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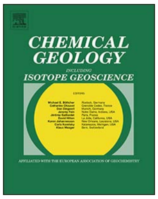

Local structure of Cu^{2+} in Cu-doped hexagonal turbostratic birnessite and Cu^{2+} stability under acid treatment

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ABSTRACT

Geochemical behaviors of heavy metal contaminants, such as Cu^{2+}, are strongly controlled by natural birnessite-like minerals in both marine and terrestrial environments. However, the mechanisms of the interaction of Cu^{2+} with birnessite are not fully understood yet. In the present study, Cu^{2+} was coprecipitated with Mn^{2+} to produce hexagonal turbostratic birnessite, which is analogous to natural birnessite. The obtained Cu-doped birnessite was characterized by powder X-ray diffraction, field-emission scanning electron microscopy, and X-ray absorption spectroscopy (XANES + EXAFS). The stability of Cu(II) in the birnessite structure was investigated by acid treatment. Increasing the dopant content reduces the mineral crystallinity in the [001] direction and the unit cell parameter b from the hexagonal layers. It also shortens the bond length of Mn—O in the $[MnO_6]$ unit and the edge-sharing Mn—Mn distance in the layers, and increases the average oxidation state (AOS) of Mn and the specific surface area. Analysis of Cu K-edge XANES and EXAFS data indicates that, only a small part of Cu(II) is inserted into the birnessite layers, while most of it is adsorbed on the vacancies. When the Cu/Mn molar ratio is increased from 0.08 to 0.23, an increasing part of Cu(II) is present as polynuclear clusters on the birnessite edge sites in the pH range of ~3.3–5.3. Reaction with H_2SO_4 solution is found to easily dissolve the polynuclear Cu clusters and the highly distorted Cu octahedra in innersphere complexes on the birnessite-water interface, with ~53% of the Cu^{2+} released into the solution. On the other hand, the reaction with HCl solution leads to reductive dissolution of the mineral matrix, the release of Mn^{2+} into solutions, the decrease in the first Mn—O and edge-sharing Mn—Mn distances and Mn AOS, in addition to the release of Cu^{2+}. The release rate of Cu^{2+} is much faster than that of Ni^{2+} in Ni-doped birnessites, owing to the lower stability of distorted $[CuO_6]$ octahedron upon proton attack. These results indicate the formation of multinuclear Cu complexes on birnessite surfaces under the investigated conditions. The results also suggest the lower stability of Cu^{2+} in these minerals and thus higher potential toxicity in acidic conditions, in comparison with other metal pollutants, such as Ni^{2+}. This study provides new insights into the interaction mechanisms between Cu^{2+} and birnessite-like minerals, and help to clarify the structural stability and geochemical behaviors of Cu^{2+} associated with birnessite-like minerals in natural environments.

1. Introduction

Copper is a trace metal important in biogeochemical cycles in the environment. For instance, it is a cofactor in various enzymes in mammals (Peña et al., 1999). However, it is also one of the most common heavy metal pollutants in soils, lakes, and groundwater systems (Spitalny et al., 1984; Barker and Senft, 1995). The toxicity of Cu^{2+} is a major concern. For example, excessive intake of Cu^{2+} is dangerous to algae. In natural environments, the interactions of Cu^{2+} with active minerals have significant effects on its geochemical behaviors. In ferromanganese crusts, Cu^{2+} tends to be more strongly associated with the Mn oxide phase than with Fe oxides. The dominant Mn oxide phase in ferromanganese crusts is vernadite (Manceau et al., 2003, 2007a, b, 2014; Peacock and Sherman, 2007a; Little et al., 2014).

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Owing to its specific characteristics (e.g., small particle size, structural defects, and unique surface charge), vernadite acts as an important heavy metal scavenger (Manceau et al., 1992a, b, 1999, 2002; Lanson et al., 2002, 2008; Villalobos et al., 2005, 2014; Villalobos, 2015; Drits et al., 2007; Feng et al., 2007; Peacock and Sherman, 2007b; Grangeon et al., 2012; Wang et al., 2012; Yin et al., 2012, 2013; Yu et al., 2012; Peña et al., 2015). Laboratory synthesized birnessite samples under different conditions are usually used as analogs to natural vernadites (Lanson et al., 2002; Manceau et al., 2002, 2014; Villalobos et al., 2014; Peacock and Sherman, 2007b; Grangeon et al., 2008, 2012; Zhu et al., 2012; Peña et al., 2015).

There are two main binding mechanisms of Cu^{2+} on birnessite surfaces: adsorption and incorporation (Manceau et al., 2002, 2014; Sherman and Peacock, 2010; Arai, 2011; Kwon et al., 2013; Little et al., 2014). The metal ions of Co^{3+}, Ni^{2+}, and Fe^{3+} are known to be partly adsorbed on birnessite vacancies and/or edge sites in the octahedron, and partly inserted into the birnessite layers (Manceau et al., 1997, 2007a, b; Peacock and Sherman, 2007a, b; Peacock, 2009; Yu et al., 2012; Kwon et al., 2013; Yin et al., 2013). In contrast, many questions remain regarding the binding of Cu^{2+} to birnessite, such as the coordination structure of Cu^{2+} in the first Cu—O shell (e.g., coordination number, CN), and whether Cu^{2+} can insert into the birnessite layers by replacing Mn atoms in the layer and/or occupying vacancies (Sherman and Peacock, 2010; Kwon et al., 2013; Little et al., 2014; Manceau and Nagy, 2015; Sherman et al., 2015). Powder and polarized extended X-ray absorption fine structure spectroscopy (EXAFS) analysis of Cu sorbed on birnessite have been carried out by equilibrating a Na-exchanged buserite suspension with Cu^{2+} at pH 4. The results showed that Cu^{2+} formed Jahn-Teller distorted six-fold triple corner-sharing (Cu_{TC}) complexes (Manceau et al., 2002). A combination of EXAFS analysis and density functional theory (DFT) calculations for Cu^{2+} sorption on synthetic vernadite concluded that all (at pH 4) or most (at pH 8) of adsorbed Cu^{2+} ions formed three- to four-fold Cu_{TC} complexes located at the vacancies (Sherman and Peacock, 2010). This was also observed in the crystal chemistry of Cu in natural ferromanganese crusts (Little et al., 2014), and further supported by improved DFT calculation using long-range solvation and a more extensive explicit solvation layer (11 water molecules over the vacancy site) (Sherman et al., 2015). Based on the five-fold coordination of aqueous Cu^{2+} identified both experimentally and theoretically (Pasquarello et al., 2001; Frank et al., 2005), another independent DFT calculation of the transition metal sorption on vacancy sites in birnessite was conducted by Kwon et al. (2013). The results showed that Cu_{TC} complexes appear to be essentially fivefold, but their structural parameters could not be distinguished from those of the octahedral complex. The value of CN = 5 or 6 for the first Cu—O(H) shell was further adopted for the crystal chemistry analysis of Cu in a mixed hydrogenetic-diagenetic deep-sea Pacific polymetallic nodule sample, which is representative of ferromanganese deposits on abyssal plains (Manceau et al., 2014), as well as in Cu^{2+}-adsorbed synthetic vernadite with small particle size (2–4 nm in the **a**–**b** plane) and a large specific surface area (SSA, 254 m^2/g) (Peña et al., 2015). However, owing to the special d^9 electronic configuration, the first coordination shell of Cu(II) suffers from Jahn-Teller distortion: it is divided into one subshell of four equatorial Cu—O(H) bonds and another subshell of two axial Cu—O(H) bonds. Bonds in the second subshell are difficult to recover from the EXAFS spectra measured at room temperature due to the significant thermal motion, especially when water molecules are involved (Cheah et al., 2000; Manceau and Nagy, 2015; Peña et al., 2015).

The incorporation of Cu(II) into birnessite layers is also poorly determined. It was found that during sorption at vernadite-water interfaces at pH 8, ~20% of Cu^{2+} was incorporated into the layer octahedral vacancies. By comparison with the crystal chemistry of Cu^{2+} adsorption at pH 4 and DFT calculations, it was proposed that the change from surface complexation to structural incorporation is a response to the protonation of oxygens surrounding the vacancy site, and this transformation should be reversible (Sherman and Peacock, 2010). In three hydrogenetic Fe—Mn crust samples, one from each of the major ocean basins (the central Pacific, northwest Atlantic, and southwest Indian Oceans), ~35% of the Cu^{2+} was in vacancy sites (Little et al., 2014). In the 10 Å vernadite in a mixed deep-sea hydrogenetic-diagenetic nodule from the Pacific Ocean, all Cu^{2+} was incorporated into the $[MnO_6]$ layers (Manceau et al., 2014). EXAFS analysis of a series of Cu-sorbed phyllomanganates (i.e., triclinic birnessite, hexagonal birnessite, and vernadite) showed that the synthetic route has little effect on the Cu partition among the layer site (Cu_E), Cu_{TC} complex, and edge site (Cu_{DC}). The Cu_E complex was formed when Cu^{2+} was adsorbed on mineral surfaces at circumneutral pH (5–7), or when Cu^{2+} was coprecipitated with Mn in triclinic birnessite at pH 10 followed by the equilibration of the mineral suspension at pH 6 or 4. The subsequent equilibration of Cu-coprecipitated triclinic birnessite at pH from 10 to 6 or 4 decreased the proportion of Cu_E and increased that of Cu_{TC} (Manceau et al., 2014). DFT calculations suggested that the increased covalency in the Cu—O bond in Cu_E complex with increasing pH reduced the energy barrier between the Cu_{TC} and Cu_E species, thus rationalizing experimental observations of increasing proportion of Cu_E. However, Cu_E is not more stable than Cu_{TC}, owing to the significant suppression of the Jahn-Teller distortion in Cu_E that provides additional stability (Kwon et al., 2013). Recently, it was reported that for Cu^{2+} adsorption on synthetic vernadite with a large amount of edge sites and Cu/Mn molar ratio from 0.01–0.26 at pH 6, the CN values (~0.5–0.6) derived from the Cu K-edge EXAFS fitting were low for the Cu—Mn shells at $R + \Delta R = 2.5$ Å. This suggested the absence of Cu_E. Detailed EXAFS analysis further suggested the existence of innersphere complexes and dimeric or polynuclear surface species (i.e., containing multiple Cu atoms) on vacancies and particle edge sites, especially the edge sites (Peña et al., 2015).

In the present study, Cu^{2+} was coprecipitated with Mn in hexagonal turbostratic birnessite with initial Cu/Mn molar ratio up to 0.20. The obtained samples were then characterized using mineralogical tools, including wet chemical analysis, powder X-ray diffraction (XRD), electron microscopy, and synchrotron-based X-ray absorption spectroscopy (XAS), in order to investigate the physicochemical properties of the mineral and the local coordination environments of Mn and Cu. Meanwhile, chemical measurement of the dissolution kinetics of Cu-doped birnessites in HCl or H_2SO_4 solutions was carried out, and the results were compared to those of Ni-sorbed analogs reported previously (Yin et al., 2012). Based on these results, we found (1) clear evidence for surface Cu polymers at high surface coverage and low pH, (2) Cu(II) innersphere surface complexes are less stable than Ni(II) complexes, and (3) an octahedral geometry is possible for Cu^{2+} in these Cu-containing birnessite minerals.

2. Materials and methods

2.1. Sample preparation

Copper-doped birnessites were prepared according to McKenzie (1971). The synthesis procedure was the same as that reported by Yin et al. (2012) with $NiCl_2{\cdot}6H_2O$ replaced by $CuCl_2{\cdot}2H_2O$. The samples were obtained with different initial Cu/Mn molar ratios of 0, 0.05, 0.10, and 0.20; and named HB, Cu5, Cu10, and Cu20. The pH values of their final suspensions were 6.37, 5.26, 3.63, and 3.31, respectively. The obtained solids were dried at 40 °C for several days, then ground, sieved (100 mesh), and stored at room temperature.

Nickel-doped birnessite Samples, Ni5 and Ni10, are from our previous work. In these birnessites, ~24% and ~34% of the total Ni existed as Ni_E species respectively (Yin et al., 2012).

2.2. Samples characterization

The obtained samples were characterized by powder XRD