



Geochemical fates and unusual distribution of arsenic in natural ferromanganese duricrust[☆]



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ABSTRACT

Preferential enrichment of arsenic in iron oxides relative to manganese oxides has been well documented. In this study, however, a distinct arsenic enrichment is revealed in natural ferromanganese duricrusts, which are commonly found in natural weathering profiles of manganese-bearing carbonate rocks. In the studied ferromanganese duricrust covering Carboniferous carbonates at Qixia Mountain in eastern China, stromatolite-like structures composed by hematite, goethite, pyrolusite and hetaerolite have been observed. Electron microprobe analysis (EMPA) mapping and synchrotron-based micro-scanning X-ray fluorescence (μ -XRF) analyses reveal that the arsenic content in manganese oxides is elevated with respect to iron oxide phases. For example, the arsenic content of pyrolusite is approximately 5 times as much as that of hematite or hetaerolite. However, the highest arsenic content (0.58 wt % As_2O_5) occurs in 2.75 (± 0.96 , $\pm \sigma$) μm micro-bands of hematite ($(\text{Fe}_x\text{Mn}^{III}_{1-x})_2\text{O}_3$, $0.75 < x < 0.83$). Although arsenic contents in the Mn-rich hematite micro-bands are extraordinarily high, the amount of hematite with a high Mn content is very low in the duricrust. Hence manganese oxides are suggested to be the major arsenic sink in the ferromanganese duricrust. Extended X-ray absorption fine structure spectra (EXAFS) further shows that all arsenic is present as oxidized As(V) and are bound to Fe/Mn oxides in bidentate binuclear bridging complexes with As–Fe and As–Mn bond distances of 3.24 Å and 3.23 Å, respectively. In addition, it is found that zinc is also more enriched in Mn oxides (besides hetaerolite) than in Fe oxides. The fine hematite crust with low contents of heavy metals could act as a protective seal to separate Mn oxides core with high Zn and As from environmental fluids. This separation could reduce the interaction between them and decrease the release of Zn and As from this ferromanganese duricrusts, which ensures long-term sequestration of heavy metals. The unique structural and mineralogical constraints on the distribution of heavy metals can provide insights into novel strategies for environmental remediation of heavy metals contaminations.

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1. Introduction

High contents of heavy metals and metalloids in natural sediments, soils and waters impose serious harm to local communities and human health. Especially in sulfide mining areas, large amount of heavy metals (e.g., arsenic, lead, zinc, and so on) are released from mine wastes due to microbial/chemical oxidation of various sulfides and then drained into groundwater, rivers and soils (Benzerara et al., 2008; Kocar et al., 2008; Lu and Wang, 2012;

Morin and Calas, 2006; Parviainen et al., 2012; Zhu et al., 2014), which has long been a worldwide environmental issue (Fendorf et al., 2010; Guo et al., 2014; Mandal and Suzuki, 2002; Nickson et al., 2005; Nordstrom, 2002; Smedley and Kinniburgh, 2002; Tamaki and Frankenberger, 1992). In general, occurrence and spatial distribution of heavy metals determine their mobility in environment (Hayes et al., 2011; Jain and Ali, 2000). In general, arsenic commonly presents as soluble ions, adsorbate on mineral surfaces, impurities accommodated into mineral lattices, and occasionally exist as certain arsenic minerals (e.g., scorodite, pharmacolite, and so on) (Lottermoser, 2007; Lu and Wang, 2012; Zhu et al., 2015). It has been found that both arsenate (As(V)) and arsenite (As(III)) can be adsorbed onto iron/manganese (oxy)hydroxides (Bowell, 1994; Deschamps et al., 2005; Han et al., 2011;

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Manning et al., 2002; Marcus et al., 2004; Villalobos et al., 2014; Zhang et al., 2007), while arsenate and arsenite exhibit different priority to adsorb onto iron/manganese minerals (Lakshminathiraj et al., 2006; Qi and Pichler, 2014; Raven et al., 1998; Szlachta et al., 2012). As(V) predominates as the oxyanion $H_2AsO_4^{2-}$ in oxidizing conditions, while under anoxic and reducing conditions As(III) dominates as $H_3AsO_3^0$. It is worthy to note that arsenite shows higher toxicity than arsenate (Hirano et al., 2003; Watanabe and Hirano, 2013). The adsorption of arsenic has been shown to depend highly on the oxidation state oxidation in the pH range of 5.5–7.5 (Ferguson and Anderson, 1974). It has been reported that As(V) reacts faster than As(III) with iron oxides, and the sorption of As(V) onto iron oxides are more favorable than As(III) (Dixit and Hering, 2003; Pierce and Moore, 1982). Furthermore, the mobility of the As(III) could be promoted higher by the presence of natural organic matter in soils (Redman et al., 2002). Thus the oxidation of As(III) into As(V) and adsorption onto Fe/Mn mineral surfaces can reduce its toxicity and immobilize arsenic. Other heavy metals, such as zinc, lead, nickel, copper and so on, are also able to adsorb to Fe–Mn oxides (Frierdich and Catalano, 2012; Fuller and Bargar, 2014; Little et al., 2014; Manceau et al., 2002, 2007).

It has been well studied that ubiquitous manganese and iron oxides/(oxy)hydroxides with microbial or chemical activities in soils and fine-grained sediments have high capacity for scavenging As, Zn, Ni and other heavy metals (Manceau et al., 2007; Marcus et al., 2004; Peacock and Sherman, 2007). The strong ability of iron oxides to scavenge toxic elements have drawn wide attention in environmental studies and engineering developments (Fendorf et al., 1997; Manning et al., 1998; Ona-Nguema et al., 2005), whereas, the oxidation and adsorption ability of manganese oxides has not been fully recognized despite that they show considerable potential to retain redox-active toxic elements in various environments (Di Christina et al., 2005; Polizzotto et al., 2008; Stuckey et al., 2016). Manganese oxides have high specific surface areas and high adsorption capacities for heavy metals. (Miyata et al., 2007; Potter and Rossman, 1979; Villalobos et al., 2005). Binary systems of iron and manganese oxides control the chemical state of a series of toxic elements through oxidation and chemical adsorption in a variety of hazardous environments (Deschamps et al., 2003; Zhang et al., 2007, 2014). For example, arsenite can be oxidized into arsenate by Mn oxides, which further enhances the subsequent binding of arsenic to the surface of Mn oxides (Amirbahman et al., 2006; Deschamps et al., 2003; Gupta et al., 2010; Manning et al., 2002; Ying et al., 2012; Zhu et al., 2009). In the situations with the presence of both birnessite and goethite, birnessite can oxidize arsenite into arsenate, which is adsorbed onto goethite surface thereafter (Ying et al., 2012). Therefore, Mn-substituted goethite and Fe–Mn binary oxides have also been identified to exhibit similar abilities to scavenge toxic elements and have been widely employed to remove arsenic from polluted waters (Deschamps et al., 2003, 2005; Lakshminathiraj et al., 2006; Singer et al., 2013; Sun et al., 1999; Szlachta et al., 2012; Zhang et al., 2007).

Binary system of manganese oxides and iron oxides are potential low cost materials used to remove heavy metals from polluted waters (Chakravarty et al., 2002), thus the interactions between arsenic species and coexisting Fe/Mn minerals have been extensively studied in lab (Ying et al., 2012, 2013). It is important to understand the mechanism of toxic metals sequestration by manganese and iron oxides in soils and sediments (Costagliola et al., 2013; Frierdich and Catalano, 2012; Manceau et al., 2004, 2007; Marcus et al., 2004). This will help us understand the geochemical fate of heavy metals in various environments.

Ferromanganese duricrust, commonly found in weathering profiles over manganese-rich sedimentary rocks and occasionally

observed in soils, consist of manganese oxides and iron oxides, and are generally enriched in heavy metals (Pracejus et al., 1988; Roy, 1997; Sethumadhav et al., 2010). Ferromanganese duricrust provide us a natural analogue to study the constraints of Fe/Mn oxides on heavy metals distribution. In Fe–Mn oxides binary systems, heavy metals may show different behavior correlated with Fe or Mn (Costagliola et al., 2013; Frierdich and Catalano, 2012; Manceau et al., 2004, 2007). However, the mineralogical constraints on the spatial distribution and partition of heavy metals among various mineral phases in natural samples are not well understood yet.

In this study, the distribution of arsenic and zinc in natural ferromanganese duricrusts sampled from Qixia Mountain in Nanjing, eastern China are well presented. The objectives of this study are to (1) identify the iron and manganese mineral phases formed in this ferromanganese duricrusts; (2) study the mineralogical constraints of As and Zn on iron and manganese minerals; and (3) propose a geochemical model to explain the retention of As and Zn in these Fe– and Mn-rich duricrusts.

2. Samples and methods

2.1. Samples of Fe–Mn duricrusts

In the low reach area of Yangtze River, manganese-enriched carbonates of the Carboniferous Huanglong formation (C_2h) largely exposed and have been weathered in various degrees. Alteration with hydrothermal fluids in some parts of the rock bodies accumulates Pb–Zn sulfides, and form a polymetallic ore deposit in the C_2h carbonate rocks (Liu and Chen, 1985; Zhang, 2015). In many outcrops, iron-manganese duricrusts derives from natural weathering cover on the Carboniferous carbonates (Xu, 2005). The studied weathering profile of Mn-rich carbonate is located at the Qixia Mountain, Nanjing, eastern China (N: $32^{\circ}09'32.5''$; E: $118^{\circ}58'06.8''$). By performing electron microprobe analysis (EMPA) of the calcite grains in a fresh C_2h carbonate rock underneath the studied duricrust, MnO content varies from 0.84% to 2.32%. C_2h carbonate has approximately >0.2 wt% FeO, 0.1 wt% MnO and 20 $\mu\text{g/g}$ Zn, and minor sulfide minerals in carbonate strata-formation contain higher contents of Zn and As (Ling and Liu, 2003; Zhang, 2015). As Qixia Mountain is a locally famous scenic region, the release of heavy metal can lead to serious contamination. Fortunately, the ferromanganese duricrusts composed of iron oxides and manganese oxides have the capacity to accommodate heavy metals (Frierdich and Catalano, 2012). Investigating the natural attenuation of heavy metals in ferromanganese duricrusts will help us to understand the fate of heavy metals in similar environments.

In the studied profile, the Fe–Mn duricrust is approximately 30 cm thick, covering on the surface of the underlying carbonate with an unclear boundary (Fig. 1b). Different contents of Fe oxides and Mn oxides are denoted with various colors (Fig. 1c), which are similar to the iron-manganese deposit found in other carbonate systems (Frierdich and Catalano, 2012; Frierdich et al., 2011). The collected duricrust samples were divided into several bulks according to the color (Fig. 1c). Samples QX-1, QX-2 and QX-3 are fragile, and appear in red or brown due to the dominant species of iron minerals. QX-4, the main component of the crusts, is dark gray and hard. Before analysis, QX-4 was filled with epoxy resin in order to perform cutting and polishing. The polished thin sections were ultrasonic cleaned in ethanol and dried at room temperature.

Sample QX-4 presents stromatolite-like cross sections (Fig. 2a and b) and core-crust cross sections (Fig. 2c and d), which may come from different section planes of a stromatolite-like structure. This microstructure is similar with the manganese stromatolites (Rossi et al., 2010), but the evidence of microbial activities, such as

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