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Sequestration of molybdate during transformation of 2-line ferrihydrite under alkaline conditions

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ABSTRACT

Hematite is a thermodynamically stable iron oxide under the aerobic conditions present in most natural surface soils and sediments. Most studies to date have focused on the capacity of hematite to adsorb trace metals and metalloids, but structural incorporation of trace metals within hematite is less recognized. This study assessed the incorporation of molybdenum within the structure of hematite during the phase transformation of 2-line ferrihydrite under alkaline conditions (pH ~10). Extended X-ray absorption fine structure analyses show molybdenum incorporated into hematite, with two Mo-O shells having a coordination number (CN) of 3 and average bond distances of 1.78 ± 0.01 and 2.08 ± 0.02 Å, respectively, as well as two Mo-Fe shells with a CN of 3 and average bond distances of 3.10 ± 0.02 Å and 3.44 ± 0.02 Å, respectively. This observation suggests the tetrahedrally-coordinated Mo in the molybdate that adsorbs onto the 2-line ferrihydrite changes to an octahedrally-coordinated Mo within the hematite with Mo possibly substituting for Fe in the hematite structure. Our findings suggest that molybdenum partitioning (low concentrations) to iron oxides in the environment can occur due to structural incorporation as well as adsorption.

1. Introduction

Molybdenum (Mo) is a naturally occurring trace element that comprises ~0.0015% of the Earth's crust (Chappell, 1975). It is an essential element for both plants and animals, but at large concentrations can be toxic and pose a major threat to living organisms (Vunkova-Radeva et al., 1988). Mo can exist in valence states from +2 to +6 and in minerals including molybdenite (MoS_2), powellite ($CaMoO_4$), and lead molybdate ($PbMoO_4$) (NRC, 1994). Weathering of igneous and sedimentary rocks containing Mo ores is a natural source to aquatic environments (groundwaters and surface waters). Natural concentrations of Mo are low (10–20 μg/L) (U.S. EPA, 1979) and well below drinking water guidelines (~70 μg/L) (WHO, 2011), but elevated concentrations as high as ~1500 mg/L are reported for many surface waters in the United States (WHO, 2011). Anthropogenic sources such as leaching from mine wastes and mill tailings, burning of fossil fuels, and fertilizers can provide considerable inputs of Mo to the environment. For example, surface waters in areas of North America affected by mining can have Mo concentrations as high as 800 mg/L (Phillips and Russo, 1978; Carpenter and Johnson, 1990; Morrison and Spangler, 1992; Morin and Hutt, 1999; U.S. EPA, 1979). Solid Mo phases (e.g., sulfides and oxides) are sparingly soluble in water (Vyskočil and Viau, 1999) and thus pose little threat to living organisms. However, these Mo sulfides and oxides can be oxidized to generate aqueous molybdate ions (MoO_4^{2-}). These molybdate ions are mobile and can be transported into streams and lakes (in the absence of a reducing agent; WHO, 2011), where Mo may then accumulate in the tissues of living organisms (Vyskočil and Viau, 1999).

Iron (Fe) oxides are of great importance for many processes that operate in surface or near surface environments, including adsorption, precipitation, and co-precipitation. They are ubiquitous in most terrestrial environments and thus play an important role in regulating trace metal speciation in soils and sediments (Schwertmann and Cornell, 1991). Iron oxides and hydroxides are lead into the environment via oxidation and hydrolysis of silicate minerals and result in the formation of insoluble Fe(III), which is precipitated as poorly crystalline 2-line ferrihydrite (hereafter ferrihydrite; nominal formula $Fe_5HO_8 \cdot 4H_2O$) (Schwertmann and Cornell, 1991). Ferrihydrite is metastable and transforms to

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crystalline phases such as goethite or hematite with respect to pH, temperature, and water chemistry (Das et al., 2011a,b). However, hematite (α-Fe_2O_3) is the most thermodynamically stable iron oxide in nature and thus is the most predominant secondary mineral (compared to other iron oxides and hydroxides, e.g., goethite (α-FeOOH), lepidocrocite (β-FeOOH), and/or maghemite (β-Fe_2O_3); Lahann, 1976; Yariv and Mendelovici, 1979; Schwertmann and Cornell, 1991) in most natural soils and sediments. Owing to its stability, moderate specific surface area (30–90 m^2/g) (Schwertmann and Cornell, 1991), and ability to sequester metals and metalloids from aqueous solutions via adsorption, hematite has been considered a viable mineral/solid by several workers for contaminant remediation (Hsi and Langmuir, 1985; Todorović et al., 1992; Goldberg et al., 1996; Horányi and Joó, 2002; Peak and Sparks, 2002; Christl and Kretzschmar, 2001; Giménez et al., 2007; Zhang et al., 2011; Grover et al., 2012; Das and Hendry, 2013).

Recent studies indicate that foreign ions such as arsenic (As) and Mo (adsorbed or co-precipitated) may be preferentially incorporated into the hematite structure (Muramatsu et al., 2012; Bolanz et al., 2013; Das et al., 2014; Brinza et al., 2015) during ferrihydrite aging. Unlike adsorption or surface precipitation, this structural incorporation mechanism cannot be reversed unless the mineral/solid into which it is incorporated (for example hematite) partially or completely dissolves (Prieto et al., 2013). More importantly, mineral dissolution is a much slower process compared to desorption (i.e., whereby a slight change in pH could quickly release adsorbed contaminants into solution) (Prieto et al., 2013). Thus, structural incorporation may be a viable permanent or long-term sink for elements of concern. As a result, there is a need to understand this incorporation mechanism with respect to toxic trace metalloids such as Mo. This study investigated Mo incorporation into the crystal structure of hematite via temperature-accelerated (75° C) aging of ferrihydrite with adsorbed Mo. Testing was conducted at pH 10 to represent *in situ* conditions generally found in mining operations (Das et al., 2011b). The results contribute new understanding of metal-mineral interactions and immobilization of toxic trace elements in the environment.

2. Materials and methods

2.1. Synthetic ferrihydrite preparation and time series transformation experiment

Three batches of ferrihydrite were synthesized according to Schwertmann and Cornell (1991) (precipitation with alkali) with slight modifications. Briefly, anhydrous $FeCl_3$ (as a substitute of $Fe(NO_3)_3 \cdot 9H_2O$) solution (20 g in 250 mL of Milli-Q water) was titrated with 1 M NaOH (as a substitute of KOH) to a pH of ~7.5. All synthesized precipitates were then washed with Milli-Q water (5–6 times) to ensure relatively chloride-free ferrihydrite (details of ferrihydrite preparation are provided in SI).

Each of these three wet ferrihydrite precipitates was then resuspended in 200 mL of Milli-Q water in individual polyethylene vessels and the slurries homogenized by stirring at room temperature. Hydrated sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) was added to each slurry under continued stirring to produce molybdate adsorbed to ferrihydrite at Fe/Mo molar ratios of 150, 600, and 4500 (details of Mo solution preparation and molar ratios calculations are provided in SI). Three pH electrodes were immersed into the individual slurries and the pH monitored after the addition of $Na_2MoO_4 \cdot 2H_2O$ and then raised to pH 10 (±0.05) by dropwise addition of trace metal grade NaOH (0.1 M) using a 10 μL pipette. A 15 mL aliquot of each slurry was then designated as the t = 0 sample (ferrihydrite with adsorbed molybdate before aging). The three polyethylene vessels were then covered with aluminum foil and transferred to a water bath preheated to 75(±2) °C. A ~15 mL aliquot of each slurry was sampled from each vessel after 1, 2, 3, 6, 7, 10, 13, 24, 50, 56, and 96 h with concurrent pH measurements. All samples were centrifuged (at 2500 rpm for 10 min), then supernatants syringe filtered (0.2 μm) and stored in a refrigerator prior to analyses. The solid precipitates were freeze-dried for 24 h and then also stored in a refrigerator.

2.2. X-ray diffraction (XRD)

XRD analyses were conducted on 36 solid and ground samples (~10 mg of each) (t = 0, 1, 2, 3, 6, 7, 10, 13, 24, 50, 56, and 96 h) from the Fe/Mo 150, 600, and 4500 systems using a PANanalytical Empyrean X-ray diffractometer equipped with a Spellman generator and Co X-ray tube set to 40 kV and 45 mA. Both divergence and receiving slits were fixed at 0.5° and the analyses (incident beam path Fe β-filter, 1° anti-scatter slit, and 0.02 mm Soller slits) were performed on a spinning reflection/transmission stage with a scan speed of 1°/min. After acquiring the diffraction patterns (10–80° with a step size of 0.0167°) raw XY data files were subsequently converted to Excel files and the data plotted as intensity (arbitrary units) versus degrees two theta.

All acquired patterns were compared to the Inorganic Crystal Structure Database (ICSD; FIZ Karlsruhe) for phase identification using XPERT HIGHSCORE PLUS LTU, 3.0. A spectral baseline was initially established for each pattern and then later refined in semi-automatic mode. These analyses were conducted on an identical set of 36 solid samples to evaluate the amount of hematite and goethite formed during aging of each individual solid and to establish the kinetics of ferrihydrite transformation. Detailed Rietveld analyses were conducted on the 96 h samples from each Fe/Mo system (X-ray powder data were refined with Rietveld program Topas 4.2, Bruker AXS) to identify *a* and *c* unit cell parameters as well as unit cell volumes of hematite and goethite. Hematite samples were indexed in a hexagonal (trigonal) symmetry (R-3c space group; #167) (Blake et al., 1966) and data were then compared with pristine hematite (as reported in the literature) to evaluate how the presence of Mo can alter the unit cell of hematite.

2.3. Raman spectroscopy

Raman spectroscopic analyses were conducted on six selected solid samples (t = 0 and 96 h from the three Fe/Mo systems) using a Renishaw InVia Raman microscope. The instrument was configured at 785 nm (A1 lens) and a 1200 lines/mm (633/780) grating with a solid state laser diode (Renishaw). Prior to any analyses, the instrument was calibrated using an internal Si sample (Raman shift of ~520 cm^{-1}). Subsequently, a few grains of freeze-dried ground samples were placed onto a glass slide and scanned under the Raman microscope for appropriate grains during analyses (Leica 20X N PLAN objective lens; NA = 0.40). The instrument was set with a 10 s detector exposure time, cosmic ray interference removed, and 0.1% laser power using Renishaw WiRe 3.2 software in the line focus confocal mode. Once the appropriate grain was identified, 32 spectral accumulations (range of 100–2000 Raman shift/cm-1) were collected for each sample with a Peltier cooled CCD detector. All six raw wxd files were later converted to xls files and the individual spectra plotted as wavenumber (cm^{-1}) versus intensity (arbitrary units) in Excel spreadsheets.

2.4. Transmission electron microscopy (TEM)

TEM images were acquired for three dried and ground solid samples (96 h from the three Fe/Mo systems) to determine grain size distribution and morphology of individual hematite