Title
Inhibition of As(III) Oxidation by Manganese Oxides in the Presence of Fe(II)

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Author
Mock, Rebecca Pettit

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Inhibition of As(III) Oxidation by Manganese Oxides in the Presence of Fe(II)

A Thesis submitted in partial satisfaction of the requirements for the degree of

Master of Science

in

Environmental Toxicology

by

Rebecca Pettit Mock

September 2017

Thesis Committee:
Dr. Samantha C. Ying, Chairperson
Dr. Haizhou Liu
Dr. David Volz
The Thesis of Rebecca Pettit Mock is approved:

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Committee Chairperson

University of California, Riverside
ABSTRACT OF THE THESIS

Inhibition of As(III) Oxidation by Manganese Oxides in the Presence of Fe(II)

by

Rebecca Pettit Mock

Masters of Science, Graduate Program in Environmental Toxicology
University of California, Riverside, September 2017
Dr. Samantha C. Ying, Chairperson

High arsenic (As) concentrations can be found in drinking water around the world, the consumption of which can lead to increased incidences of skin cancers, arsenicosis, and cardiovascular disease. The source of arsenic in contaminated regions is geogenic, where its fate and transport is affected by other naturally-occurring mineral constituents within the soil solid phase. Manganese (Mn) oxides within soil profiles are strong oxidants of many metals and metalloids found in soil, including As, where the more mobile and more toxic arsenite [As(III)] form can be oxidized to the less mobile and less toxic arsenate [As(V)]. Within redox transition zones in soil profiles, including the diffusion-limited matrix of soil aggregates, Fe(II) can come into contact with Mn oxides, altering the reactivity of the Mn oxides. This change in reactivity of Mn oxides may therefore alter the impact of Mn oxides on the fate and transport of arsenic in these interfacial zones. In the current study, we quantitatively demonstrate the impact of the formation of a potentially passivating Fe(III)-oxide coat on Mn-oxide mediated contaminant oxidation. By simulating diffusion-limited transport using a Donnan cell reactor, we investigated the oxidation of As(III) by Mn-oxides after exposure to varying concentrations of Fe(II). Our findings show
that Fe(II) treatment of birnessite, a poorly-crystalline Mn oxide, leads to the formation a combination of Fe(III) oxides with a range of crystallinities as determined by Fe EXAFS analysis. Concomitant reduction of birnessite leads to formation of hausmannite, a Mn(II, III) oxide. Reaction of the resultant Fe-Mn oxide with As(III) shows decreased rate of As oxidation as compared to systems without Fe. Additionally, increasing Fe(II) concentrations exposed to birnessite by two folds leads to a five fold decreases in As(III) oxidation rate. During As(III) oxidation, hausmannite is rapidly reductively dissolved, resulting in increased aqueous Mn concentrations; continued As(III) oxidation is then mediated by birnessite. Furthermore, our results show that a higher concentration of arsenic partitions into the solid phase at high Fe(II) treatment due to the tendency of arsenic to bind preferentially to Fe oxides as compared to Mn oxides.
Table of Contents

1. Introduction 1
2. Materials and Methods 5
3. Results 9
4. Discussion 26
5. Conclusions 30
List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Donnan Schematic</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Aqueous Mn and Fe Concentrations Pre-As</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>High Fe Aqueous Concentrations</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>Low Fe Aqueous Concentrations</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>Aqueous Arsenic Speciation</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>Pres-As Solid Phase Speciation</td>
<td>17</td>
</tr>
<tr>
<td>7</td>
<td>Post-As Solid Phase Speciation</td>
<td>17</td>
</tr>
<tr>
<td>8</td>
<td>Pre-As Mn and Fe EXAFS</td>
<td>19</td>
</tr>
<tr>
<td>9</td>
<td>Post-As Mn and Fe EXAFS</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>As XANES Spectra and Proportion High Fe Concentration</td>
<td>21</td>
</tr>
<tr>
<td>11</td>
<td>As XANES Spectra and Proportion Low Fe Concentration</td>
<td>23</td>
</tr>
<tr>
<td>12</td>
<td>SEM Images of Solids</td>
<td>25</td>
</tr>
</tbody>
</table>
List of Tables

Table 1  Solid State Phase Proportions  22
Table 2  Mn Phase Contributions to As Oxidation  29
Introduction

Arsenic (As) is a naturally occurring human toxin found in hazardous concentrations in drinking water around the world with particular severity in Southeast Asia (Smith et al., 2000; Yu et al., 2003; Fendorf et al., 2010). In Bangladesh, 62% of tube wells were found to have concentrations of As above 100 μg L\(^{-1}\) which greatly exceeds the World Health Organization’s recommended level of 10 μg L\(^{-1}\) (British Geological Survey, 2001). Chronic consumption of elevated levels of As results in increased risk of heart disease, cancers of the skin, lung, kidney and bladder disease, neurological effects and skin lesions (Quansah et al., 2015; Flanagan, 2011).

The concentration of dissolved As in groundwater is dependent upon the interaction of As with minerals found in soil and sediments including manganese (Mn) and iron (Fe) hydroxides, oxyhydroxides, and oxides (hereon referred to collectively as oxides). Arsenic is present in soils and sediments in two predominant forms including arsenite (As (III)) and arsenate (As(V)) at a pH 7. As(III) is weakly adsorbed onto Fe oxides through the formation of outer-sphere complexes, while As(V) is able to bind strongly to a variety of minerals including Fe and Al oxides (Gupta and Chen, 1978). Due to the difference in sorption strength of As(V) and As(III) on mineral phases, redox reactions facilitated by the presence of strong oxidants, such as Mn(III/IV) oxides, impact the mobility of As in soil and sediment systems.

Various species of Mn oxides are found in soils globally and have high oxidative capacity even under reducing conditions (Ehlert, 2016; Ying 2013; Appelo and Postma, 2000; Myers et al., 1988). Birnessite is a common Mn(III/IV) poorly crystalline, layer-type oxide found in soils which can oxidize and sequester many trace metals found in nature (Myers et al., 1988; Young and Harvey, 1992; Toner et al., 2006; Tournassat et al., 2002). The
oxidation reaction of As(III) by birnessite is a two-step process where Mn(IV) is reduced to Mn(III) to form a MnOOH intermediate reaction product followed by the reaction of As(III) with MnOOH producing Mn²⁺ and As(V) (Nesbitt et al., 1998).

Previous studies indicate that as Mn oxides interact with As(III) the oxidative capacity of the Mn oxides is reduced (Scott and Morgan, 1995; Tournassat et al., 2002; Manning et al., 2002). This passivation can be contributed to several mechanisms which occur when As(III) is oxidize. Initially birnessite contains both Mn(IV) and Mn(III) binding sites on its surface; as As(III) is oxidized Mn(IV) sites are converted Mn(III) sites, which are less reactive in terms of As(III) oxidation (Zhu et al., 2009). Additionally, binding sites are physically blocked by the presence of As(V) that sorbs onto the surface after oxidation (Tournassat et al., 2002). Mn(II) which is released in during initial oxidation of As(III) is also sorbed and can contribute Mn(III) binding sites to the surface (Lafferty et al., 2010).

In soils and sediments, water and solutes will flow advectively through large pores as well as diffuse through soil aggregates into microsites in the soil. These microsites are a result of the heterogeneous nature of soils and result in novel and unexpected interactions between minerals. In natural soil profiles under certain geochemical conditions Mn and Fe reduction zones can be stratified, creating a distinct layer of Mn oxides. These are found in deposits of aquifer sands (Koljonen et al., 1976; Larsen and Postma, 1997), and in surface layers of marine sediments (Froelich et al., 1979; Canfield et al., 1993). The stratification of Mn and Fe oxides can lead to diverse redox conditions in a spatially constrained area (Appelo and Postma, 2000). Under these conditions Fe(II) can be released into soil pore water which then diffuses into zones containing Mn(III/IV) oxides resulting in the oxidation of Fe(II) by Mn oxides.
A similar mechanism has also be observed at in a smaller scale within soil aggregates (Ying et al., 2013). Within the core of soil aggregates, suboxic to anoxic conditions formed from anaerobic microbial respiration, while oxic conditions remain near the surface of the aggregate (Sextone, 1985). This redox zonation is formed by the slow transport of oxygen from advective flow path on the exterior of the aggregate moving diffusively into the center of the soil aggregate. This indicates that Fe(II) from the core of an aggregate can diffuse into soil pore water through diffusion limited transport and subsequently come into contact with oxidized Mn(IV) at the exterior of the aggregate.

Iron(III) oxides are strong sorbents that have high capacity for As and other soil contaminants. A previous study examined biotic and abiotic mechanisms responsible for secondary iron oxide transformation of ferrihydrite in the presence of Fe(II). Using ferrihydrite-coated sand columns, Hansel et al. (2003) generated various concentrations of aqueous Fe(II) through anaerobic microbial reduction of Fe(III) oxides. Through abiotic pathways, lepidocrocite, goethite, and magnetite were formed upon ferrihydrite exposure to Fe(II); the mineral transformation occurred as a function of Fe(II) concentration, with lepidocrocite and goethite forming at relatively lower concentrations due to phase transformation through dissolution-reprecipitation mechanisms (Pedersen et al. 2005); while the presence of relatively higher concentrations of Fe(II) lead to the formation of magnetite through solid state transition.

Mn oxide exposure to Fe(II) can lead the precipitation of a variety of Fe(III) oxides depending on the Mn oxide crystallinity and the concentration of Fe(II). A recent study by Gao et al. (2015) examined the oxidation of Fe(II) by birnessite, a poorly-crystalline Mn(III/IV) oxide commonly found in soils, which demonstrated that under anoxic conditions various Fe(III) oxides are formed due to differences in Fe(II) concentration and reaction
time. In the presence of 20 mM Fe(II), poorly-crystalline Fe oxides (ferrihydrite) precipitated rapidly, followed by lepidocrocite and goethite formation after two hours of reaction. Their results showed that the presence of aqueous Mn(II) facilitated the transition from lepidocrocite to goethite.

To our knowledge, no investigations have examined the reactivity of Fe(II)-treated birnessite and the ability of these altered oxides to oxidize trace metals and metalloids such as arsenic. Better understanding of these systems will provide invaluable information regarding the impact of reduced constituents on Mn oxides oxidative power within redox interfaces along with the effect of this chemical interaction on the rate of transformation of redox active contaminants within soils. In this study, we examine the interactions between Fe(II) and Mn oxides and subsequent effects on As speciation and transport. We hypothesize that Fe(II) is oxidized to Fe(III) upon contact with birnessite, initially precipitating poorly crystalline Fe oxides followed by secondary transformation to more crystalline Fe oxides upon higher addition of Fe(II), ultimately resulting in the formation of a partial Fe(III)-oxide coat on the birnessite surface. We expected that exposure of the Fe-Mn oxide would lead to partial passivation of the surface of the Mn oxides, surface transformations, along with the presence of Mn(III) likely lead to decreased As(III) oxidation rate and therefore As(III) oxidation extent after a defined time period. To determine the mechanisms involved in this reaction, we simulated the diffusion-limited transport of Fe(II) into Mn oxide-rich zones within soil aggregates using a Donnan cell reactor where two continuously homogenized chambers are separated by a semi-permeable membrane through which aqueous constituents can pass diffusively. We employed a combination of solid phase analyses including X-ray absorption spectroscopy (i.e., XANES and EXAFS), SEM-EDX, and acid digestion in combination with aqueous
phase analyses (HG-ICP) to monitor the changes in both aqueous and solid phase speciation. Our findings show that Fe(II) reaction with Mn oxides leads to a series of Mn oxide mineral transformations concurrent with Fe oxide precipitation and secondary Fe oxide transformation due to Fe(II) exposure overtime. We demonstrate that despite the presence of Fe oxides precipitated on the surface of Mn oxides, As(III) oxidation continues and is not completely inhibited. The rate of oxidation is dependent upon the concentration of Fe in the system, where the presence of higher Fe(II) levels resulted in a slower oxidation rate possibly indicating a greater passivation of the birnessite surface.

2 Materials and Methods

2.1 Synthesis and characterization of Birnessite

Birnessite was synthesized according to the method provided by McKenzie (1971). Briefly, 63 g of KMnO₄ was dissolved in 1 L of double deionized (DDI) water and heating the solution to 90°C. The solution was then combined with 66 mL concentrated HCl in a 5 L flask. The solution was allowed to react at 90°C for 10 minutes before cooling for 30 minutes and filtering with a 50µm ashless filter paper. The filtered oxide solids were resuspended in DDI to wash any entrained potassium and refiltered. This process was repeated until the filtrate solution ran clear. The solids were then dried and crushed with a mortar and pestle. Birnessite structure was confirmed using X-ray diffraction analysis. Birnessite structure was confirmed using X-ray diffraction analysis. Surface area was determined with Brunauer–Emmett–Teller (BET) analysis to be 47.0842 m²g⁻¹.

2.2 Experimental Conditions

All experiments were conducted at room temperature under anoxic conditions (i.e., 95% N₂:5% H₂ atmosphere) in an anaerobic glove bag (Coy Laboratory). The Donnan reactor was constructed of 5.08 cm interior diameter PVC fittings (Figure 1) first acid washed in a
3.7% HCl bath. A 0.1 μm isopore polycarbonate filter (Millipore) is installed to act as a semi-permeable membrane between the two chambers to mediate diffusion-limited transport of aqueous constituents. 300 ml of deoxygenated 10 mM PIPES buffer and 0.1 M NaCl were added to each chamber to maintain solution pH at 7 and simulate soil pore water ionic strength. 1.0 g of birnessite was added to one of the chambers and was stirred for 24 hours at approximately 400 rpm before reaction initiation. Two concentrations of Fe(II) were used to compare the effects on As oxidation rate. For the high concentration treatment, ferrous chloride was added into the chamber opposite of the birnessite chamber in four injections 1.44 mM at hour 0, 2.84 mM at hour 36, 1.84 mM at hour 72, and 2.06 mM at hour 108 for a total of 8.18 mM Fe or a mass ratio of 0.54 Fe/Mn was reached. For the low Fe(II) treatment, two Fe(II) injections of 2.045 mM were added, one at 0 hours and one at 36 hours until a total of 4.09 mM concentration of Fe(II) was reached with a mass ratio of 0.27 Fe/Mn. 36 hours of reaction time was allotted between each Fe(II) dose injection to allow for maximum reaction of Fe(II) with birnessite. Ferrozine assays were performed to ensure complete oxidation of Fe(II) by birnessite after each injection. Once the final addition of Fe(II) had been injected, an additional 48 hour period of reaction time was allowed to ensure complete oxidation of Fe(II) by birnessite. To examine the oxidation of As(III) by Fe(II) reacted birnessite, 500 μM As(III) (sodium arsenite) was then added to the chamber opposite of the Fe(II) reacted birnessite and was allowed to diffuse and react for 91.5 hours, with solid and aqueous samples taken throughout the duration of the experiment.
2.3 Aqueous Phase Analysis

At each sampling point, a total of 10 mL were removed from each chamber. For aqueous analyses, 6 mL samples were taken from the birnessite chamber and 10 mL samples were taken from the Fe(II) and As(III) injection chamber. An additional 4 mL sample was taken from the birnessite chamber for solid phase analyses described below. Aqueous samples were filtered (0.2 μm Sartorius) and acidified for Mn, Fe, and total As content using inductively coupled plasma optical emission spectrometry (ICP-OES, axial view). Sodium concentrations were monitored to ensure instrument stability. Aqueous As speciation at each sampling was determined using the method provided by Masscheleyn et al. (1991) as modified by Jones et al. (2000). 0.6 mL of 2 M Tris (pH 6.0) were added to 3 mL of sample while the samples were continuously purged with N₂. Two additions of 0.3 mL of
3% (w/v) NaBH₄ in 1 M NaOH were added to the sample, with 5 min of N₂ purging between additions. The resulting samples were analyzed for aqueous As(V) concentrations using ICP-OES. Aqueous As(III) concentrations were determined by subtracting As concentrations in hydride-treated samples from total As concentrations.

2.4 Solid Phase Analysis

At each time point 4 mL of sample were collected from the birnessite chamber for solid phase analysis. 2 mL were used for acid digestion to determine the amount of As adsorbed to solids. The samples were allowed to dry at 80° C for 2 days in acid-washed borosilicate tubes. Dried solids were then resuspended in 2 mL HCl and heated to 90° C until all solids were completely dissolved. The acid digested samples were diluted and analyzed for Mn, As, Fe, and Na content using ICP-OES.

2 ml of sample were filtered onto ashless filter paper for XAS and SEM analysis to determine the Mn and Fe oxide mineralogy overtime. The membranes were then stored in petri dishes until dry and were then sealed into 0.5 mil Kapton tape and stored under anoxic conditions until analysis. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamlines 7-2, 11-2, 4-1, and 4-3 with a Si (220) monochromator. Fluorescence signal was collected with a Lytle detector. EXAFS were collected for Fe and Mn speciation. Spectra were collected for Fe from 200 eV below and 800 eV above the inflection point of 7112 eV. Mn spectra were collected from 190 eV below and 770 eV above the inflection point of 6539 eV. XANES analysis was used for the As speciation and spectra were collected from 200 eV below and 332 eV above the As inflection point of 11867 eV. The Kapton enclosed samples were frozen in liquid nitrogen and scanned in a 25° K chamber during the scanning process to prevent
the oxidation of As by the X-Rays. Linear combination fitting was completed using the Athena program (Ravel and Newman, 2005) to determine the As(III)/As(V) ratio and Mn and Fe structure.

3 Results

3.1 Aqueous Dynamic within the Donnan

3.1.1 Fe(II) and Birnessite Interactions

Diffusion-limited transport of Fe(II) at two concentrations followed by reaction with Mn oxides was simulated using a Donnan reactor, where Fe(II) was injected into a chamber separated from Mn oxides by a semi-permeable membrane filter (Figure 1). At high Fe(II) concentrations, 1.44 mM Fe(II) was initially injected into the Donnan reactor, decreasing to concentrations below detection limit by 1.5 days (36 hrs.) after removal from aqueous phase through oxidation by with birnessite as determined by Ferrozine assay (Figure 2A). Subsequent Fe(II) injections at 1.84 and 2.06 mM Fe(II) was added at day 3 (72 hrs.) and 4.5 (108 hrs.), respectively, and decreased to concentrations below detection limit within 36 hrs. and 48 hrs. An additional injection was made at 36 hrs. of 2.84 mM (Ferrozine data not shown; Fe(II) concentrations were confirmed to have decreased to below detection limit before injection was made). Concomitantly, aqueous Mn increased gradually within the Fe injection chamber from 0 to 2.56 mM over the course of 6 days (Figure 2A), closely reflecting the aqueous Mn concentrations in the birnessite chamber (Figure 2B). No aqueous Mn was detected after the first two injections, but reached 1.6 mM by day 4 and 2.56 by day 6.

During the low Fe(II) treatment, initial Fe(II) concentrations were 2.05 mM and decreased to below detection limit by 1.5 days (36 hrs.) (Figure 2C). A second injection at 1.5 days increased aqueous Fe concentrations to 2.35 mM and decreased to below detection by
day 4.5 (108 hrs.). Similar to high Fe(II) treatment, no aqueous Mn was initially detected within either chamber, but by 4.5 days had reached 0.23 mM in the injection chamber and 0.34 in the birnessite chamber (Figure 2). Aqueous Fe concentrations were below detection limit within the birnessite chamber throughout the injection period for both Fe concentration treatments (Figure 2B and 2D).

Fig. 2: Aqueous Fe and Mn concentrations in the Fe injection chamber (A,C) and the birnessite chamber (B,D) with initial total Fe injection of 8.18 mM (A,B) and 4.09 mM (C,D). Samples were taken during the formation of Fe coated birnessite with 1.67 g L-1 birnessite.
3.1.2 Aqueous As Dynamics in the Donnan

Fe(II) was allowed to react with birnessite for an additional 48 hrs. after the last Fe injection before As(III) was introduced to the system at 500 μM. After As(III) injection into the high Fe(II) treatment system, total As concentrations decreased from a high of 0.52 mM to 0.35 mM by 20 hrs. Arsenic diffusion into the birnessite chamber was seen over the first 13 hrs. with total As concentrations rising from 0 to 0.16 mM by 13 hrs. By 80 hours, the system reached pseudo-steady state with total As concentrations remaining 0.12 mM within both chambers (+/- 0.002 mM). Aqueous Mn concentrations rose from 2.52 mM prior to As(III) addition to a maximum of 3.10 mM within the injection chamber at 91.5 hrs. and 3.23 mM within the birnessite chamber at 77.5 hrs. Aqueous Fe concentrations remained near or below detection limit (0 to 0.02 mM) throughout the rest of the reaction time in both chambers. (Figures 3 and 4).

3.1.3 Oxidation of As(III) rate

Aqueous As speciation was performed using hydride-generation ICP (HG-ICP) method (Masscheleyn et al, 1991; Jones et al., 2000). As(V) concentrations were determined by subtracting As concentrations measured in sodium borohydride treated samples from total As concentrations. At high Fe additions, aqueous As(V) concentration remained lower than the As(III) concentration throughout the duration of the experiment reaching a concentration of 42 μM, while As(III) concentration was 64 μM at the last time point (95.1 hrs). At low Fe additions, As(V) concentration [74 μM As(V)] surpasses As(III) concentration [62 μM As(III)] after 7 hours, demonstrating a greater extent of As(III) oxidation than under high Fe treatment. Aqueous As(V) concentration plateaus after 22 hours post-As addition while As(III) concentration continues to decrease due to adsorption on the Fe-Mn oxide (Figure 5).
To determine the quantitative dependence of the rate of oxidation of As(III) upon Fe(II) concentration, we first calculated As(III) oxidation rate by determining the change in As(V) concentration \([\text{mM As(V)}]\) overtime \((\text{s})\) within the initial time points of the experiment. Using a simple linear function, we calculated the initial rate of As(III) oxidation in the low Fe system was \(2.27 \times 10^{-6} \text{ mmol L}^{-1} \text{ sec}^{-1}\) and was approximately five times slower in the high Fe system at \(4.62 \times 10^{-7} \text{ mmol L}^{-1} \text{ sec}^{-1}\).
Fig. 3. Aqueous As (A,B), Mn (C,D), and Fe (E,F) concentrations in the 8.18 mM total Fe concentration experiment. Fe injection chamber (A,C,E) and birnessite chamber are both represented. Samples were taken after the formation of Fe coated birnessite and immediately following the addition of As(III) to the system.
Fig. 4. Aqueous As (A,B), Mn (C,D), and Fe (E,F) concentrations in the 4.09 mM total Fe concentration experiment. Fe injection chamber (A,C,E) and birnessite chamber (B,D) are both represented. Samples were taken after the formation of Fe coated birnessite and immediately following the addition of As(III) to the system.
Fig. 5. Speciated aqueous As concentrations in the injection chamber (A, C) and birnessite chamber (B, D) at the 8.18 mM concentration (A, B) and 4.09 mM concentration (C, D). A μmol representation of the speciated As concentrations in birnessite chambers at the 8.16 mM and 4.09 mM Fe concentration (E, F).
3.2 Solid Phase Acid Digestion Analysis

2 mL of suspended solids were taken at each sample point to determine solid phase concentrations of As, Mn, and Fe using strong acid (HCl) digestion. At the high Fe(II) additions, solid phase Fe increase to 721 µmol g⁻¹ by 3 days, reaching a maximum of 404 µmol g⁻¹ by day 6 and 66 µmol g⁻¹ by day 4.5 for the low concentration. Total solid phase Mn decrease from ~1000 µmol g⁻¹ at day 0 to 585 µmol g⁻¹ by day 6 during high Fe treatment and 535 µmol g⁻¹ by day 4.5 at low Fe additions (Figure 6).

Arsenic concentrations rise from 0 to 8.1 µM within the first 4 hours after As(III) injection. Under high Fe treatment, solid phase As reaches a maximum of 31 µmol g⁻¹ by 29 hours post As(III) injection (Figure 7A). Under low Fe treatment, solid phase As concentration was more than four times lower, reaching a maximum of 7 µmol g⁻¹ at 38 hours after As injection. Solid phase Fe concentrations fluctuated between a low 226 µmol g⁻¹ at 13 hours post-As injection to a high of 432 µmol g⁻¹ at 29 hours after As injection for the high Fe treatment and 41 µmol g⁻¹ at 22 hours and 102 µmol g⁻¹ at 38 hours at the low Fe treatment but remain within error (Figure 7B). Solid Mn concentrations remain between 414 µmol g⁻¹ and 648 µmol g⁻¹ at the high Fe concentration and 459 µmol g⁻¹ and 676 µmol g⁻¹ at the low concentration (Figure 7C).
3.3 EXAFS and XANES speciation of solids

Extended X-ray absorption fine structure spectroscopy was used to determine changes in Fe and Mn oxide mineralogy after Fe(II) and As(III) addition to birnessite in the high Fe treatment experiment (EXAFS on low Fe treatment was not performed). After 4.28 mM Fe(II) was injected and allowed to react for 72 hours, 91% of Fe oxide was identified as ferrihydrite, 3% as lepidocrocite, and 5% as goethite. By day 6 after 8.18 mM Fe(II) was added, the percentage of ferrihydrite decreased slightly (to 89%) while goethite
percentage increased (from 5 to 7%), and lepidocrocite remained the same (4%). The reduction of the birnessite during Fe(II) oxidation led to the formation of hausmannite, a mixed valence Mn oxide represented by the unit formula Mn(2+, 3+).O. Prior to Fe(II) addition, EXAFS analysis confirms that Mn oxide phase is 100% birnessite; by day 6 after Fe(II) addition, the Mn oxide was composed of 82% birnessite and 17% hausmannite. EXAFS spectra were also collected after As(III) addition to the subsequently formed Fe-Mn oxides. Fe EXAFS reveal that the percentage of goethite decreases from 7 to 4% over the course of the experiment, while the percentage of lepidocrocite showed an increasing trend (5 to 7%), while ferrihydrite fluctuated between 88 and 91%. At 0.5 hours post As injection, solid phase Fe oxide was identified as composed of 6% goethite, which decreased slightly to 3% by 91.5 hours. Lepidocrocite percentage increased from 5% at 0.5 hours to 7% at the end of the experiment (91.5 hrs.) (Figure 8). However, it should be noted that these percentage changes in oxide composition as determined by linear combination fitting are within sensitivity limits (~2%) and therefore, these results likely demonstrate that Fe oxide mineralogy does not change after As(III) addition. In contrast, Mn EXAFS analysis shows that at 0.5 hours post-As injection, solid phase Mn oxide was still composed of a sizable percentage of hausmannite (18%), while the rest identified as birnessite (82%). After 0.5 hours, the percentage of hausmannite then continually decreased and by 22 hours post-As addition, only birnessite was detected (Figure 9).
Fig. 8. EXAFS analysis for Fe (A) and Mn (B) during the formation of Fe coated birnessite with 8.18 mM Fe concentration. EXAFS of Fe (C) and Mn (D) standards.
Arsenic K-edge XANES analysis was performed on solid phases for both high and low Fe treatment systems, where we were able to determine the fraction of As(III) and As(V) associated with the Fe-Mn oxide over time (Figure 10 and 11). In the high Fe system, As(III) oxidation on the solid phase was rapid with 37% As(III) and 67% As(V) adsorbed on the Fe-Mn oxide 5 minutes after As(III) injection. The percentage of As(V) in the solid phase increased to a maximum of approximately 90% after 7 hours. After this point the percentage of As(III) remained between 10 and 15% as As(V) remained between 85 and
90% (Figure 9, Table 1). In the low Fe treatment system, solid phase As(III) and As(V) percentages were 7% and 93% respectively 5 minutes after As(III) injection. The concentration of As(V) subsequently decreased over the next 4 hours until reaching 80%. The As(III) concentrations fluctuated between 11% and 20% until the end of the experiment (Figure 11).

Fig. 10. Fractional representation of As(III)/AS(V) speciation in the solid phase at 8.18 mM Fe concentration (A). XANES analysis of As(III)/AS(V) speciation on the Fe coated birnessite at the 8.18 mM Fe concentration (B).
### Table 2

EXAFS speciation for Fe and Mn during the formation of Fe treated birnessite at the 8.18 mM Fe concentration (A), including fit accuracy (reduced chi squared), EXAFS for Fe and Mn after As addition (B). XANES speciation of As(III)/As(V) as oxidation occurs, throughout the experiment (C).

#### A

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>Lepidocrocite</th>
<th>Ferrohydrite</th>
<th>Geohite</th>
<th>Reduced Chi Sqrd</th>
<th>Birnessite</th>
<th>Hausmannite</th>
<th>Reduced Chi Sqrd</th>
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#### B

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<th>Time (hours)</th>
<th>Lepidocrocite</th>
<th>Ferrohydrite</th>
<th>Geohite</th>
<th>Reduced Chi Sqrd</th>
<th>Birnessite</th>
<th>Hausmannite</th>
<th>Reduced Chi Sqrd</th>
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<td>98.80%</td>
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<td>89.61%</td>
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#### C

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<tr>
<th>Time (hours)</th>
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<th>As(V)</th>
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<td>10.90%</td>
<td>89.10%</td>
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3.4 SEM Imaging of Oxides

SEM imaging was utilized to visualize the morphology of solids collected from the high Fe treatment system before injecting Fe(II) (day 0), at the midpoint of the Fe treatment (day 3), 36 hours after the final Fe(II) injection (day 6) (Figure 12). The morphology of oxides confirm our findings from EXAFS analysis and reveal the heterogeneous nature of the resulting oxide mixture. Images of the solid at day 0 show small ridged spherical clusters
typical of birnessite (Figure 12A). At Day 3 after 4.28 mM of Fe(II) was added, both poorly-crystalline (ferrihydrite and lepidocrocite) and rod-like (goethite) Fe oxide structures beginning to form on the birnessite (Figure 12B). After 8.18 mM of Fe(II) was added (day 6), increasingly more rod structures and small angular crystals appear confirming an increase in goethite content (Figure 12C). Increasingly more hausmannite (Mn oxides with less pronounced ridges) can be seen in the system as a function of Fe(II) addition. However, unreacted birnessite (Figure 12 B and C) can still be seen after Fe(II) treatment (Figure 12C), indicating that the birnessite surfaces are not completely passivated by the Fe oxides even upon high Fe(II) treatment.

SEM images were also taken of solids from the system 13 hours after As(III) was injected, as well as the endpoint of the experiment (95.1 hours). At both of these time points the oxide morphologies are consistent with our EXAFS findings. There are observable small crystalline structures (ferrihydrite and lepidocrocite) and relatively fewer rod like structures. The structures also appear more evenly distributed than those viewed at earlier time points.
Fig. 12. Birmessite before Fe(II) addition (A). Solid phase after 4.28 mM were added and allowed to react (B). Solid phase after 8.18 mM were added and allowed to react (C). Solid phase 13 hours after As(III) injection (D). Solid phase 91.5 hours after As(III) injection.
4 Discussion

Manganese oxides are found in nearly all soils and sediments and can act as strong oxidants and sorbents for metals and metalloids. Alteration of Mn oxide minerals by other soil constituents such as Fe(II) at redox interfaces can impact their reactivity and thus affect their oxidative capacity. Our results illustrate that in the presence of increasing aqueous Fe(II) concentrations, surface passivation of poorly crystalline Mn oxides, birnessite, contribute to decreased As(III) oxidation rate. Concomitant with Fe(II) oxidation, the reduction of birnessite results in the formation of a second Mn oxide phase, hausmannite, a more crystalline Mn(II/III) oxide. The rate of As(III) oxidation by the resulting Fe-Mn oxide is significantly slowed drastically compared to the rate of As(III) oxidation by birnessite alone (3.9 x 10^{-4} mmol L^{-1} sec^{-1} versus 4.62 x 10^{-7} mmol L^{-1} sec^{-1}) (Scott and Morgan, 1995) likely due to a number of reasons, including the formation of Fe oxides on the surface of the birnessite, a decrease in overall redox potential of the system upon Fe(II) addition, and the presence of Mn(II) and Mn(III) reactive sites on any exposed birnessite surface. The rate is decreased to a point such that, under the described experimental conditions, As(III) is not completely oxidized by the Fe-Mn oxide at both the high and low concentrations over 91.5 hrs. demonstrating the impact that reduced constituents like Fe(II) can have on reactive phases within soils.

4.1 Fe(II) reaction with birnessite

The reaction between Fe(II) and birnessite results in the removal of aqueous Fe(II) through the formation of both poorly-crystalline and crystalline Fe(III) oxides during reductive dissolution of birnessite, resulting in an increase in aqueous Mn(II) (Figure 3 and 4). Interface of aqueous Mn(II) and Mn oxides has been shown to result in both no change in mineralogy (Elzinga, 2016) and formation of secondary mineral phases. Treatment of
vernadite (randomly stacked birnessite, δ-MnO₂), was shown to undergo continuous reprecipitation and dissolution as the mineral structure remained the same (Elzinga, 2016). Our results, however, shows that a second Mn mineral phase of decreased oxidation state is formed.

Fe EXAFS indicate that ferrihydrite remained the dominant oxide throughout the experiment with much lower fractions of goethite and lepidocrocite (Table 1, Figure 8 and 9). The presence of these species is consistent with previous studies which reported that goethite and lepidocrocite form as secondary mineral structures when ferrihydrite is exposed to relatively low concentrations of aqueous Fe(II) (Hansel et al., 2003).

The addition of Fe(II) into the system and subsequent oxidation by birnessite also decreases the overall redox potential of the birnessite (Manning et al., 2002; Scott and Morgan, 1995). This results in a slowing of the oxidation rate resulting from the decrease of the redox potential in addition to the surface passivation by Fe(III) oxides. There are therefore 2 mechanisms which are slowing the overall oxidation of As(III). A chemical mechanism in the reduced overall oxidative potential of birnessite upon reaction with Fe(II) and a physical blockage of binding sites on the birnessite surface by adsorbed Fe(III) oxides.

4.2 Oxidation of As(III) by Fe-Mn oxide and Mn dynamics

By taking into account aqueous As speciation, the percentage of hausmannite and birnessite determined by Mn EXAFS analysis, and reported average oxidation states of both Mn oxides (Feng et al., 2006), we are able to determine the contribution of hausmannite versus birnessite to As(III) oxidation over time.

While the exact process of oxidation of As(III) by hausmannite is unknown, birnessite has been shown to oxidizes As(III) by the following two-step process (Nesbitt et al. 1998):
1) \(2\text{Mn}^{\text{III}}\text{O} + \text{HAs}^{\text{III}}\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Mn}^{\text{IV}}\text{OOH} + \text{HAs}^{\text{IV}}\text{O} + \text{H}_2\text{O} \quad \text{Eq. 1.}
\)

2) \(2\text{Mn}^{\text{III}}\text{OOH} + \text{HAs}^{\text{III}}\text{O}_3 + 3\text{H}^+ \rightarrow 2\text{Mn}^{\text{II}}(\text{aq}) + \text{HAs}^{\text{V}}\text{O}_4^- + 3\text{H}_2\text{O} \quad \text{Eq. 2.}
\)

Therefore, Mn(III) reactive sites within the hausmannite fraction may undergo further reduction to Mn(II) under a similar one electron transfer in the presence of As(III) as shown in Eq. 2.

Our calculations show that interaction of the Fe-Mn solids with As(III) results in electron transfer to both the hausmannite and birnessite (Table 2). The total amount of As(III) oxidized over the course of the experimental time was much greater than the oxidative capacity of the total mass of hausmannite in the system, indicating the large contribution of reactive sites from birnessite responsible for As(III) oxidation. Hausmannite is a Mn(II)/Mn(III) oxide in which Mn has an average oxidation state (AOS) of 2.66 (Feng et al., 2006). Thus, 3.03 molecules of hausmannite are needed to convert one molecule of As(III) to As(V). Birnessite is a Mn(III)/Mn(IV) Mn oxide with an average oxidation state of 3.96 (Feng et al., 2006), and therefore slightly more than 1.02 molecules of birnessite is needed to oxidize As(III) to As(V). Using these values, we show that the amount of hausmannite formed in the system was not sufficient to account for all of the oxidation of As(III) that occurred and that only 6.96% of the total As(III) oxidation can be mediated by hausmannite (Table 2). Thus both hausmannite and birnessite act as electron acceptors in the oxidation of As(III) within the Fe-treated system, with hausmannite playing a role for only a short period after As(III) exposure. EXAFS analysis indicates that nearly all of the hausmannite is oxidized within 4 hrs. (95%) and completely depleted by 7 hours of the reaction (Table 1). Oxidation of As(III) to As(V) continues after complete dissolution of hausmannite, indicating that birnessite acts as the major electron acceptor in the system.
Our findings also agree with previous research that oxidation of As(III) is entirely mediated by Mn oxides under anoxic conditions with no contribution of oxidation from Fe(III) oxides (Oscarson et al., 1981). This is confirmed by the consistency of Fe oxide phase composition throughout the experiment (Figure 10, Table 1) and concentration of Fe found in the solid phase (Figure 6). Ultimately, these findings demonstrate the transient nature of lower oxidation state Mn oxide phases that is contributing to oxidation reactions within soil redox interfaces.

<table>
<thead>
<tr>
<th>Mn Species</th>
<th>$\AOS$</th>
<th># of Moles Needed to Oxidize One Mole As(III)</th>
<th>mmol MnO$_x$ available at As injection</th>
<th>As(III) Oxidized (mmol)</th>
<th>Total As(III) Oxidized (mmol)</th>
<th>% of Total As(III) Oxidized</th>
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<tbody>
<tr>
<td>Hausmannite Mn(II/III)$_2$O$_4$</td>
<td>2.66</td>
<td>3.03</td>
<td>0.1113</td>
<td>0.0368</td>
<td>0.5277</td>
<td>6.564%</td>
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<tr>
<td>Birnessite Mn(III/IV)O$_2$</td>
<td>3.96</td>
<td>1.02</td>
<td>0.534152749</td>
<td>0.4910</td>
<td>0.5277</td>
<td>93.036%</td>
</tr>
</tbody>
</table>

Table 2. Electrons that can be accepted by each Mn oxide and how many millimoles of As(III) were oxidized by each. This could be determined because of the complete dissolution of Hausmannite.

Previous studies indicate that hausmannite has a much lower oxidative capacity than birnessite (Feng et al., 2006; Zhu et al., 2009). This is reflected in our results with the rapid dissolution of the previously formed hausmannite upon contact with As(III). Additionally, Feng et al. indicated a higher release of Mn(II) into the aqueous phase than birnessite as a result of the Mn(II)/Mn(III) structure of hausmannite which leads to the spontaneous release of Mn(II) when Mn(III) is reduced and released. Indeed, in our experiment aqueous Mn(II) concentrations increased more rapidly in the first 7 hours after As(III) was added to the system (Figure 7C).

70% of the As(III) originally injected into the high Fe(II) treatment system was oxidized into As(V) by the end of the experiment. This was determined by comparing the total As(V)
mass at the end of the experiment in both aqueous and solid phase to As(III) mass at the initial injection time. At the 4.09 mM Fe concentration 81% of As(III) was oxidized.

Our results show a marked decrease in As(III) oxidation rate with increasing Fe(II) concentrations. This indicates that at soil redox interfaces with high Fe(II), As(III) oxidation would proceed at a rate which is comparable to or slower than diffusion. Under these conditions the rate of As(III) oxidation would be transport limited.

Our results also demonstrate that the formation of Fe(III) oxides increases the sorption capacity of the system upon Fe(II) interaction with birnessite. Aqueous As concentrations decrease within the injection chamber as a function of diffusion rate, and is also dependent upon the rate of As(III) oxidation by Mn oxides and subsequent sorption on the Fe-Mn solids. An approximately 5-fold decrease is seen in the rate of As(III) oxidation in the presence of only two times greater aqueous Fe(II) concentration. Although a lower total mass of As(III) was oxidized to As(V) at the high Fe concentration, more of the As(V) was proportionately adsorbed onto the solids than at the low Fe concentration. As(V) is has been shown to preferentially bind to Fe oxides (Deschamps et al.; 2003, Dixit et al., 2003; Ying et al., 2012) and the presence of a higher concentration of solid Fe oxides results in increased incorporation and adsorption of As(V) into the solid phase.

5 Conclusions

Diverse reactions between Mn and Fe occur in soils due the physical and biogeochemical heterogeneity of soils. Our results show that the interaction between Fe and Mn results in only a partial passivation of the oxidative power of Mn oxides and that a physical barrier of Fe on the surface of the Mn does not prevent electron transfer from occurring. Diffusion limited transport of geogenic metals and metalloids which interact with these Fe coated solids will therefore continue to undergo oxidation. However, the rate of oxidation is
affected by the presence of Fe on the surface of the Mn oxides, where the rate is decreased as a function of Fe concentration in the system. Our experiments indicated that As(III) was more rapidly oxidized to As(V) when a lower concentration of Fe(II) was present. However, more As(V) was partitioned into the solid phase at the high concentration due to preferential binding to Fe Oxides. This indicates that despite the reduced oxidative power of the birnessite at high Fe concentrations, there is actually more As removed from the aqueous phase due to increased As(V) loading onto Fe-oxides.

Using EXAFS and the XANES analysis, we determined that the oxidation of Fe(II) by the birnessite results in the formation of hausmannite, a second Mn oxide phase. There are two possible reactions that could produce the hausmannite. The first is that the hausmannite is being formed directly from the birnessite during the redox reaction and will be found in at the Mn/Fe interface. The second is that it is being re-reduced from the aqueous phase and is being formed within the Fe matrix during the oxidation of Fe(II). In conclusion, our study demonstrates that the interaction of Mn and Fe in soils and sediments can greatly impact the prediction of As speciation and transport and that consideration of such ternary systems can be informative toward better characterizing complex elemental interactions in soils and sediments.
References


Elzinga, Evert J. “$^{54}$Mn Radiotracers Demonstrate Continuous Dissolution and Reprecipitation of Vernadite (6-MnO$_2$) during Interaction with Aqueous Mn(II).” Environmental Science & Technology 50, no. 16 (August 16, 2016): 8670–77. doi:10.1021/acs.est.6b02874.


Oscarson, D. W., P. M. Huang, C. Defosse, and A. Herbillon. “Oxidative Power of Mn(IV) and Fe(III) Oxides with Respect to As(III) in Terrestrial and Aquatic Environments.” Nature 291, no. 5810 (May 7, 1981): 50–51. doi:10.1038/291050a0.


