Effect of Zn coprecipitation on the structure of layered Mn oxides

Shiliang Zhao[a], Qian Wang[b], Jingying Sun[c], Olaf J. Borkiewicz[d], Rixiang Huang[a], Emily M. Saad[a], Benjamin Fields[a], Shuo Chen[c], Mengqiang Zhu[b], Yuanzhi Tang[a,*]

[a] School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, United States
[b] Department of Ecosystem Science and Management, University of Wyoming, Laramie, WY 82071, United States
[c] Department of Physics and Texas Center for Superconductivity, University of Houston, Houston, TX 77204, United States
[d] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, United States

ARTICLE INFO

ABSTRACT

Mn oxides (MnO_x) are a group of ubiquitous metal oxides in the environment and can significantly affect the biogeochemical cycles of metals, nutrients, and contaminants. Due to their negative surface charge across a wide range of environmental conditions, metal cations have strong affinities for MnO_x, and the presence of metal cations during or after the formation of MnO_x might significantly affect their structure and reactivity. This study systematically investigates the effects of Zn^{2+} presence during mineral formation (i.e. coprecipitation) on the structure of acid birnessite and δ-MnO_2, two synthetic analogs that are structurally similar to fresh biogenic MnO_x but with different crystallinity. For both acid birnessite and δ-MnO_2, Zn^{2+} existed as surface adsorbed species at vacancy sites, interrupted layer stacking along c axis, and caused reductions of the lateral particle size. Zn^{2+} also reduced Mn(III) contents in δ-MnO_2 layers, leaving more vacancy sites (capped by adsorbed Zn^{2+}). The reduction of layer stacking was more obvious for acid birnessite, while the modification of layer structure was more significant for δ-MnO_2. These structural changes will likely lead to modified reactivity of MnO_x in natural systems.

1. Introduction

Manganese (Mn) oxides (MnO_x) are a group of metal oxides that are ubiquitous in nearly all environmental settings, such as fresh waters, marine nodules, soils, and sediments (Bargar et al., 2009; Bodeï et al., 2007; Lanson et al., 2008). MnO_x can form through the oxidation of Mn (II) and this process is much faster when catalyzed by mineral surfaces, microorganisms, or reactive oxygen species. Previous studies have shown that the initial biogenic MnO_x phases produced by bacteria (Learman et al., 2011a; Learman et al., 2011b; Villalobos et al., 2006) and fungi (Bargar et al., 2005; Grangeon et al., 2010; Saratovsky et al., 2009) at circumneutral pHs are typically highly disordered and nano-crystalline phases that are structurally similar to hexagonal phyllomanganates (e.g. acid birnessite and δ-MnO_2) (Tebo et al., 2004). Due to their high surface area, large amount of vacancy sites, and negative surface charge across a wide range of pHs, MnO_x are highly reactive for the adsorption and redox transformation of metals (e.g. Pb, Ni, Cr) (Charlet and Manceau, 1992; Gadde and Laitinen, 1974; Kawashima et al., 1986; Li et al., 2015; Nico and Zasoski, 2000), metalloids (e.g. As, Se) (Chang et al., 2012; Manceau et al., 2007), and organic compounds (Kung and McBride, 1988; Stone and Morgan, 1984), and can exert

significant influences on the biogeochemical cycles of many important elements. From the materials chemistry aspect of view, hexagonal phyllomanganates are also important layered octahedral molecular sieves (OMS). The design of OMS with specific composition, structure, and morphology is of great interest for environmental, chemical, and material science research, due to their wide applications as catalysts, battery electrodes, adsorbents, and semiconductors (Lee et al., 2007; Li et al., 2006; Poizot et al., 2000; Yin et al., 2011a).

Metal cations such as Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} can either adsorb onto and/or incorporate into the layer vacancies and edge sites of birnessite (Drits et al., 2002; Hinkle et al., 2017; Lanson et al., 2002b; Manceau et al., 2002; Manceau et al., 1997; Peña et al., 2015; Peña et al., 2010; Silvester et al., 1997; Simanova et al., 2015; Villalobos et al., 2005). Adsorption of non-redox sensitive metals on MnO_x was shown to have limited effects on MnO_x layer structure (Power et al., 2005; Villalobos et al., 2014b) (except a recent study on Zn^{2+} sorption (Grangeon et al., 2012), as discussed later). Although numerous studies have examined the sorption and/or incorporation of metal cations on pre-formed MnO_x (i.e. sorption system), much remain unknown on the impact of metal cation presence during MnO_x formation (i.e. coprecipitation system) on the oxide structure, reactivity, and transformation,

despite the obvious relevance in complex environmental settings. Several recent studies demonstrated significant impacts of metal coprecipitation on the structural properties of MnO_x, such as Mn(II, III) contents, vacancy site density, crystallinity, thermal stability, and surface area (Kamimura et al., 2013; Yin et al., 2011a; Yin et al., 2015b; Yin et al., 2014; Yin et al., 2013; Yin et al., 2011b; Yin et al., 2015c; Yin et al., 2012). For biogenic phyllomanganates, the presence of Ni^{2+} can enhance vacancy site formation while Ca^{2+} and Na^+ were shown to stabilize layer Mn(III) (Zhu et al., 2010). For abiotic hexagonal birnessite, coprecipitation of Ni, Co, Fe, and V were found to modify the surface area, layer stacking, oxidation state, and coherent scattering domain size of MnO_x (Yin et al., 2011a; Yin et al., 2015b; Yin et al., 2014; Yin et al., 2012). These influences were shown to be metal specific and dependent on the compatibility of foreign metal ions with the MnO_x structure (e.g. size/charge similarities to the structural Mn(III)/(IV) ions, crystal field stability energy), which was previously suggested to be reflected in the ratio of incorporated vs. surface complexed metal (i.e. incorporation / (incorporation + complexation)) (Yin et al., 2011a; Yin et al., 2015b; Yin et al., 2013; Yin et al., 2015c; Yin et al., 2012). The degree of compatibility and amount of metal ion incorporation was found to increase in the order of $Zn^{2+} < Cu^{2+} < Ni^{2+} < Co^{3+}$, with the metal impact on structure modification in the reverse order (Yin et al., 2011a; Yin et al., 2013; Yin et al., 2012). These modified structural properties were shown to lead to differences in adsorptive capacities towards metal cations (e.g. Pb^{2+}, Zn^{2+}) (Li et al., 2015; Yin et al., 2015b; Yin et al., 2014; Yin et al., 2011b; Yin et al., 2012) and anions (e.g. arsenate) (Villalobos et al., 2014b), oxidative capability, as well as catalytic (Wang et al., 2016; Yin et al., 2015a) and electrochemical properties (Liu et al., 2015).

Among the transition metals (e.g. Co, Ni, Cu, Fe, Zn) that are commonly found to associate with MnO_x in natural environments, Zn shows the least structural compatibility (Kwon et al., 2013; Yin et al., 2011a; Yin et al., 2013; Yin et al., 2012). Zn^{2+} has not been found to incorporate into the layer vacancy sites of synthetic or biogenic birnessite, but instead predominantly adsorbs above/below the vacancy sites. Interestingly, the coordination environment of Zn^{2+} on MnO_x is dependent on Zn^{2+} concentration as well as MnO_x crystallinity (Grangeon et al., 2012). Tetrahedrally coordinated Zn^{2+} (Zn^{IV}) at low Zn^{2+} concentrations can change to octahedral coordination (Zn^{VI}) with increasing Zn^{2+} loading (Manceau et al., 2002; Toner et al., 2006; Trivedi et al., 2001). A recent study showed that adsorbed Zn^{2+} can reduce the amount of Mn(III) ions in δ-MnO_2 layers, leaving more vacancy sites (capped by adsorbed Zn^{2+}) (Grangeon et al., 2012). Zn^{2+} adsorption can also cause the dissolution of birnessite and result in smaller coherent scattering domain size in the *a-b* plane as calculated by X-ray diffraction (XRD) fitting (Grangeon et al., 2012). Only two previous studies have examined the effect of Zn^{2+} coprecipitation on MnO_x structure, but no consensus was reached. Yu et al. found that the presence of Zn^{2+} during the formation of fungal MnO_x inhibited the crystal growth and modified the layer stacking of MnO_x (Yu et al., 2013). Boonfueng et al. found that the presence of Zn^{2+} during biogenic MnO_x formation resulted in large Zn^{2+} sequestration (likely due to surface sorption), but with no obvious changes in MnO_x local structure (Boonfueng et al., 2009). Given the low compatibilities of Zn^{2+} with phyllomanganate structure, as well as its unique dependence of coordination environment on phyllomanganate crystallinity, a systematic study is highly desired to reveal the impact of this environmentally abundant element on the composition, surface properties, morphology, structural properties, as well as subsequent reactivity (e.g. sorptive, redox) of MnO_x.

This study examines the impact of Zn^{2+} coprecipitation on the structural properties of two phyllomanganates with different structural order, acid birnessite and δ-MnO_2. Zn^{2+} association with natural MnO_x was found to be 0–0.5% (Zn/Mn molar ratio) in marine nodules (Childs, 1975; Jenkyns, 1970; Marcus et al., 2004) and soils (Manceau et al., 2003). This ratio can reach 3% in coal mine drainage treatment systems

where Mn(II)-oxidizing microbes thrive (Tan et al., 2010), and can be as high as 46% in contaminated sediments (Lanson et al., 2008). This ratio can be even higher locally (Manceau et al., 2007). Since Zn^{2+} sequestration is known to be affected by phyllomanganate structure and crystallinity, this study compared acid birnessite and δ-MnO_2, two structurally similar phyllomanganate phases but with different structural order. Compared to δ-MnO_2, acid birnessite has better crystallinity, more layer stacking along *c* axis, larger layer dimension, and lower surface area (Manceau et al., 2013; Villalobos et al., 2003). Because Zn^{VI} stabilization is weaker between incoherently stacked and laterally smaller layers (Kwon et al., 2009), its prevalence on δ-MnO_2 was shown to be two times lower than on acid birnessite at similar Zn/Mn loadings (Grangeon et al., 2012; Yu et al., 2013). Therefore, it is possible that Zn^{2+} coprecipitation can have different effects on the structural properties of these two MnO_x phases with different crystallinity.

Compared to previous studies on Zn sorption on pre-formed MnO_x (Boonfueng et al., 2009; Drits et al., 2002; Grangeon et al., 2012; Lanson et al., 2002b; Manceau et al., 2002; Silvester et al., 1997; Toner et al., 2006), in this study Zn was added during the formation of Mn oxides (i.e. Zn coprecipitation). Although Zn was also found to exist as surface adsorbed species in this coprecipitation system (details in results section), more significant effects were observed on MnO_x structure compared to Zn sorption system. By exploring two synthetic MnO_x phases with similar structure but different structure order, our system eliminated the potential toxicity effects associated with biogenic MnO_x systems, and allowed thorough investigation on the effect of MnO_x structure order. We conducted systematic characterization of the Zn-coprecipitated MnO_x phases, by combining a suite of complementary techniques that are capable of probing mineral surface properties, morphology, and structure order at varied ranges, including BET surface area analysis, zeta-potential measurements, Zn and Mn X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), pair distribution function (PDF) analysis of X-ray total scattering, and high resolution transmission electron microscopy (HRTEM). Information obtained from this study provides a better understanding of the impacts of Zn^{2+} coprecipitation on the structural properties of two environmentally relevant MnO_x phases, and points to the importance of considering metal coprecipitation effects for studies centered on MnO_x reactivity in natural systems.

2. Methods

2.1. Synthesis of δ-MnO_2 and acid birnessite in the presence of Zn^{2+}

Both δ-MnO_2 and acid birnessite phases were synthesized in the absence or presence of a range of Zn^{2+} concentrations. δ-MnO_2 synthesis followed a previous procedure (Zhu et al., 2012) where 160 mL $MnSO_4$ solution (0.30 mol L^{-1}) was pumped into a mixture of 160 mL $KMnO_4$ (5.0 g) and 180 mL NaOH (3.5 g) solutions at a speed of 25 mL min^{-1} under vigorous stirring. Calculated amounts of $ZnSO_4$ was dissolved in the $MnSO_4$ solution to achieve Zn:total Mn molar ratio of 0–20%. For acid birnessite synthesis, $ZnSO_4$ was dissolved in 45 mL of 6 mol L^{-1} HCl solution to achieve Zn/total Mn molar ratio of 0–20%. This solution was then pumped at 1 mL min^{-1} into 300 mL of boiling 0.667 mol L^{-1} $KMnO_4$ solution under vigorous stirring (Villalobos et al., 2003). Previous studies on Mn oxide formation in the presence of Zn^{2+} used Zn/Mn ratios of ~1–22% (Yu et al., 2013). After synthesis, the suspensions were allowed to cool down (for birnessite) and the solid precipitates vacuum filtered (0.2 μm), rinsed with deionized (DI) water, dialyzed, and freeze-dried. Samples were labeled according to the starting Zn/Mn molar ratio and are referred to as pure or Zn-coprecipitated samples (see Table 1 for details). A portion of the dried solids was digested by aqua regia and analyzed for elemental composition using inductively coupled plasms – mass spectrometry (ICP-MS). Samples were also characterized for their morphology, surface, and