Dissolution and phase transformation processes of hausmannite in acidic aqueous systems under anoxic conditions

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ABSTRACT

Hausmannite is the most widely distributed spinel-structured manganese oxide in soils and sediments. The transformation of this metastable manganese oxide to Mn(IV) oxides with higher adsorption capacity has attracted much research interest, while the transformation mechanisms and influencing factors still remain largely unknown, especially under acidic condition. In this work, the transformation processes of hausmannite at different pH values and the influence of cations were studied. Results indicated that hausmannite was transformed into manganite at pH 5.0–9.0. The dissolution of hausmannite was initiated and promoted by protons ($\leq$ 7.0), and the decrease of pH accelerated its conversion to Mn(IV) oxides. The tunnel-structured Mn(IV) oxide was generated via two steps during the dissolution process of hausmannite at pH $\leq$ 3.0. Hausmannite was disproportionated to δ-MnO$_2$ at first, which was then transformed to nsutite in the presence of Na$^+$ and H$^+$ through the transfer of electrons from adsorbed Mn(II) to structural Mn(IV). The disproportionation of hausmannite to δ-MnO$_2$ was not affected by other cations, while the presence of K$^+$ promoted the further transformation of δ-MnO$_2$ to cryptomelane. The structural rearrangement process of δ-MnO$_2$ was the rate-determining step for the formation of final products. This work expands the understanding of the formation, transformation and geochemical processes of manganese oxides in supergene environments.

1. Introduction

Manganese oxides are widely distributed in soils and sediments. Their specific physicochemical properties influence the migration, transformation, and fate of organic pollutants and toxic metalloids/metals such as As(III,V), Cr(III,VI), and Se(IV,VI) (Katsoyiannis et al., 2004; Saputra et al., 2013; Scott and Morgan, 1996; Weaver and Hochella, 2003). The interaction processes are responsible for the biogeochemical cycling of corresponding active elements. Crystal structure plays an important role in the adsorption and oxidation reactivity of manganese oxides (Landrot et al., 2012; Luo et al., 2017; Post, 1999; Qiu et al., 2011; Weaver and Hochella, 2003). Compared with todorokite, manganite and cryptomelane, layered birnessite exhibits the highest reactivity for sulfide oxidation (Luo et al., 2017; Qiu et al., 2011). Although δ-MnO$_2$ and acid birnessite both show hexagonal layer symmetry, the Cr(III) oxidation capacity of acid birnessite is higher than that of δ-MnO$_2$ (Landrot et al., 2012). The reactions between seven manganese oxides and Cr(III) indicated that hausmannite and birnessite have the highest Cr(III) oxidation ability (Weaver and Hochella, 2003). Hence, the formation and conversion of manganese oxides are hot topics of research in soil science, environmental chemistry and mineralogy.

Hausmannite, the fifth most common manganese oxide minerals in soil profiles (McKenzie, 1972), is a mixed-valent spinel manganese oxide with Mn(III) in the distorted octahedral coordination and Mn(II) in the tetrahedral coordination (Giovanoli et al., 1976; Jarosch, 1987). Metastable hausmannite can be generated from the abiotic oxidation of Mn(II) or reduction of manganese oxides (Murray et al., 1985; Lefkowitz et al., 2013). In oxygen-containing natural waters, Mn(II) is easily oxidized to Mn$_3$O$_4$ and β-MnOOH (Murray et al., 1985). Reaction with Mn(II) causes the reduction of birnessite to β-MnOOH, and the subsequent transformation into hausmannite would occur at pH 8.0–8.5 (Lefkowitz et al., 2013). Thus, hausmannite is easily generated and is ubiquitous in supergene environments.
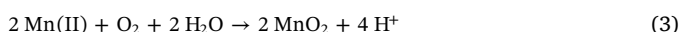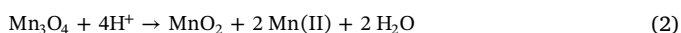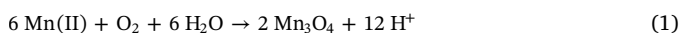
Due to the presence of Mn(III) in the structure, hausmannite can act as an oxidizing and reducing agent (Madison et al., 2013). The reaction of hausmannite with As, Cr, and Pu can affect their mobility and toxicity (Cantu et al., 2014; Feng et al., 2006; Garcia et al., 2014; Shaughnessy et al., 2003; Weaver and Hochella, 2003). Hausmannite, which comprises both Mn(II) and Mn(III), has a higher Cr(III) oxidation

reactivity than tunnel-structured manganese oxides including crypto-melane and pyrolusite (Weaver and Hochella, 2003). The highest Cr(III) and Cr(VI) binding capacities of hausmannite were achieved at pH 4.0 and 3.0, respectively (Cantu et al., 2014). Thermodynamic analysis indicated an adsorption process, but activation energy analysis indicated a chemisorption process for Cr(III,VI) (Cantu et al., 2014), however, the final products after an hour of reaction was not identified for further understanding the reaction mechanism. When the pH was controlled between 2.0 and 6.0, the maximum binding capacities of hausmannite for As(III) and As(V) were respectively 13.5 and 7.5 mg g^{-1} at pH 3.0 (Garcia et al., 2014). Hausmannite can work as an excellent adsorbent for heavy metals, especially at low pH values, but the adsorption mechanisms are not fully understood. The adsorption process may be related to the pH-dependent changes in the structure and transformation compositions of metastable hausmannite, which have been largely ignored in previous studies.

Hausmannite is considered as a vital intermediate in the oxidation process of Mn(II) to Mn(IV) oxides. Mn(III) in the structure of hausmannite can be disproportionated to Mn(IV) as indicated by a thermodynamic model (Hem and Lind, 1983). A two-step cycle for a final product of MnO_2 includes (Hem, 1978): oxidation of Mn(II) to Mn_3O_4 (Eq. (1)), and disproportionation of Mn_3O_4 to MnO_2 (Eq. (2)). The total reaction may be expressed as Eq. (3). These equations are listed as follows.

$$6\,Mn(II) + O_2 + 6\,H_2O \rightarrow 2\,Mn_3O_4 + 12\,H^+ \tag{1}$$

$$Mn_3O_4 + 4H^+ \rightarrow MnO_2 + 2\,Mn(II) + 2\,H_2O \tag{2}$$

$$2\,Mn(II) + O_2 + 2\,H_2O \rightarrow 2\,MnO_2 + 4\,H^+ \tag{3}$$

The incongruent dissolution processes of hausmannite induced by hydrolysis and protonation have been extensively studied under oxic conditions. The dissolution of hausmannite occurs first, and 7-Å phase birnessite is then precipitated in high-concentration NaOH and KOH solution, while dilute alkaline solution facilitates the transformation of hausmannite to manganite (Cornell and Giovanoli, 1988). In acidic solution, conversion of hausmannite to manganite is also dominant at pH ≥ 4.0, and Mn(IV) oxide precipitates are the major secondary mineral phases at lower pH (Giovanoli et al., 1976; Hem and Lind, 1983). Bricker found that γ-MnO_2 is produced in intense acidification and δ-MnO_2 is produced in mild acidification (Bricker, 1965), but the transformation mechanism from hausmannite to δ- and γ-MnO_2 has not been clarified yet. In previous studies, the above reaction processes were mainly monitored by conventional characterization methods such as Mn average oxidation state (Mn AOS), X-ray diffraction (XRD), and transmission electron microscopy (TEM) for the long-term reaction products. Besides the limitation of technology, the features of manganese oxides, including fine particles, poor crystallinity, and indistinguishable crystal phases, make it extremely difficult to identify the reaction intermediates, resulting in a poor understanding of the transformation mechanisms. Synchrotron radiation XRD (SR-XRD) and Mn K-edge X-ray absorption near edge structure (XANES) spectroscopy were also used to analyze the dissolution products of hausmannite (Peña et al., 2007). Manganite, which was observed by XRD in aged hausmannite products for several weeks or a year at pH ≥ 6.0, was identified by SR-XRD but not by XANES in the 1-week dissolution product at pH 6.0 (Peña et al., 2007). The low content of transformation products also leads to the poor understanding of reaction process. Collectively, hausmannite can be transformed to manganese (hydr) oxides under a wide range of environmental conditions. Although the final products have been well analyzed, the detailed transformation mechanism, especially the short-term intermediates and crystal growing process, still remains unknown.

In the present work, we examined the dissolution and phase transformation processes of hausmannite with various pH values and aqueous cations including H^+, Na^+, and K^+. Our objectives are to

understand the mineralogy in the entire reaction to identify the possible intermediates and clarify the growth of tunnel-structured Mn(IV) oxides.

2. Materials and methods

2.1. Synthesis of manganese oxides

Hausmannite was synthesized following the modified procedure of Mckenzie (Feng et al., 2007; McKenzie, 1971). The $Mn(OH)_2$ precipitate from $MnSO_4 \cdot H_2O$ and NaOH was oxidized by oxygen in air to obtain the final product. The XRD pattern and Fourier transform infrared spectroscopy (FTIR) spectrum of synthesized product indicated that pure-phase hausmannite was generated (Fig. S1). The Brunauer-Emmer-Teller surface area was measured to be 22 m^2 g^{-1}. The preparation of references, including cryptomelane (α-MnO_2), nsutite (γ-MnO_2), feit-knechtite (β-MnOOH), manganite (γ-MnOOH), and δ-MnO_2, is described in Supporting Information, and the results of XRD and Mn K-edge extended X-ray absorption fine structure (EXAFS) are shown in Fig. S2.

2.2. Mineral dissolution experiments

Dissolution experiments of hausmannite were performed at a pH range of 3.0–9.0. The whole experiments were conducted under anoxic conditions. Distilled deionized water (DDW, 18 MΩ cm resistance) was boiled for 20 min and cooled to room temperature by bubbling high-purity nitrogen gas (99.999%, Wuhan Iron and Steel (Group) Corp., China) before use. About 0.50 g of hausmannite (4.4 mmol L^{-1}) was added to 500 mL 0.1 mol L^{-1} Na_2SO_4 solution in a five-neck bottle with one neck for pH monitoring, one capped with a rubber stopper equipped with a port for pH adjustment and sampling, one for bubbling of nitrogen and the remaining two were sealed. The reaction solutions were stirred vigorously with a magnetic stir bar throughout the experiments to ensure thorough mixing. The pH of the reaction systems was continuously adjusted manually in the first 12 h using NaOH (0.01 and 0.1 mol L^{-1}) and H_2SO_4 solution (0.1 and 1.0 mol L^{-1}), and was then adjusted three times a day. After the prescribed time, 3.0 mL suspension was collected from the port of the bottle by a syringe and filtered through a 0.22 μm microporous membrane filter. The reaction system was continuously purged with high-purity nitrogen gas in the first 12 h, and the nitrogen pressure inside the reactor was maintained to be slightly higher than the atmospheric pressure to prevent air ingress. After 12 h of reaction, the reactor was transferred to an anaerobic glove box to maintain anoxic conditions. Wet samples were identified by XRD soon after the reaction. The samples in membrane filter were washed with deoxygenated DDW for three times, dried in a vacuum oven at 40 °C for 12 h, and stored in a vacuum bag for further analyses including FTIR, TEM, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectra (XAS).

To examine the influence of cations on the hausmannite transformation process under acidic conditions, parallel experiments were conducted in 0.1 mol L^{-1} K_2SO_4 solution or without background cation under the same experimental conditions.

2.3. Characterization of intermediates

Wet samples were directly pasted onto the glass slides for XRD (Bruker D8 ADVANCE) data collection using Cu Kα (λ = 0.15418 nm) and an operation voltage of 40 kV and current of 40 mA at a scanning rate of 2° min^{-1}. Fourier transform infrared spectroscopy (FTIR, Bruker VERTEX 70) was conducted with a Bruker Equinox 55 model spectro-photometer by making pellets with KBr powder. The Mn AOS of hausmannite was measured by the oxalic acid method (Kijima et al., 2001). About 0.1 g of sample was dissolved into 10 mL H_2SO_4 (0.5 mol L^{-1}) and an excess of 10 mL $H_2C_2O_4$ (0.5 mol L^{-1}) to reduce