



Effect of Zn(II) coprecipitation on Mn(II)-induced reductive transformation of birnessite

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ABSTRACT

Mn oxides (MnOx) are ubiquitous metal oxide minerals in nearly all environmental settings. They play important roles in the transport and fate of many environmental components such as metals, organics, and nutrients. In the presence of dissolved Mn(II), MnOx phases can undergo ripening and transformation, resulting in the formation of phases with higher structural order, thus strongly affect the reactivity of MnOx over extended time scale. In natural environments, metal cations can strongly interact with MnOx through mechanisms such as sorption, incorporation, and/or coprecipitation, yet much still remain unknown about the effect of metal coprecipitation on the transformation of MnOx. This study investigates the effects of Zn coprecipitation on Mn(II)-induced reductive transformation of birnessite, a common MnOx mineral phase. Pure and Zn-coprecipitated acid birnessite phases were synthesized and their transformation kinetics and pathways in the presence of Mn(II) was investigated under oxic or anoxic conditions. During the transformation process, Zn-coprecipitated birnessite showed higher capability toward Mn(II) uptake, likely due to smaller particle size and the fast consumption of Mn(II) and precipitation of a new phase heterolite. The formation of an intermediate phase, feitknechtite, was faster for Zn-coprecipitated birnessite than pure birnessite, which is the opposite of Zn-sorbed birnessite system. Transformation from the intermediate phase feitknechtite to the final stable phase manganite was slower for Zn-coprecipitated birnessite, due to the lower Mn(II) concentration which catalyzed the transformation. This study revealed the importance of understanding the influence of metal cation impurities on the structural stability and long term reactivity of Mn oxide minerals.

1. Introduction

Mn oxides (MnOx) are ubiquitous metal oxide minerals in nearly all environmental settings, such as fresh waters, marine nodules, soils, and sediments (Bodeř et al., 2007; Bargar et al., 2009; Lanson et al., 2008). They are generally produced through the oxidation of Mn(II), and this process is much faster when catalyzed by mineral surfaces, microorganisms (Tebo et al., 2004), or reactive oxygen species (ROS) (Learman et al., 2011; Jung et al., 2017a, 2017b). Microorganisms are highly effective in catalyzing MnOx production (Learman et al., 2011; Jung et al., 2017a, 2017b; Murray et al., 2007; Bargar et al., 2005), and the initial biogenic MnOx are typically highly reactive hexagonal phases with high surface area, negative surface charge, and large amount of vacancy sites (Tebo et al., 2004). Dissolved Mn(II) can react with structural Mn(IV) to produce Mn(III) (Bargar et al., 2005; Zhu et al., 2010; Tang et al., 2014; Zhao et al., 2016), resulting in the ripening and transformation of the hexagonal birnessite phases and the formation of phases with different symmetry (i.e. triclinic birnessite) or

oxidation states (i.e. Mn(III)-bearing oxides and hydroxides) (Webb et al., 2005; Post, 1999). Such reductive transformation can strongly affect the sorptive and redox reactivity of the MnOx. For example, newly produced Mn(III) can incorporate at the vacancy sites of MnOx and decrease the sorption capacity toward metal cations (e.g. Pb, Cu, Zn, and Cd) (Wang et al., 2012). Mn(III)-bearing minerals are less reactive compared to Mn(IV)-bearing minerals toward the adsorption of As(III, V) (Zhu et al., 2009). The availability of Mn(III) in MnOx structure is also important during the oxidation of Cr(III) by MnOx (Landrot et al., 2012; Nico and Zasoski, 2000).

The reductive transformation process is controlled by factors such as dissolved Mn(II) concentration, pH, and the presence of oxygen (O₂). At low Mn(II) concentrations, biotic and abiotic hexagonal birnessite can react with Mn(II) to form Mn(III), which can order within the layer and change the layer symmetry from hexagonal to triclinic (Bargar et al., 2005; Zhu et al., 2010; Zhao et al., 2016). With higher Mn(II) concentration and under anoxic conditions, such reductive transformation can lead to the formation of manganite (γ -MnOOH) at pH 7.0–8.0 and

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hausmannite ($\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$) at pH 8.0–8.5, both with the presence of an intermediate phase feitknechtite ($\beta\text{-MnOOH}$) (Elzinga, 2011; Lefkowitz et al., 2013). Under oxic conditions, hexagonal birnessite can react with concentrated Mn(II) and precipitate nsutite ($\gamma\text{-Mn}^{\text{III,IV}}(\text{O,OH})_2$) and ramsdellite (MnO_2) at pH 2.4, cryptomelane ($\text{K}_{1.3-1.5}\text{Mn}_8^{\text{III,IV}}\text{O}_{16}$) at pH 4.0, groutite ($\alpha\text{-MnOOH}$) at pH 6.0, and feitknechtite and manganite at pH 7–7.5 (Tu et al., 1994; Mandernack et al., 1995). The presence of oxygen generally increases the uptake of Mn(II) by birnessite, due to mineral-surface catalyzed oxidation of Mn(II) by O_2 in addition to the direct electron transfer reaction between Mn(II) and birnessite (Elzinga, 2011; Lefkowitz et al., 2013).

Birnessite minerals have high affinities for metal cations due to their low point of zero charge (PZC) (Tebo et al., 2004; Spiro et al., 2009) and negatively charged surface across a wide range of pH conditions. Adsorbed and/or incorporated metal impurities in birnessite are likely to affect the above-mentioned transformation processes. A few studies have examined the effects of metal sorption and/or presence on the reductive transformation process. Ni adsorption on biogenic birnessite (Zhu et al., 2010) was shown to inhibit the formation of Mn(III) and favor the hexagonal symmetry; whereas Na and Ca presence during the transformation of biogenic MnOx can stabilize layer Mn(III) and favor the triclinic symmetry (Zhu et al., 2010). Zn adsorption on birnessite was found to slow down the transformation from birnessite to feitknechtite under anoxic condition (Lefkowitz and Elzinga, 2015).

Coprecipitation of metal cations (e.g. Ni, Zn, Fe, and Co) is known to modify birnessite structural properties (e.g. average oxidation state, surface area, vacancy site density) (Yin et al., 2015a, 2013, 2014, 2012, 2011). For example, Zn coprecipitation with fungal MnOx was shown to interrupt layer stacking and result in thinner flake-shaped particles (Yu et al., 2013). Our recent study also showed that Zn coprecipitation with abiotic phyllosulfates ($\delta\text{-MnO}_2$ and birnessite) resulted in reduced layer stacking and/or lateral layer size (Zhao and Wang, n.d.). Such effects, though previously observed for Zn adsorption on MnOx (Grangeon et al., 2012), were not as significant as the Zn coprecipitation system (Zhao and Wang, n.d.). Yet, despite the commonly observed structural modifications induced by metal coprecipitation with MnOx and the obvious environmental relevance, no studies have investigated how the structural modifications caused by metal coprecipitation would influence the long-term reductive transformation processes of MnOx.

In this study, we systematically compared the Mn(II)-induced transformation kinetics and pathways of pure and Zn-coprecipitated birnessite, and compared the effects to a previous study on the transformation of Zn-adsorbed birnessite (Lefkowitz and Elzinga, 2015). The roles of light and oxygen were also investigated by conducting experiments under light vs. dark conditions and oxic vs. anoxic conditions. To our knowledge, this is also the first study on the effects of Zn-birnessite interaction on birnessite reductive transformation under oxic conditions. Results from this study can help understand how metal impurities affect the long-term stability and reactivity of Mn oxides, thus Mn geochemical cycling in natural environments. For example, the formation of intermediate Zn-containing MnOx mineral phases as well as the overall transformation kinetics and pathways might significantly affect the sorptive and redox activities of the MnOx phases over extended time, and might also affect microbial anaerobic respiration of these oxides depending on the redox reactivity of the products.

2. Methods

2.1. Synthesis of pure and Zn-coprecipitated acid birnessite

Acid birnessite was synthesized following a previous study (Villalobos et al., 2003) by adding 45 mL of 6 M HCl to a boiling 300 mL of 0.667 M KMnO_4 solution under vigorous stirring. For Zn-coprecipitated birnessite samples, calculated amount of ZnSO_4 was mixed with the HCl solution before the addition of KMnO_4 , to achieve Zn:Mn_{total} molar ratio of 0.01, 0.1, and 0.2. These samples are labeled as 0.01

cppt, 0.1 cppt, and 0.2 cppt birnessite, respectively. At the end of reaction, the suspension was allowed cooling down and settling. The brown precipitates were collected by vacuum filtration (0.2 μm), washed and dialyzed with deionized (DI) water, and freeze dried. A portion of the solids were digested by aqua regia and measured for Zn and Mn concentrations using inductively coupled plasma–mass spectrometry (ICP-MS).

2.2. Mn(II)-induced transformation of birnessite phases

Parallel experiments were conducted to investigate the kinetics and pathways of Mn(II)-induced reductive transformation of pure and Zn-coprecipitated birnessite under oxic or anoxic conditions. For oxic experiments, 20 mg of pure or Zn-coprecipitated birnessite was suspended in a 200-mL solution containing 20 mM HEPES and 10 mM NaCl, with a solids/liquid ratio of 0.1 g/L. pH of the suspension was adjusted to 7.5 using NaOH and HCl solutions. The suspension was ultrasonicated for 3 min and equilibrated for 3 h by shaking at 150 rpm. To initiate the reaction, 200 μL of 1 M MnSO_4 stock solution was added to the suspension to achieve 1 mM Mn(II) concentration. Reaction bottles were consistently agitated on an orbital shaker at 150 rpm for 18 days. At certain time point, aliquots of the reaction suspension were collected and vacuum-filtered (0.22 μm). Mn(II) concentration in the filtrate was determined using a colorimetric method (Madison et al., 2011) using a UV–vis spectrometer (Cary 60, Agilent). Zn concentration was analyzed using ICP-MS. Filtered solids were repeatedly rinsed with DI water and freeze-dried for later structural characterization. For anoxic experiments, all reactions were conducted inside a glove box (Coy) filled with 95% N_2 and 5% H_2 . All solutions used for the experiments were boiled and cooled down under N_2 bubbling before transferring into the glove box. The transformation experiments above were conducted under dark conditions (bottles wrapped with aluminum foil). To investigate the potential influence of Mn oxide photo-reduction, the effect of light was also investigated using transparent plastic bottles under ambient lab lighting with other conditions same as above.

2.3. Solid phase characterization

A suite of complementary techniques were used to analyze the morphology and structure of the pure and Zn-coprecipitated birnessite, as well as their transformation products. X-ray diffraction (XRD) analysis was conducted using a Panalytical Empyrean multipurpose diffractometer with $\text{Cu K}\alpha$ radiation and a PIXcel 3D-Medipi $\times 3 \times 1 \times 1$ detector. Freeze-dried samples were placed on a zero-background holder, and data collection was conducted at $0.03^\circ 2\theta$ interval with 4 s counting time per step. Fourier transformed infrared (FT-IR) spectroscopy analysis was conducted on a Bruker Vertex 80 V spectrometer using KBr pellets at $800\text{--}1250 \text{ cm}^{-1}$. FTIR spectra were normalized by the highest peak intensity in each spectrum, according to previous studies (Elzinga, 2011; Lefkowitz et al., 2013; Lefkowitz and Elzinga, 2015). High resolution transmission electron microscopy (HRTEM) analysis was conducted on a JEOL 2010F TEM. Solid samples were suspended in ethanol and ultrasonicated for 1 min, then a single drop of the suspension was added on a 200-mesh Cu grid with a holey-carbon support film and air dried. Image focus was obtained on the carbon film adjacent to the particles of interest to avoid beam damage, then the beam was moved to the sample for image collection.

For Mn and Zn K-edge XAS analysis, wet pastes of the synthesized birnessite samples were vacuum filtered using a 0.22 μm membrane, rinsed with DI water, and mounted in an acrylic sample holder covered with Kapton tape. Samples were stored at -20°C before analysis. XAS experiments were conducted at Beamline 4-1 at Stanford Synchrotron Radiation Lightsource (SSRL, Menlo Park, CA) and beamlines 5-BM-D and 12-BM-B at Advanced Photon Source (APS; Argonne National Laboratory, Lemont, IL). Energy calibration used the corresponding Mn or Zn metal foil. Spectra of reference foils were collected

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