganate that occurs in diverse natural environments, such as soils, sediments and Mn-rich ore deposits in oceans (Vodyanitskii, 2009). Because of their natural ubiquity, large amounts of structural defects and negative charges, high redox potential and large specific surface area, birnessites play an important role in the geochemical fate of heavy metals (Manceau et al., 1997; Feng et al., 2007; Peacock and Sherman, 2007a,b; Zhu et al., 2010b; Villalobos et al., 2014) and other pollutants (Li et al., 2015) in the environment. Birnessite is also the precursor of other Mn oxides, such as todorokite (Bodei et al., 2007; Feng et al., 2010; Atkins et al., 2014; Manceau et al., 2014). Natural birnessite is typically highly disordered and occurs in a finely dispersed state, commonly mixed with other phases such as phyllosilicates and Fe oxyhydroxides, thus varieties synthesized under various physicochemical conditions in the laboratory are considered

analogs of natural birnessites (Manceau et al., 2000) and are used to conduct mineralogical research and to model naturally occurring redox and adsorption processes.

Birnessites consist of layers of edge-sharing $[MnO_6]$ octahedra, and these layers are stacked along the c^* axis in various orders and are separated from each other by interlayer hydrated cations and water molecules (Drits et al., 2007). Birnessite layer symmetry can be either orthogonal (in-plane lattice parameter $a > \sqrt{3}$ b based on a C-centered two-dimensional unit cell) or hexagonal ($a = \sqrt{3}$ b). The orthogonal birnessite layers are composed of $[Mn(IV)O_6]$ and $[Mn(III)O_6]$ with or without minor vacancies, and the layer symmetry results from the systematic elongation of distorted $[Mn(III)O_6]$ octahedra along the same direction (cooperative Jahn–Teller effect). The negative charge of these layers is mainly due to the presence of a high amount of Mn(III) cations in the layers, and is compensated by protons, alkali and alkaline earth metals, such as Na^+ or K^+, Ca^{2+} and Mg^{2+} (Drits et al., 1997, 2007; Manceau et al., 1997; Lanson et al., 2000, 2002; Gaillot et al., 2005). When the birnessite layers are mainly composed of $[Mn(IV)O_6]$, a large quantity of vacancies, and no or a small amount of $[Mn(III)O_6]$, or if the layers

contain a lot of elongated [Mn(III)O$_6$] but these octahedra are randomly oriented, the layers have a hexagonal symmetry. The large layer charge deficit mainly originating from the vacancies is neutralized by interlayer cations such as H$^+$, K$^+$ and Mn$^{2+/3+}$ (Silvester et al., 1997; Lanson et al., 2000, 2008; Gaillot et al., 2004, 2005; Villalobos et al., 2006; Grangeon et al., 2008, 2010, 2012). Hexagonal symmetry is found to be common among most birnessites formed from both biotic and abiotic pathways (Jones and Milne, 1956; Villalobos et al., 2003; Lanson et al., 2008; Grangeon et al., 2010; Zhu et al., 2010a, 2010b).

The geochemical interactions of birnessites with transition metals (TMs) occur mainly by adsorption and coprecipitation. The effects of TMs on the structure and properties of birnessites and the crystal chemistry characteristics of these TMs in birnessite structures are strongly dependent on the birnessite layer composition and ion types of the TMs (Peacock and Sherman, 2007b; Yin et al., 2012, 2013; Manceau et al., 2014). When adsorbed on hexagonal birnessite, Co^{2+} is quickly oxidized to Co^{3+} and most Co^{3+} migrates into the layers (Co$_E$), with the remaining portion adsorbed on vacancies as triple corner-sharing complexes (Co$_{TC}$) (Manceau et al., 1997; Yu et al., 2012; Kwon et al., 2013). Coprecipitation of Co with Mn during birnessite crystallization may also affect the birnessite properties. For turbostatic birnessite with hexagonal layer symmetry, Co doping has little effect on layer symmetry and micromorphology, but reduces the crystallinity and decreases the Mn average oxidation state (Mn AOS). Co K-edge EXAFS analysis shows that most of the Co (71–80%) exists in the layers (Yin et al., 2013).

Several previous studies have also explored the coprecipitation of TMs with Mn during synthesis of triclinic birnessites (Cai and Suib, 2001; Cai et al., 2002; Manceau et al., 2014). The synthesis of birnessite with orthogonal layer symmetry in these studies occurred through oxidation of Mn^{2+} by air at alkaline conditions. The presence of Fe^{3+}, Co^{2+}, and Ni^{2+} during the synthesis facilitates the formation of birnessite at low air flow rates, and the obtained birnessites have similar morphologies and particle sizes to those of the undoped triclinic birnessite, but the thermal stability is reduced (Cai and Suib, 2001; Cai et al., 2002). However, very little careful examination has been made on the layer symmetry of these TM-doped birnessites and the crystal chemistry characteristics of these TMs in the birnessite structures. In this work, Co^{2+} was added into the initial reactants during the synthesis of birnessite through oxidation of Mn^{2+} by O$_2$ at high pH. The obtained

birnessites were characterized by a combination of powder XRD, wet chemical analysis, N$_2$ adsorption, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and XAS to elucidate the effects of Co on the layer symmetry and physicochemical properties of the birnessites, and the spatial location of Co in the birnessite structure. The results provide further insights into the interactions between TMs and birnessites with different layer symmetries.

2. Materials and methods

2.1. Sample preparation

Triclinic birnessite is usually synthesized at a very high NaOH concentration by the oxidation of Mn^{2+} by various oxidizers, followed by equilibration at high pH (8–10). Usually the oxidizers are either air or O$_2$ (Giovanoli et al., 1970a, 1970b; Yang and Wang, 2002; Feng et al., 2004) or MnO$_4^{-}$ (Mckenzie, 1971; Luo et al., 1998; Villalobos et al., 2003). Here Co-doped birnessites were synthesized by oxidation of Mn^{2+} by O$_2$. For a typical synthesis, 250 mL of cold (~0 °C) 5.5 mol · L^{-1} NaOH solution was quickly added to 200 mL of 0.5 mol · L^{-1} (MnCl$_2$ + CoCl$_2$) solution with the Co/Mn molar ratios of 0, 0.05, 0.10 and 0.20. All the above solutions were mixed at a temperature held below 10 °C to prevent the formation of low valence Mn oxide impurities, such as hausmannite (Yang and Wang, 2002; Feng et al., 2004). Then, O$_2$ was bubbled through the mixtures at a rate of 2 L · min^{-1} and the reaction went on under vigorous mechanical stirring (450 r · min^{-1}) for 5 h. The obtained birnessite samples were named Co0, Co5, Co10 and Co20, respectively.

All the obtained samples were washed thoroughly with distilled deionized water and then dried at 40 °C for several days. The dried samples were ground in an agate mortar to particle sizes below 100 mesh and stored at room temperature in polyethylene plastic tubes.

2.2. Sample characterization

Powder X-ray diffraction analysis of the Co-doped birnessites was carried out on a Bruker D8 Advance diffractometer using Ni-filtered, Cu Kα radiation (λ = 0.15418 nm). The diffractometer was operated at a tube voltage of 40 kV and a current of 40 mA with 10 s counting
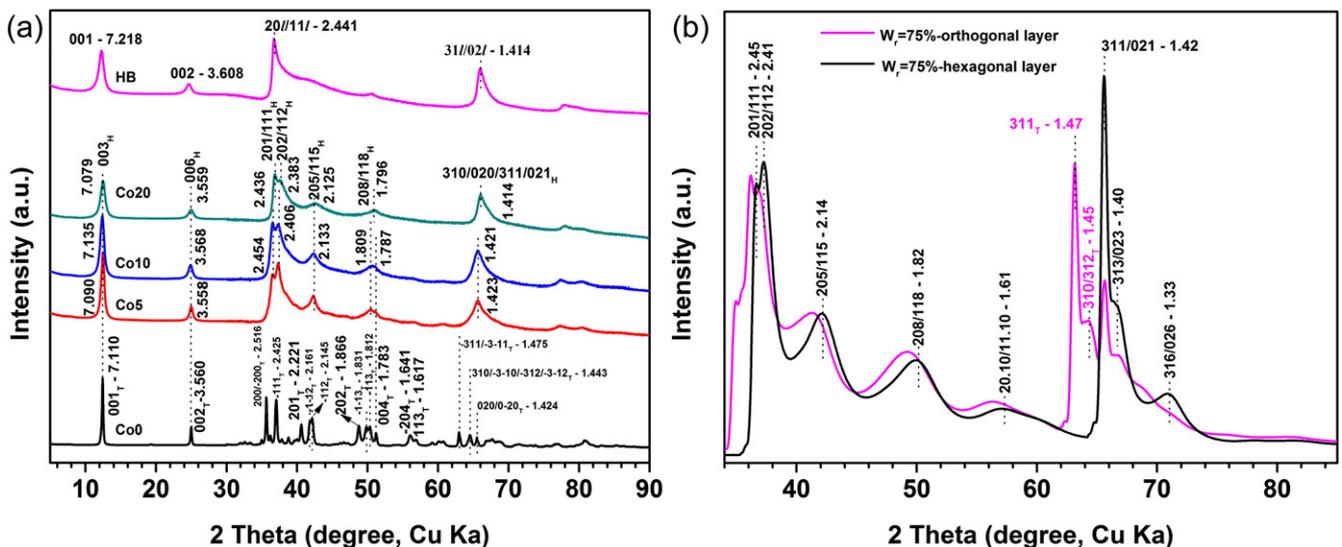

Fig. 1. (a) Powder XRD patterns of Co-doped birnessites. For a better examination of the evolution of the XRD traces with Co content, the low angle region (5–30° 2θ Cu Kα) of Co0 was scaled by a factor 0.04, and the high angle regions (30–90° 2θ Cu Kα) of Co5, Co10, Co20 and hexagonal turbostatic birnessite HB (Yin et al., 2012) were scaled by a factor 10. (b) Theoretical calculations of birnessites with 75% random stacking faults (W$_r$) with orthogonal and hexagonal layer symmetry based on the model of Lanson et al. (2002). The base-centered unit cell parameters for the birnessite with the orthogonal layer symmetry are a = 5.174 Å, b = 2.848 Å, c = 7.334 Å, α = 90.53°, β = 103.20°, and γ = 90.07° while those for the variety with the hexagonal layer symmetry are b = 2.848 Å, a = $\sqrt{3}$ b = 4.933 Å and c = 7.128 Å. For both birnessite varieties, the same coherent scattering domain (CSD) sizes were used: 100 Å radius disks within the a–b plane and an average of 15 layers along the c* axis (lognormal distribution). Unit for d-spacing is Å.