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Geochimica et Cosmochimica Acta 192 (2016) 220–234

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Structural response of phyllomanganates to wet aging and aqueous Mn(II)

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Received 24 May 2016; accepted in revised form 30 July 2016; available online 6 August 2016

Abstract

Naturally occurring Mn(IV/III) oxides are often formed through microbial Mn(II) oxidation, resulting in reactive phyllomanganates with varying Mn(IV), Mn(III), and vacancy contents. Residual aqueous Mn(II) may adsorb in the interlayer of phyllomanganates above vacancies in their octahedral sheets. The potential for interlayer Mn(II)-layer Mn(IV) comproportionation reactions and subsequent formation of structural Mn(III) suggests that aqueous Mn(II) may cause phyllomanganate structural changes that alters mineral reactivity or trace metal scavenging. Here we examine the effects of aging phyllomanganates with varying initial vacancy and Mn(III) content in the presence and absence of dissolved Mn(II) at pH 4 and 7. Three phyllomanganates were studied: two exhibiting turbostratic layer stacking (δ-MnO_2 with high vacancy content and hexagonal birnessite with both vacancies and Mn(III) substitutions) and one with rotationally ordered layer stacking (triclinic birnessite containing predominantly Mn(III) substitutions). Structural analyses suggest that during aging at pH 4, Mn(II) adsorbs above vacancies and promotes the formation of phyllomanganates with rotationally ordered sheets and mixed symmetries arranged into supercells, while structural Mn(III) undergoes disproportionation. These structural changes at pH 4 correlate with reduced Mn(II) uptake onto triclinic and hexagonal birnessite after 25 days relative to 48 h of reaction, indicating that phyllomanganate reactivity decreases upon aging with Mn(II), or that recrystallization processes involving Mn(II) uptake occur over 25 days. At pH 7, Mn(II) adsorbs and causes limited structural effects, primarily increasing sheet stacking in δ-MnO_2. These results show that aging-induced structural changes in phyllomanganates are affected by aqueous Mn(II), pH, and initial solid-phase Mn(III) content. Such restructuring likely alters manganese oxide reactions with other constituents in environmental and geologic systems, particularly trace metals and redox-active compounds.

Keywords: Manganese oxides; Birnessite; Phyllomanganates; Redox reactions

1. INTRODUCTION

Many naturally-occurring manganese oxides are nanoparticulate, poorly crystalline, and highly reactive minerals (Krumbein and Jens, 1981; Emerson et al., 1982; Villalobos et al., 2003; Saratovsky et al., 2006; Bargar et al., 2009; Clement et al., 2009; Dick et al., 2009; Grangeon et al., 2010; Tan et al., 2010). Manganese oxide formation in natural systems is often controlled by microbial Mn(II) oxidation, as abiotic Mn(II) oxidation is kinetically slow (Morgan and Stumm, 1964; Nealson et al., 1988; Tebo, 1991; Wehrli et al., 1995; Tebo et al., 1997; Von Langen et al., 1997; Bargar et al., 2000; Nelson and Lion, 2003; Morgan, 2005; Luther, 2010). Biogenic manganese oxides are typically phyllomanganates with birnessite-type structures, consisting of negatively charged octahedral sheets separated by hydrated interlayers (Krumbein and Jens, 1981; Emerson et al., 1982; Villalobos et al., 2003; Bargar et al., 2005, 2009; Webb

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http://dx.doi.org/10.1016/j.gca.2016.07.035

0016-7037/

et al., 2005a; Saratovsky et al., 2006; Clement et al., 2009; Dick et al., 2009; Grangeon et al., 2010; Tan et al., 2010; Santelli et al., 2011). The negative layer charge develops as a result of Mn(IV) vacancies, Mn(III) substitutions, or a combination thereof, with vacancy and Mn(III) content varying substantially among phyllomanganates. To compensate the negative charge, exchangeable cations are adsorbed in the interlayer. These phyllomanganates exhibit high adsorption capacities for many cations, including Mn (II) (Morgan and Stumm, 1964; McKenzie, 1980; Murray et al., 1984), which often bind above vacant sites in the octahedral sheets (Toner et al., 2006; Peacock and Sherman, 2007; Manceau et al., 2007b; Peacock, 2009; Zhu et al., 2010b) and can enter into the phyllomanganate structure over time (Peacock, 2009).

Phyllomanganates coexist with aqueous Mn(II) in regions with active manganese cycling; for example, at hydrothermal vents, redox interfaces in soils or sediments, or in oxic regions of stratified soils, sediments, and water columns as a result of upward diffusion of Mn(II) (Graybeal and Heath, 1984; Rajendran et al., 1992; Burdige, 1993; Van Cappellen et al., 1998; Tebo et al., 2004, 2005). Abiotic reactions involving Mn(II) adsorption onto phyllomanganates are likely common in these environments (Shimmield and Price, 1986; Canfield et al., 1993), and could involve Mn(II) incorporation into vacant sites or electron transfer via Mn(II)–Mn(IV) comproportionation reactions, resulting in increased structural Mn(III). Several studies have identified that aqueous Mn(II) induces phyllomanganate phase transformations to a wide range of Mn(III) or Mn(IV/III) oxide minerals, including nsutite [$Mn(O,OH)_2$], ramsdellite [MnO_2], cryptomelane [$K_x(Mn^{IV},Mn^{III})_8O_{16}$], groutite [$\alpha$-MnOOH] (Tu et al., 1994), hausmannite [Mn_3O_4] (Lefkowitz et al., 2013), feitknechtite [β-MnOOH] (Bargar et al., 2005; Elzinga, 2011; Lefkowitz et al., 2013; Elzinga and Kustka, 2015), or manganite [γ-MnOOH] (Tu et al., 1994; Elzinga, 2011; Lefkowitz et al., 2013; Elzinga and Kustka, 2015). A recent study has observed Mn isotope exchange between aqueous Mn(II) and a solid Mn(IV) oxide during conversion to Mn (III) oxyhydroxides, indicating that some Mn(III) formed during reaction undergoes disproportionation (Elzinga and Kustka, 2015).

Many natural systems with active manganese cycling are associated with Mn(IV/III) phyllomanganates, even in the presence of elevated dissolved Mn(II) (Wehrli et al., 1995; Friedl et al., 1997; Manceau et al., 2007a, 2007b; Dick et al., 2009; Tan et al., 2010; Frierdich and Catalano, 2012), suggesting that Mn(II)-induced phase transformations of birnessite-type phyllomanganates are uncommon. Prior research on Mn(II)–phyllomanganate interactions with Mn(II) to Mn(IV) ratios that do not induce phase transformations is limited. Some studies do indicate that Mn(II) alters sheet stacking behaviors (Lefkowitz et al., 2013) and symmetries (Bargar et al., 2005; Zhu et al., 2010a; Zhao et al., 2016). This indicates that structural Mn(III) was produced during reaction, as its larger size and Jahn–Teller distortion are expected to alter the mineral structure. However, the systematic relationship between Mn(II) concentrations and phyllomanganate structural changes at low to circumneutral pH (conditions relevant to soils and many natural waters) is unclear.

Identifying the structural response of phyllomanganates to dissolved Mn(II) is needed because the reactivity and trace metal scavenging behavior of manganese oxides is largely controlled by their structure (Post, 1999). In this paper, changes to phyllomanganate structures are examined following aging for 25 days in the presence and absence of Mn(II) at acidic and neutral pH, with Na^+ as the dominant cation. Because Mn(II) likely adsorbs above vacancies, three birnessite-type phyllomanganates with varying vacancy content and layer stacking are investigated. δ-MnO_2, the synthetic analogue of vernadite [$(Ca,Na,K)(Mn^{4+},\square)O_2 \cdot nH_2O$] (Villalobos et al., 2006), has high vacancy content and turbostratic stacking; c-disordered H^+ birnessite (a hexagonal-type birnessite) (‘HexB’) [$(Ca,Na,K)(Mn^{4+},Mn^{3+},\square)O_2 \cdot nH_2O$] has vacancies (Silvester et al., 1997; Lanson et al., 2000), Mn(III) substitutions, and turbostratic stacking; triclinic birnessite (‘TriB’) [$(Ca,Na,K)(Mn^{4+}{}_x Mn^{3+}_{1-x})O_2 \cdot nH_2O$] has primarily Mn(III) substitutions, few vacancies, and ordered layer stacking (Post and Veblen, 1990; Drits et al., 1997; Post et al., 2002; Lopano et al., 2007). The role of pH is also examined because Mn(II)–Mn(IV) comproportionation reactions exhibit a pH dependence, with comproportionation promoted with increasing pH (Mandernack et al., 1995). The effects of aging and Mn(II) on phyllomanganate sheet structures were explored using X-ray absorption fine structure (XAFS) spectroscopy and powder X-ray diffraction (XRD). To assess differences in Mn(II) uptake upon aging versus adsorption over short time scales, macroscopic Mn(II) adsorption isotherms onto the solids at differing pH values were also obtained.

2. METHODS AND MATERIALS

2.1. Mn oxide syntheses

Manganese oxide minerals were synthesized using modified, previously published procedures, as described in detail below. δ-MnO_2 was synthesized using a redox method, which involves the reduction of $KMnO_4$ and the oxidation of $MnCl_2$ under alkaline conditions, outlined by Villalobos et al. (2003). Briefly, a solution of 2.50 g $KMnO_4$ in 80 mL deionized water (>18.2 MΩ·cm) was added to a solution of 1.75 g NaOH in 90 mL deionized water over approximately five minutes. While stirring this mixture vigorously, a solution of 4.70 g $MnCl_2 \cdot 4H_2O$ in 80 mL deionized water was added slowly, over approximately 35 min. The mixture was allowed to settle for four hours, after which point the pH of the suspension was checked to ensure it was around a pH of 7, and the suspension was centrifuged, discarding the supernatant. The suspension was subjected to at least four 1 M NaCl washes, as described in Villalobos et al. (2003), followed by at least six deionized water washes.

A poorly crystalline hexagonal birnessite was synthesized following the c-disordered H^+-birnessite synthesis procedure described in Villalobos et al. (2003). This synthesis is similar to the δ-MnO_2 synthesis described above (including the NaCl and deionized water washes), except