The Role of Dissolved Fe(II) Concentration in the Mineralogical Evolution of Fe
(hydr)oxides During Redox Cycling

Elizabeth J. Tomaszewski¹; S. Sarah Cronk²; Christopher A. Gorski²; Matthew Ginder-
Vogel^{1*}

Keywords: Redox cycling; Iron (hydr)oxides; X-ray spectroscopy

¹ The University of Wisconsin-Madison
Department of Civil and Environmental Engineering
Environmental Chemistry and Technology Program
660N Park St
Madison, WI 53706

² The Pennsylvania State University
Department of Civil and Environmental Engineering
212 Sackett Building
University Park, PA 16802

*Corresponding Author
Email: mgindervogel@wisc.edu
Phone: 608-262-0768

Abstract

Iron (Fe) (hydr)oxides play a key role in sediment biogeochemical cycling, particularly in dynamic environments that periodically undergo redox oscillations. The length of redox half cycles varies, depending on environment, and is often brief in upland tropical soils, the vadose zone and at the sediment/plant root interface. One reaction that impacts Fe (hydr)oxide mineralogy in these environments is the Fe(II) catalyzed transformation of ferrihydrite. This reaction leads to the production of more crystalline phases under strictly anaerobic conditions and in cycling studies with relatively long anaerobic and/or oxic periods (e.g., 7 to 90 days). Ferrihydrite transformation has been investigated under strictly anaerobic conditions, or during a few (1-3), longer redox cycles; however, there is limited information describing the transformation of ferrihydrite, over multiple, short, sequential exposures to chemical reductants (e.g., dissolved Fe(II)) and oxidants (e.g., O₂). Here, we examine the mineralogical evolution of ferrihydrite over eight redox cycles during which it reacts with dissolved Fe(II) in the absence of oxygen (anaerobic conditions) for 48 hours and is subsequently exposed to air (oxic conditions) for 18 hours. Using X-ray absorption spectroscopy (XAS) and ⁵⁷Fe Mössbauer spectroscopy, the abundance of each mineral phase present after each anaerobic or oxic period, is quantified. Our results demonstrate that rapid redox cycling limits the extent of ferrihydrite transformation leading to disequilibrium between mineral phases while magnetite stoichiometry increases throughout the study despite periodic exposure to oxygen. A deeper understanding of poorly crystalline Fe (hydr)oxide transformation

during multiple, short redox cycles can provide insight into reactions controlling the speciation of redox active nutrients and contaminants in soils and sediments.

1. Introduction

Ferrihydrite ($\text{Fe}(\text{OH})_3$), a poorly crystalline Fe(III) (hydr)oxide, transforms to more crystalline phases such as goethite ($\alpha\text{-FeOOH}$) and/or magnetite (Fe_3O_4) when reacted with dissolved Fe(II) under anaerobic conditions (Boland et al., 2014, 2013; Hansel et al., 2005; Pedersen et al., 2005; Postma, 1993; Yang et al., 2010; Yee, 2006). However, many environments including riparian zones, and wetlands are not infinitely anaerobic. These environments experience fluctuating water table levels, influencing the diffusion of oxygen into the sediment column and causing changes in redox conditions. Often, the influence of redox cycling on iron mineralogy is examined over extended (5 to 90 day) half cycles (Couture et al., 2015; Mejia et al., 2016; Stewart et al., 2015, 2009; Thompson et al., 2006; Yang et al., 2012). Yet, redox oscillations in many environments occur on much shorter time scales (e.g., hours to days) (Pett-Ridge and Firestone, 2005; Reddy et al., 1989; Schuur and Matson, 2001; Van Cappellen et al., 1998; Hansen et al., 2011).

In anaerobic environments, Fe(III) (hydr)oxides are terminal electron acceptors for microbial respiration, resulting in the production of dissolved Fe(II), which in turn leads to mineralogical transformation (Hansel et al., 2004, 2003; Roden, 2012, 2004, 2003). The molar ratio of dissolved Fe(II) to ferrihydrite is a key factor in determining which mineral phases form (Boland et al., 2014; Hansel et al., 2005; Stewart et al., 2009; Yang et al., 2010). Goethite, the primary product when this ratio is ≤ 0.072 , has a smaller surface area and thus, a smaller number of surface sites per unit mass than ferrihydrite (Roden, 2003; Roden and Zachara, 1996). When the molar ratio of dissolved Fe(II):ferrihydrite is ≥ 0.72 , the primary product is magnetite ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$), which

reductively transforms many contaminants such as Cr(VI), As(V) and U(VI) and nitrobenzene (Gorski and Scherer, 2009; Peterson et al., 1997a, 1997b, 1996).

A transition back to oxidizing conditions after only a short exposure to Fe(II) may impede the formation of more crystalline phases by oxidation and subsequent precipitation of dissolved Fe(II) as Fe(III) (hydr)oxides. Once anaerobic conditions are restored, reduction of Fe(III) (hydr)oxides produces fresh dissolved Fe(II), which can catalyze further transformation. For example, in natural sediment, four cycles of seven days of biological reduction followed by seven days of oxidation by O₂ (air) results in the transformation of nano-crystalline goethite to microcrystalline goethite and hematite (Thompson et al., 2006). Similarly, when ferrihydrite or lepidocrocite (γ -FeOOH) is exposed to four cycles of microbial reduction each lasting for 19 days followed by 5-days of oxidation by either O₂ or NO₃⁻, transformation into goethite and/or non-stoichiometric magnetite occurs (Mejia et al., 2016). Clearly, longer half cycles (>14 days) of microbial reduction followed by chemical oxidation (by either O₂ or NO₃⁻) leads to an increase in crystallinity; however, the pathway of Fe(III) (hydr)oxide mineral transformation driven by abiotic processes during shorter half cycles remains ambiguous.

Fe(III) (hydr)oxide mineralogical evolution during chemical and/or biological redox cycling is dependent on a variety of factors including starting mineral, reduction mechanism (e.g., biological vs. chemical), length of half cycles and the presence of other contaminant species (Couture et al., 2015; Stewart et al., 2015, 2009; Yang et al., 2012). Stewart et al. (2009) examines uranium incorporation during ferrihydrite remineralization during four complete redox cycles. Reducing half cycles ranged from 5 to 90 days with reduction being initiated by addition of either 3 or 10 mM FeSO₄, while oxidizing half-

cycles last 5 days and are initiated by aeration. Iron (hydr)oxide mineralogy is only characterized following reduction for 5 or 30 days and oxidation for 5 days. Goethite is observed after reduction with 3 mM FeSO₄ and a mixture of magnetite and goethite is produced by reduction with 10 mM FeSO₄. Lepidocrocite is the predominant oxidation product in both systems, likely due to the elevated SO₄²⁻. Iron mineralogy is not characterized beyond the first redox cycle and the stoichiometry of the magnetite is not determined. Another study examines the mobility of Cr, As, Se, Sb and U during redox oscillations of natural sediments (Couture et al., 2015). In this study, half cycles last seven days each, with a total of three complete redox cycles, and lead to changes in contaminant solubility and oxidation state (Couture et al., 2015); however, investigation of changes in iron (hydr)oxide mineralogy are limited due to the complexity of the natural sediments and focus on contaminant speciation. Finally, Yang et al. (2012) investigates the redox cycling of technetium (Tc) and Fe-bearing clay minerals during bioreduction of Fe in clay minerals over three redox cycles. The half cycles last ~400 hours, leading to changes in the reduction rate of Tc(VIII) by reactive Fe(II) in the clay mineral (Yang et al., 2012). Developing an understanding of electron transfer reactions in redox active environments is critical to predicting contaminant mobility these systems; however, their inclusion in cycling studies may limit the general applicability of the observed transformations.

The objective of this study is to determine the impact of short half cycles on the mineralogical evolution of ferrihydrite over eight redox cycles, at two dissolved Fe(II) concentrations. Dissolved and solid-associated Fe(II) are quantified throughout each redox cycle, while the abundance of Fe (hydr)oxide minerals and the stoichiometry of

magnetite are quantified with extended X-ray absorption fine structure (EXAFS) and Mössbauer spectroscopies. This work demonstrates that multiple, short, abiotic, redox cycles influence mineralogy by disrupting transformations, introducing disequilibrium between solid phases and enriching lattice Fe(II) content in magnetite despite the frequent introduction of oxygen. Surface passivation caused by continued mineral transformation and formation during redox cycling, could alter sorption processes of contaminant species such as Cr(VI), As(V) or U(VI), and influence electron transfer with lattice Fe(II). Determining mineral transformation as a result of redox cycling is important in understanding the chemical and physical processes that influence contaminant flux in redox active environments and could potentially lead to the creation of long term remediation solutions.

2. Materials and Methods

2.1 Synthesis of anaerobic media and 2-line ferrihydrite

Anaerobic, synthetic groundwater was comprised of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mM), $\text{Ca}(\text{NO}_3)_2$ (0.5mM), KCl (0.05 mM), NaClO_4 (100 mM) and PIPES (1,4 piperazinediethanesulfonic acid) (10.0 mM) in $18.2 \text{ M}\Omega \text{ cm}^{-1}$ water and was adjusted to pH 7.0 with HCl (12 N) and NaOH (1 M). Sodium perchlorate was utilized to maintain a similar ionic strength at the two different Fe(II) concentrations. As prepared, the ionic strength was 0.172 M in the low Fe(II) reactors and 0.195 M in high Fe(II) reactors. The media was heated to a rolling boil and then sparged with N_2 that had passed over hot copper filings to remove trace oxygen. The media was immediately capped and transferred to an anaerobic chamber (COY), with a 5% H_2 and 95% N_2 atmosphere.

Ferrihydrite ($\text{Fe}(\text{OH})_3$) was synthesized by rapidly titrating 0.5 M ferric chloride with 0.4 M NaOH to a final pH of 7 while not exceeding pH 7.5. The resulting slurry was centrifuged and resuspended four times with ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) (Schwertmann, 2000). The ferrihydrite was then resuspended in anaerobic, synthetic groundwater media and bubbled with N_2 , scrubbed of O_2 , prior to use. Ferrihydrite was used within 48 hours of synthesis. The purity of 2-line ferrihydrite was confirmed by X-ray diffraction (Figure A.1).

2.2 Abiotic Redox Oscillations in Batch Reactors

Duplicate batch reactors were prepared in 1 L glass media bottles. These bottles and all other supplies that came into contact with anaerobic solutions were equilibrated inside the anaerobic chamber for at least 24 hours prior to use. Ferrihydrite was added as an anaerobic slurry in deionized water to a final concentration of 15.0 mM to the artificial groundwater media. Redox cycling began with an anaerobic period, where $\text{Fe}(\text{II})$, as FeCl_2 dissolved in anaerobic groundwater media, was added to a final concentration of either 1.0 mM or 10.0 mM. The molar ratio of $\text{Fe}(\text{II})_{\text{added}}:\text{Fe}_{\text{Total}}$ was 0.46 ± 0.13 in the high $\text{Fe}(\text{II})$ reactors or 0.08 ± 0.03 in the low $\text{Fe}(\text{II})$ reactors during the experiment (Appendix A, Table A.1).

After 48 hours under anaerobic conditions, the aqueous phase was decanted, to minimize the amount of dissolved $\text{Fe}(\text{II})$ present during oxic periods, leaving a slurry. Aqueous $\text{Fe}(\text{II})$ was measured prior to the beginning of each oxic period to calculate the amount of additional Fe (hydr)oxide that may form during oxidation (Appendix A, Tables A.5 & A.6). In the low $\text{Fe}(\text{II})$ reactors, oxidation of residual aqueous $\text{Fe}(\text{II})$ may account for $\sim 1\%$ of the solids present in the reactor after each oxic phase, while it may

account for ~ 10% of the solids present at the conclusion of oxic periods in the high Fe(II) reactors. Oxic (saturated with air) groundwater media was then added to the slurry inside the anaerobic chamber, and the reactors were stirred outside the anaerobic chamber for 18 hours (dissolved O₂ concentration was approximately 9.9 mM). After 18 hours, the media was decanted, again preserving the solid phase. Subsequent anaerobic periods were initiated by the addition of anaerobic media and Fe(II). After media addition, and prior to Fe(II) addition, reactors were sparged with scrubbed N₂ for 2 hours, and then transferred to the anaerobic chamber. Reactors were stirred continuously throughout the experiment. The pH remained in the range of 6.7 ± 0.24 for 1.0 mM Fe(II) and 6.4 ± 0.23 for 10 mM Fe(II) reactors for the duration of the experiment (Appendix A, Table A.2).

Solid phase samples were obtained at the conclusion of each anaerobic and oxic period by removing 20 ml of slurry and filtering it through a 0.2 μ m nylon filter. The solid samples were then dried and stored under anaerobic conditions until further analysis. Slurry samples were collected immediately after dissolved Fe(II) addition, as well as 24 and 48 hours after Fe(II) addition, as well as at the beginning and end of each oxic period, by pipetting directly from the reactor. Slurry samples were then either: (1) dissolved in 12N HCl for quantification of total Fe; (2) extracted with 1M HCl for 14 days and then filtered for quantification of sorbed Fe(II); or (3) immediately filtered through 0.2 μ m PTFE disk filter with the filtrate diluted into 5 % HCl volume for aqueous Fe(II) determination.

2.3 Analytical Techniques

Ferrous iron was determined in aqueous samples and solid phase extracts using a modified version of the ferrozine method (Stookey, 1970) (Appendix B), and the

absorbance was measured at 562 nm. Although samples diluted into both 1M HCl and 5% HCl volume were filtered, the high solubility of poorly crystalline Fe(III) (hydr)oxides resulted in the presence of dissolved Fe(III) in samples collected at early time points. Excessive dissolved Fe(III) alters the measurement of Fe(II) by ferrozine and therefore the data was corrected as described in Appendix B. Total Fe was determined by the addition of equal volumes of 1.4 M NH_2OH and sample dissolved in 12 N HCl to a mixture of 5 mL ferrozine reagent buffered to pH 6 with 50 mM HEPES and 500 μL of 4.0 M ammonium acetate buffer.

X-ray diffraction patterns were collected using a Rigaku D/Max Rapid II diffractometer equipped with a Mo X-ray tube, operating at 50 kV and 50 mA. To limit exposure to oxygen, dried solids were prepared in silica capillary tubes in the anaerobic chamber, sealed with vacuum grease and stored in glass vials sealed with butyl stoppers prior to analysis. Crystalline mineral phases were identified using Match! (Crystal Impact Version 2.44) (Figure A.2). Dried solid samples were mixed with boron nitride (~ 0.5 mg Fe/mg BN), sealed with Kapton polyamide tape in the anaerobic chamber and stored anaerobically until analysis by X-ray absorption spectroscopy (XAS). XAS measurements were performed at the Advanced Photon Source (APS). GeoSoilEnviroCARS (GSE-CARS) Beamline 13BM-D employs a bending magnet source and a Si (111) monochromator. N_2 filled gas ionization chambers were used to collect transmission spectra. Spectra were collected at the Fe k-edge (7112 eV) from $k=2$ - $14 \text{ \AA}^{-1}$ (Figure A.3). Linear combination fitting (LCF) of k^3 weighted EXFAS spectra was performed using iron (hydr)oxide standards (Figure A.4) (Benner et al., 2002; Hansel et al., 2005, 2003) to quantify the mole percent of each Fe-bearing phase in the system

(Newville, 2001). Principal component analysis (PCA) was performed to determine the maximum number of standards to be included in each LCF. Iron (hydr)oxide standards for each LCF included the starting material and the crystalline phases that were detected using XRD. This fitting technique has an error of approximately $\pm 5\%$ for each phase that is fit, agreeing with the error associated with LCF of XAS in previous studies (Hansel et al., 2003). Although it was not detected in the XRD patterns, maghemite was included in LCF analysis to account for non-stoichiometric magnetite. Each fit was optimized by minimizing σ^2 .

Cryogenic ^{57}Fe Mössbauer spectra were collected for a subset of samples to determine magnetite stoichiometry (Appendix A, Figures A.5-A.8) and confirm the Fe mineralogy determined using EXAFS. Magnetite stoichiometry was determined using only Mössbauer and was compared to the mineralogy as determined by EXAFS data. Samples were prepared by placing the dry powder inside an aluminum washer sealed on both sides with 5 Mil Kapton tape. Oxygen sensitive samples were prepared inside an anaerobic glovebox chamber (MBraun Unilan Workstation, 100% N_2 atmosphere, <0.1 ppm O_2). Spectra were collected using a SVT400 cryogenic Mössbauer system (SEE Co., USA). The ^{57}Co radioactive source (~ 50 mCi) was in an Rh matrix at room temperature. Spectra were collected for each sample at both 140 K and 5 K. All hyperfine parameters were relative to α -Fe foil collected at room temperature.

The spectra were fit using Recoil Software (University of Ottawa, Ottawa, Canada) and the Voigt-based model (Rancourt and Ping, 1991). Goethite, magnetite and/or lepidocrocite in varying proportions were identified by modeling the spectra using established hyperfine parameters (Cornell and Schwertmann, 2006). Samples were fit by

pure goethite and those parameters were then used as a starting point for fitting magnetite, assuming the goethite in samples with and without magnetite was similar. Fits are adjusted based on the data collected at two temperatures (5 and 140 K) as well as EXAFS data to refine site assignments when there was ambiguity. After determining which phases were present, the relative phase abundances were quantified by floating the center shift (CS), quadrupole splitting (QS), hyperfine field (H), hyperfine field distribution, and spectral area for each phase. In some cases, the CS, QS, or H was held constant during fitting because the optimized fit provided unrealistic values for these parameters. At 140 K, the goethite signal was fit using a two-component sextet due to inner-line broadening. The Fe^{2+} content in the magnetite was calculated by comparison of the spectral areas of the two magnetite sextets, which represent (1) octahedral $\text{Fe}^{2.5+}$ and (2) octahedral and tetrahedral Fe^{3+} (Gorski and Scherer, 2010). The stoichiometry of magnetite is then calculated according to equation 1.

$$x = \frac{0.5^{Oct} Fe^{2.5}}{0.5^{Oct} Fe^{2.5} + {}^{Oct,Tet} Fe^{3+}} \quad (1)$$

Stoichiometric magnetite has a value of $x=0.5$ and when it is fully oxidized (e.g., maghemite) it has a value of $x=0$. At 5 K, we first modeled pure nanoparticulate magnetite using 4 sites, then used these hyperfine parameters to fit subsequent mixed-phase samples. The Lorentzian linewidth was held at 0.148 mm/s during fitting, as it was the linewidth measured on the spectrometer for an ideally thick α -Fe foil.

Results

3.1 Fe(II) During Cycling

The concentration of Fe(II) is measured in the aqueous and solid phase throughout the experiment. In reactors where 10 mM Fe(II) is added, the concentration of aqueous Fe(II) during anaerobic periods ranges from 8.1 to 11.0 mM, while sorbed Fe(II) ranges from 0 to 4.2 mM (Figure 1A). Fe(II) concentration in solution remains higher than sorbed

Figure 1. Fe(II) partitioning (A) and mineralogy (B) during redox cycling of ferrihydrite with 10 mM Fe(II). EXAFS data and fits used to generate (B) are shown in Figure A.2. Shaded areas indicate time periods with reducing conditions. The amount of Fe(II) added at the beginning of each anaerobic period is also indicated in (A).

Fe(II) throughout the experiment. The concentration of dissolved Fe(II) is quite variable within each of the first five anaerobic periods. This coincides with extensive solid-phase transformation (Figure 1B), which causes changes in both surface site availability and particle size, leading to variability in the amount solid-phase associated Fe(II) (Figure 1). During the sixth and subsequent anaerobic periods aqueous Fe(II) decreases by at least 0.4 mM within each

Figure 2. Fe(II) partitioning (A) and mineralogy (B) during redox cycling of ferrihydrite with 1 mM Fe(II). EXAFS data and fits used to generate (B) are shown in Figure A.2. Shaded areas indicate time periods with reducing conditions. The amount of Fe(II) added at the beginning of each anaerobic period is also indicated in (A).

individual anaerobic cycle, accompanied by only minor changes in mineralogy (Figure 1). Despite the variability in aqueous Fe(II) throughout the experiment, solid phase Fe(II) increases from 0.72 mM at the start of the first anaerobic cycle, reaching 3.8 mM at the end of the 8th anaerobic cycle (Figure 1A).

In the low Fe(II) reactors, immediately after Fe(II) addition, the concentration of sorbed Fe(II) (0.66 mM) is larger than aqueous Fe(II) (0.29 mM) (Figure 2A). Within this first anaerobic cycle, aqueous Fe(II) concentration increases to 0.65 mM after 24 h and continues increasing to 0.79 mM after 48 h of reaction (Figure 2A). During subsequent anaerobic cycles, sorbed Fe(II) is consistently lower than aqueous Fe(II) (Figure 2A). With the exception of the second anaerobic period, aqueous and solid associated Fe(II) is smaller than the amount of Fe(II) added for the remainder of the experiment. For anaerobic periods 5-8, the average concentration of aqueous and sorbed Fe(II) is 0.64 mM, ~ 50% of added Fe(II) (Figure 2A).

3.2 Iron Mineralogy

While Mössbauer and XAS provide similar results, XAS can distinguish between ferrihydrite and goethite, when the latter is the dominant phase, while Mössbauer cannot (Appendix A, Table A.3).

Figure 3. Magnetite stoichiometry (○) obtained from Mössbauer spectroscopic analysis (left axis) and Fe (hydr)oxide mineralogy (right axis) determined using linear combination fitting of EXAFS spectroscopic data. Data and fits for Mössbauer and EXAFS analysis are available in Appendix A. Blue shaded areas indicate anaerobic periods.

Therefore, the mineralogy in Figures 1B & 2B is based only on fits of EXAFS data. The XRD patterns reveal that in the low dissolved Fe(II) reactors (1.0 mM), goethite and lepidocrocite become the dominant crystalline phases; while in the high dissolved Fe(II) reactors (10 mM), goethite and magnetite are formed (Appendix A, Figure A.2). Maghemite was not detected as a separate phase in the XRD patterns; however, it is used in EXAFS fitting to account for the non-stoichiometric nature of the magnetite in our system.

3.2.1 High Fe(II) Reactors

After the first anaerobic period, goethite is the dominant mineral phase (79 mole %), with residual ferrihydrite (21 mole %) in the 10 mM Fe(II) reactors (Figure 1B). The amount of ferrihydrite increases slightly (33 to 41 mole %) from the conclusion of the first anaerobic period to the conclusion of the second anaerobic period. During the third anaerobic period, magnetite forms, reaching 11 mole %, while ferrihydrite decreases (from 33 to 16 mole %) (Figure 1B). After the third oxic period, partial oxidation of magnetite is observed, while goethite continues to dominate the mineral assemblage (66 mole %). At the conclusion of the fourth redox cycle, the amount of goethite has decreased, while the amount of magnetite and partially oxidized magnetite increase. At the conclusion of the eighth oxic period, goethite (45 mole %), and non-stoichiometric magnetite 47 mole % (25 mole % magnetite and 22 mole % maghemite) are the most abundant phases, followed by ferrihydrite (8 mole %) (Figure 1B).

Mössbauer confirms the formation of non-stoichiometric magnetite in high Fe(II) reactors during the second anaerobic period, while the other mineralogical results are similar to results from LCF analysis of EXAFS spectra (Table A.3). As expected,

magnetite stoichiometry increases from one anaerobic period to the next (Figure 3) and decreases during the 5th and 7th oxic periods. Although magnetite stoichiometry decreases within individual oxic periods, there is a net increase in stoichiometry throughout redox cycling. For example, after the 7th oxic period it is higher (0.33) than after the 5th oxic period (0.29) (Figure 3). Unfortunately, Fe(II) sorbed to goethite is not detectable by Mössbauer, and therefore not included in this analysis. In the XAS data, the changes in magnetite stoichiometry are reflected by changes in the mole ratios of magnetite to maghemite, with the amount of maghemite increasing as the magnetite stoichiometry decreases (Figure 3); however, this trend is not a quantitative substitute for determination of magnetite stoichiometry by Mössbauer spectroscopy.

3.2.2 Low Fe(II) Reactors

At the conclusion of the first anaerobic period, in the low Fe(II) reactors, the mineral assemblage is dominated by goethite (52 mole %), with lesser amounts of lepidocrocite (27 mole %) and ferrihydrite (22 mole %) (Figure 2B). While lepidocrocite is present after the first anaerobic period (27 mole %) and first oxic period (23 mole %) (Figure 2B), it is not detected in later cycles. During the second anaerobic period, the amount of ferrihydrite (~22 mole %), lepidocrocite (~23 mole %) and goethite (~54 mole %) remain relatively constant. During the 3rd anaerobic period in the low Fe(II) reactors, additional Fe(II) is introduced to test the stability of ferrihydrite; however, the formation of magnetite is not observed, despite it being an expected product of a high ratio system. Over the course of the experiment, goethite dominates the mineralogy after oxic and anoxic periods (> 50 mole %) (Figure 2B), and ferrihydrite is also detected (~20 mole %). Goethite and lepidocrocite are detected by Mössbauer spectroscopy after the

first anaerobic and oxic periods (Table A.3). In samples collected at the conclusion of the 4th oxic period and 8th anaerobic period, Mössbauer only detects goethite. However, the combined amount of ferrihydrite and goethite from LCF of the EXAFS data is similar to the amount goethite detected by Mössbauer, which is not able to differentiate between ferrihydrite and goethite at these concentrations.

4. Discussion

In this study, we investigate the effect of varying Fe(II) concentration during anaerobic conditions on Fe (hydr)oxide mineralogy over multiple, short abiotic redox cycles, where ferrihydrite is the initial mineral phase. Redox oscillations on similar time-scales to our study are commonly observed in the environment. For example, in upland tropical forests, soils are more likely to undergo redox cycling on a time scale ranging from 24 hours to 4 days (Pett-Ridge and Firestone 2005). Rapid redox oscillations are also observed in the vadose zone as a result of rainfall events. Hansen et al., (2011) shows that redox conditions can change from reducing to oxidizing conditions as rainwater transports electron acceptors such as dissolved oxygen deeper into the system. Generally, E_h values became more positive in response to rainfall events but redox conditions are typically restored to previous background levels within a day (Hansen et al 2011).

Although, changes in Fe (hydr)oxide mineralogy are characterized during redox cycling in previous studies, often one or more factors limit the ability to draw conclusions regarding the evolution of poorly crystalline Fe (hydr)oxide minerals during rapid abiotic redox cycling. For example, Stewart et al. (2009) examines the incorporation of uranium into the products of redox cycling of ferrihydrite; however, Fe (hydr)oxide mineralogy

was only characterized at a single time point. Couture et al. (2015) examines the fate of multiple contaminants during redox cycling of natural, Fe rich sediments; however, Fe (hydr)oxide mineralogy was not characterized as part of the study. Mejia et al. (2016) and Thompson et al. (2006) utilize relatively long, biologically driven redox cycles (weeks to months), while Byrne et al. (2015) initiates the study by biological oxidation of magnetite. Information regarding the fundamental reaction of dissolved Fe(II) catalyzed transformation of poorly crystalline Fe(III) (hydr)oxides over multiple, short redox cycles is lacking.

Under anaerobic conditions, the products of Fe(II) catalyzed transformation of poorly crystalline Fe(III) (hydr)oxides have been well characterized and are determined by the concentration of dissolved Fe(II); a low molar ratio of Fe(II): ferrihydrite (≥ 0.072) leads to the formation of lepidocrocite and goethite while a high molar ratio (≤ 0.72) leads to the formation of goethite and magnetite. (Boland et al., 2014, 2013; Handler et al., 2014, 2009; Hansel et al., 2005, 2004; Jeon et al., 2003; Latta et al., 2012; Liu et al., 2007; Pedersen et al., 2005; Postma, 1993; Usman et al., 2012; Yang et al., 2010; Yee, 2006). Here, we observe similar mineralogical transformations during the initial Fe(II) catalyzed transformation of ferrihydrite; however, as short redox cycles continue we observe that the limited reaction time between dissolved Fe(II) and Fe(III) (hydr)oxides results in limited mineralogical transformation. We also observe solid-phase disequilibrium between ferrihydrite and goethite at low Fe(II) concentrations, and magnetite and maghemite at high Fe(II) concentrations. Finally, elevated dissolved Fe(II) leads to an overall increase in the stoichiometry (i.e., Fe(II) content) of magnetite despite periodic exposure to excess oxidant during every oxidizing half cycle.

4.1 Mineral Assemblage Reactivity With Fe(II)

In natural systems, the ratio of dissolved Fe(II) to total Fe varies based on a number of biogeochemical parameters including the composition of the microbial community as well as the bioavailability of carbon and iron. This ratio is an important variable driving mineralogical transformation (Boland et al., 2014, 2013; Hansel et al., 2005, 2004; Yang et al., 2010; Yee, 2006). Here, we constrain this ratio to 0.46 ± 0.13 Fe(II)_{added}:Fe_{Total} in the high Fe(II) reactors or 0.08 ± 0.03 in the low Fe(II) reactors throughout the experiment to allow us to examine the impact of redox cycling on mineralogical transformation rather than the impact of varying Fe(II) to total Fe ratios. The molar ratio of Fe(II):total Fe, with the exception of the 3rd anaerobic period in the low Fe(II) reactors, remains within these values in both sets of reactors (Appendix B, Table A.1). During the 3rd anaerobic period in the low Fe(II) reactors, additional Fe(II) is introduced to test the stability of ferrihydrite; however, the formation of magnetite is not observed, despite it being an expected product of a high ratio system. Therefore, while the ratio is elevated during the 3rd anaerobic period in the low Fe(II) reactors, two redox cycles at lower dissolved Fe(II) concentration appear to limit the transformation of ferrihydrite into magnetite. The lack of a transformation may be due to limited Fe(II) interaction with ferrihydrite, caused by the passivation of the ferrihydrite surface by goethite formation and/or extensive sorption of Fe(II) to goethite (Boland et al., 2014; Hiemstra and van Riemsdijk, 2007), thereby limiting the amount of Fe(II) available to react with ferrihydrite to form magnetite. Furthermore, the short length of the anaerobic periods used here (48 hours) and interruption of the transformation process by the introduction of O₂ may not have allowed for sufficient time for magnetite formation.

Trends in aqueous Fe(II), both within an individual cycle and between different cycles, reveal differences in sorption trends and incorporation of Fe(II) into the solid, corresponding to changes in the mineral assemblage (Figures 1A, 2A). In high dissolved Fe(II) reactors, ~80% of Fe(II) remains in solution during the first anaerobic period (Figure 1A). However, due to the mineralogical transformation occurring during the first anaerobic period (Figure 1A) dissolved Fe(II) concentrations are quite variable within the period itself. This variability continues during subsequent anaerobic periods; however, by the 6th anaerobic period, aqueous Fe(II) decreases during the second 24 hours of the anaerobic period, indicating stabilization of the mineral assemblage (Figure 1A).

During the first anaerobic period in the low Fe(II) reactors, when ferrihydrite is the only phase present, Fe(II) sorption is rapid. Half of the initial 1.0 mM Fe(II) is removed from solution prior to the collection of the first sample (~ 2 minutes) (Figure 2A). An increase in aqueous Fe(II) occurs at 48 hours of the first anaerobic period, likely due the formation of goethite (Figure 2). After the amount of goethite stabilizes, Fe(II) sorption rates decrease, and the changes in aqueous Fe(II) are measureable on the timescale of our experiment (Figure 2A). Slower incorporation of Fe(II) onto/into the solid results in slower Fe(III) dissolution, contributing to the preservation of ferrihydrite throughout redox cycling in the low Fe(II) reactors (Figure 2B).

Incomplete conversion of ferrihydrite also occurs also under solely anaerobic conditions (Hansel et al., 2005). Fe(III) associated with secondary mineral formation may be surface bound, resulting in goethite formation on top of the pre-existing solid, while preserving ferrihydrite in the interior. TEM and SEM imaging reveal acicular goethite crystals growing out of ferrihydrite, (Boland et al., 2014; Hansel et al., 2005) suggesting

that spatially heterogeneous mineral assemblages form without complete starting material dissolution. It is unlikely that the ferrihydrite surface are completely passivated by a layer of secondary minerals, as the nomenclature “ferrihydrite core” might suggest, instead, the assemblage is likely heterogeneous with regions of the more crystalline phases forming around ferrihydrite but not completely passivating the surface. Here, the introduction of O_2 disrupts the conversion of ferrihydrite to goethite and/or magnetite by limiting its exposure time to dissolved Fe(II). The formation of magnetite in the high Fe(II) reactors is delayed until the 3rd anaerobic period (Figure 1). The combination of secondary mineral surface growth and short reaction times leads to limited mineral transformation within each anaerobic period. The time necessary for complete conversion of ferrihydrite to goethite or magnetite is dependent on the ratio of Fe(II):Fe_{total}. At pH 6.9 and a ratio of Fe(II):Fe_{total} of 0.11, higher than that of the low Fe(II) reactors here, a near complete conversion of ferrihydrite to goethite is observed after 25 hours of reaction (Boland et al., 2014). At a ratio of 0.072, the conversion of ferrihydrite to goethite and lepidocrocite is near complete after 140 hours (Hansel et al., 2005). The conversion of ferrihydrite coated on glass microspheres to magnetite at high concentrations of Fe(II) (18 mM) takes 150 hours and takes 9 days at a low concentration of Fe(II) (0.36 mM). In our systems, we do not observe the complete transformation of ferrihydrite into magnetite and goethite.

4.2 Disequilibrium Between Mineral Phases

The formation and persistence of a diverse mineral assemblage indicates that oscillating redox conditions create disequilibrium between mineral phases. In low Fe(II) reactors, after the first complete redox cycle (one anaerobic and one oxic period), goethite forms, and then persists along with ferrihydrite throughout the experiment

(Figure 1B). In redox active environments, where half cycles are short, it appears that a reactive pool of a poorly crystalline Fe(III) (hydr)oxide may persist.

In the high Fe(II) reactors, magnetite of varying stoichiometry forms during the 3rd redox cycle; however, stoichiometric magnetite does not form under the conditions of this study. Similarly, this non-stoichiometric magnetite is not completely oxidized after 18 hours of exposure to air (Figures 1B, 2B). During anaerobic periods, the lattice Fe(II) content of magnetite increases (Figures 1B, 3); however, it does not reach that of stoichiometric magnetite. During oxic periods, sufficient O₂ (~9.9 mM) is introduced to completely oxidize the 3.3 mM magnetite present (Equation 2); however, only incomplete oxidation is observed.

This is likely due to the slow kinetics of structural Fe(II) oxidation and/or mineral surface passivation due to the formation of ferric (hydr)oxide (e.g., ferrihydrite), on the mineral surface.

This incomplete conversion indicates that, within the timescale of our experiment, equilibrium between solid phases within the mineral assemblage is not reached (Figure 1B). If equilibrium had been reached, the formation of either fully oxidized or stoichiometric magnetite would be observed. The ratio of magnetite to oxidized magnetite (fit as maghemite in XAS analysis) varies throughout redox cycling ranging from 0.3 after the fifth oxic period to 6.7 at the conclusion of the sixth oxic period. Mössbauer indicates that at the conclusion of successive anaerobic periods, overall magnetite stoichiometry increases, despite the exposure to excess oxygen during each oxic period (Figure 3). During oxic periods, Mössbauer reveals a decrease in magnetite

stoichiometry (Figure 3), while EXAFS data reveals an increase in maghemite (Figure 1B); however, fully oxidized magnetite is not formed. The mixture of the phases indicates incomplete reduction during anaerobic periods and incomplete oxidation during oxic periods. Thus, during short redox cycles, reduced mineral phases may persist under oxic conditions and oxidized mineral phases under reducing conditions.

4.3 Solid Phase Fe(II) Content Increases During Redox Cycling

The addition of higher dissolved Fe(II) concentration (10.0 mM Fe(II)) leads to the formation of goethite, and partially oxidized magnetite (maghemite and magnetite by EXAFS), with lattice Fe(II) content of magnetite increasing throughout redox oscillations. Analysis of Mössbauer spectra confirms increasing magnetite stoichiometry from the second anaerobic period (0.24) through the eighth oxic period (0.46) (Figure 3). Magnetite stoichiometry also varies during microbial redox cycling experiments in which non-stoichiometric magnetite is the starting mineral (Byrne et al., 2015). In Byrne et al., 2015 and our study, electron density is added during anaerobic periods (by either dissolved Fe(II) or microbial species), leading to an increase in stoichiometry and withdrawn during oxic periods (by either O₂ or microbial species) leading to a decrease in stoichiometry. When abiotic or microbial processes drive redox cycling, overall, magnetite stoichiometry increases during redox oscillations. Here, magnetite stoichiometry decreases during oxic periods, however; its stoichiometry after the seventh oxic period is higher than after the third oxic period, demonstrating Fe(II) is building up in the lattice despite some oxidation by O₂. Not only does magnetite act as a “battery” by donating and accepting electrons to and from microbial species (Byrne et al., 2015), but

is also capable of building up electron density or charge when formed abiotically during redox oscillations, as demonstrated by stoichiometry measurements made here.

Increasing solid Fe(II) content in magnetite greatly increases its reductive capacity. For example, magnetite with higher stoichiometry reduces organic compounds such as nitrobenzene more readily (Gorski and Scherer, 2009). Furthermore, Fe(II) in magnetite is accessible to Fe(II) oxidizing bacteria in redox active environments (Byrne et al., 2015) and the more Fe(II) in the lattice, the more reactive magnetite will be towards these microbial species.

5. Environmental Implications

Rapid redox oscillations occur in upland tropical soils (Pett-Ridge and Firestone 2005), at plant root surfaces (Emerson et al., 1999, Weiss et al., 2003) and in the vadose zone as a result of rainfall events

(Hansen et al 2011). Despite the formation of crystalline phases, ferrihydrite transformation remains incomplete after multiple, short redox cycles. The persistence of ferrihydrite in redox active systems, even in the absence of stabilizing agents (e.g., silica), may provide reactive surface area for

contaminant and/or nutrient sorption, as well as electron transfer reactions. As solid Fe(II) content increases, the reduction capacity of the mineral assemblage increases.

Figure 4. Schematic illustration of ferrihydrite transformation into a mixed mineral assemblage when cycled with 1 mM Fe(II) (left) or 10 mM Fe(II) (right) during anaerobic half cycles and $O_{2(aq)}$ during oxic half cycles. Low Fe(II) leads to a mixture of ferrihydrite and goethite while high Fe(II) leads to the formation of non-stoichiometric magnetite. Additional ferrihydrite and/or goethite likely forms during oxic periods from oxidation of sorbed or aqueous Fe(II).

Species such as Cr(VI) (Peterson et al., 1997a, 1997b) , As(V) (Coker et al., 2006), and organic contaminants (Gorski and Scherer, 2009) may be more readily reduced by solid phases after several redox cycles as opposed to after only one or two. However, continued surface passivation by goethite formation could potentially impede electron transfer reactions between contaminant species and lattice Fe(II). Continued work with this fundamental Fe(II) and Fe(III) (hydr)oxide system and chemical contaminants will further the understanding of electron transfer reactions during Fe (hydr)oxide redox cycling.

Acknowledgments

This work was funded by a grant from the Wisconsin Alumni Research Foundation. X-ray absorption spectroscopy was also performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation-Earth Sciences (EAR-1128799) and Department of Energy-GeoScience (DE-FG02094ER14466). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Thank you to the Advanced Photon Source scientists Matt Newville and Antonio Lanzorotti for excellent beamline support. We thank Jacqueline Mejia, Sarah Balgooyen and Megan McConville for their valuable contributions in both experimental design and manuscript edits. Additionally, we thank Kathleen Ginder-Vogel for her thoughtful editorial input.

References

- Benner, S.G., Hansel, C.M., Wielinga, B.W., Barber, T.M., Fendorf, S., 2002. Reductive dissolution and biomineralization of iron hydroxide under dynamic flow conditions. *Environ. Sci. Technol.* 36, 1705–1711.
- Boland, D.D., Collins, R.N., Glover, C.J., David Waite, T., 2013. An in situ quick-EXAFS and redox potential study of the Fe(II)-catalysed transformation of ferrihydrite. *Coll. Surf. A* 435, 2–8. doi:10.1016/j.colsurfa.2013.02.009
- Boland, D.D., Collins, R.N., Miller, C.J., Glover, C.J., Waite, T.D., 2014. Effect of solution and solid-phase conditions on the Fe(II)-accelerated transformation of ferrihydrite to lepidocrocite and goethite. *Environ. Sci. Technol.* doi:10.1021/es4043275
- Byrne, J.M., Klueglein, N., Pearce, C., Rosso, K.M., Appel, E., Kappler, A., 2015. Redox cycling of Fe(II) and Fe(III) in magnetite by Fe-metabolizing bacteria. *Science* 347, 1473–1476. doi:10.1126/science.aaa4834
- Coker, V.S., Gault, A.G., Pearce, C.I., van der Laan, G., Telling, N.D., Charnock, J.M., Polya, D.A., Lloyd, J.R., 2006. XAS and XMCD Evidence for species-dependent partitioning of arsenic during microbial reduction of ferrihydrite to magnetite. *Environ. Sci. Technol.* 40, 7745–7750. doi:10.1021/es060990+
- Cornell, R.M., Schwertmann, U., 2006. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*. John Wiley & Sons.
- Couture, R.-M., Charlet, L., Markelova, E., Madé, B., Parsons, C.T., 2015. On–off mobilization of contaminants in soils during redox oscillations. *Environ. Sci. Technol.* doi:10.1021/es5061879
- Emerson, D., Weiss, J.V., Megonigal, P.J., 1999. Iron-oxidizing bacteria are associated with ferric hydroxide precipitates (Fe-plaque) on the roots of wetland plants *Appl. Environ. Microb.* 65, 6, 2758–2761.
- Gorski, C.A., Scherer, M.M., 2010. Determination of nanoparticulate magnetite stoichiometry by Mossbauer spectroscopy, acidic dissolution, and powder X-ray diffraction: A critical review. *Am. Mineral.* 95, 1017–1026. doi:10.2138/am.2010.3435
- Gorski, C.A., Scherer, M.M., 2009. Influence of magnetite stoichiometry on FeII uptake and nitrobenzene reduction. *Environ. Sci. Technol.* 43, 3675–3680. doi:10.1021/es803613a
- Handler, R.M., Beard, B.L., Johnson, C.M., Scherer, M.M., 2009. Atom exchange between aqueous Fe(II) and goethite: an Fe isotope tracer study. *Environ. Sci. Technol.* 43, 1102–1107. doi:10.1021/es802402m
- Handler, R.M., Friedrich, A.J., Johnson, C.M., Rosso, K.M., Beard, B.L., Wang, C., Latta, D.E., Neumann, A., Pasakarnis, T., Premaratne, W.A.P.J., Scherer, M.M., 2014. Fe(II)-catalyzed recrystallization of goethite revisited. *Environ. Sci. Technol.* doi:10.1021/es503084u
- Hansel, C.M., Benner, S.G., Fendorf, S., 2005. Competing Fe(II)-induced mineralization pathways of ferrihydrite. *Environ. Sci. Technol.* 39, 7147–7153. doi:10.1021/es050666z
- Hansel, C.M., Benner, S.G., Neiss, J., Dohnalkova, A., Kukkadapu, R.K., Fendorf, S., 2003. Secondary mineralization pathways induced by dissimilatory iron reduction

- of ferrihydrite under advective flow. *Geochim. et Cosmochim. Acta* 67, 2977–2992. doi:10.1016/S0016-7037(03)00276-X
- Hansel, C.M., Benner, S.G., Nico, P., Fendorf, S., 2004. Structural constraints of ferric (hydr)oxides on dissimilatory iron reduction and the fate of Fe(II). *Geochim. Cosmochim. Acta*. 68, 3217–3229. doi:10.1016/j.gca.2003.10.041
- Hansen, D.J., McGuire, J.T., Mohant, B.P., 2011. Enhanced biogeochemical cycling and subsequent reduction of hydraulic conductivity associated with the soil-layer interfaces in the vadose zone. *J. Environ. Qual.* 40, 6, 1941
- Hiemstra, T., van Riemsdijk, W.H., 2007. Adsorption and surface oxidation of Fe(II) on metal (hydr)oxides. *Geochim. Cosmochim. Acta* 71, 5913–5933. doi:10.1016/j.gca.2007.09.030
- Jeon, B.-H., Dempsey, B.A., Burgos, W.D., 2003. Kinetics and mechanisms for reactions of Fe(II) with iron(III) oxides. *Environ. Sci. Technol.* 37, 3309–3315. doi:10.1021/es025900p
- Latta, D.E., Gorski, C.A., Scherer, M.M., 2012. Influence of Fe²⁺-catalysed iron oxide recrystallization on metal cycling. *Biochem. Soc. T.* 40, 1191–1197. doi:10.1042/BST20120161
- Liu, H., Li, P., Zhu, M., Wei, Y., Sun, Y., 2007. Fe(II)-induced transformation from ferrihydrite to lepidocrocite and goethite. *J Solid State Chem.* 180, 2121–2128. doi:10.1016/j.jssc.2007.03.022
- Mejia, J., Roden, E.E., Ginder-Vogel, M., 2016. Influence of oxygen and nitrate on Fe (hydr)oxide mineral transformation and soil microbial communities during redox cycling. *Environ. Sci. Technol.* 50, 3580–3588. doi:10.1021/acs.est.5b05519
- Newville, M., 2001. EXAFS analysis using FEFF and FEFFIT. *J Synchrotron Radiat.* 8, 96–100. doi:10.1107/S0909049500016290
- Pedersen, H.D., Postma, D., Jakobsen, R., Larsen, O., 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim. Cosmochim. Acta* 69, 3967–3977. doi:10.1016/j.gca.2005.03.016
- Peterson, M.L., Brown, G.E., Parks, G.A., 1996. Direct XAFS evidence for heterogeneous redox reaction at the aqueous chromium/magnetite interface. *Coll. Surf. A.* 107, 77–88.
- Peterson, M.L., Brown Jr., G.E., Parks, G.A., Stein, C.L., 1997a. Differential redox and sorption of Cr (III/VI) on natural silicate and oxide minerals: EXAFS and XANES results. *Geochim. Cosmochim. Acta* 61, 3399–3412. doi:10.1016/S0016-7037(97)00165-8
- Peterson, M.L., White, A.F., Brown, Parks, G.A., 1997b. Surface passivation of magnetite by reaction with aqueous Cr(VI): XAFS and TEM results. *Environ. Sci. Technol.* 31, 1573–1576. doi:10.1021/es960868i
- Pett-Ridge, J., Firestone, M.K., 2005. Redox Fluctuation structures microbial communities in a wet tropical soil. *Appl. Environ. Microb.* 71, 6998–7007. doi:10.1128/AEM.71.11.6998-7007.2005
- Postma, D., 1993. The reactivity of iron oxides in sediments: A kinetic approach. *Geochim. Cosmochim. Acta* 57, 5027–5034. doi:10.1016/S0016-7037(05)80015-8

- Rancourt, D.G., Ping, J.Y., 1991. Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy. *Nucl. Instrum. Meth. B* 58, 85–97. doi:10.1016/0168-583X(91)95681-3
- Reddy, K.R., Patrick, W.H., Lindau, C.W., 1989. Nitrification-denitrification at the plant root-sediment interface in wetlands. *Limnol. Oceanog.* 34, 1004–1013. doi:10.4319/lo.1989.34.6.1004
- Roden, E.E., 2012. Microbial iron-redox cycling in subsurface environments. *Biochem. Soc. T* 40, 1249–1256. doi:10.1042/BST20120202
- Roden, E.E., 2004. Analysis of long-term bacterial vs. chemical Fe(III) oxide reduction kinetics. *Geochim. Cosmochim. Acta* 68, 3205–3216. doi:10.1016/j.gca.2004.03.028
- Roden, E.E., 2003. Fe(III) Oxide Reactivity toward biological versus chemical reduction. *Environ. Sci. Technol.* 37, 1319–1324. doi:10.1021/es026038o
- Roden, E.E., Zachara, J.M., 1996. Microbial reduction of crystalline iron(III) oxides: influence of oxide surface area and potential for cell growth. *Environ. Sci. Technol.* 30, 1618–1628. doi:10.1021/es9506216
- Schuur, E.A.G., Matson, P.A., 2001. Net primary productivity and nutrient cycling across a mesic to wet precipitation gradient in Hawaiian montane forest. *Oecologia* 128, 431–442. doi:10.1007/s004420100671
- Schwertmann, U., 2000. Iron oxides in the laboratory: preparation and characterization, 2nd completely rev. and extended ed. ed. Wiley-VCH, Weinheim ; New York.
- Stewart, B.D., Cismasu, A.C., Williams, K.H., Peyton, B.M., Nico, P.S., 2015. Reactivity of uranium and ferrous iron with natural iron oxyhydroxides. *Environ. Sci. Technol.* doi:10.1021/acs.est.5b02645
- Stewart, B.D., Nico, P.S., Fendorf, S., 2009. Stability of uranium incorporated into Fe (hydr)oxides under fluctuating redox conditions. *Environ. Sci. Technol.* 43, 4922–4927. doi:10.1021/es803317w
- Stookey, L.L., 1970. Ferrozine—a new spectrophotometric reagent for iron. *Anal. Chem.* 42, 779–781.
- Thompson, A., Chadwick, O.A., Rancourt, D.G., Chorover, J., 2006. Iron-oxide crystallinity increases during soil redox oscillations. *Geochim. Cosmochim. Acta* 70, 1710–1727. doi:10.1016/j.gca.2005.12.005
- Usman, M., Abdelmoula, M., Hanna, K., Grégoire, B., Faure, P., Ruby, C., 2012. FeII induced mineralogical transformations of ferric oxyhydroxides into magnetite of variable stoichiometry and morphology. *J. Solid State Chem.* 194, 328–335. doi:10.1016/j.jssc.2012.05.022
- Van Cappellen, P., Viollier, E., Roychoudhury, A., Clark, L., Ingall, E., Lowe, K., Dichristina, T., 1998. Biogeochemical cycles of manganese and iron at the oxic-anoxic transition of a stratified marine basin (Orca Basin, Gulf of Mexico). *Environ. Sci. Technol.* 32, 2931–2939.
- Weiss, J. V., Emerson, D., Backer, S.M., Megonigal, P.J., 2003. Enumerations of Fe(II)-oxidizing and Fe(III)-reducing bacteria in the root zone of wetland plants: Implications for a rhizosphere iron cycle. *Biogeochemistry.* 64, 1, 77-96.

- Yang, J., Kukkadapu, R.K., Dong, H., Shelobolina, E.S., Zhang, J., Kim, J., 2012. Effects of redox cycling of iron in nontronite on reduction of technetium. *Chem. Geol.* 291, 206–216. doi:10.1016/j.chemgeo.2011.10.013
- Yang, L., Steefel, C.I., Marcus, M.A., Bargar, J.R., 2010. Kinetics of Fe(II)-catalyzed transformation of 6-line ferrihydrite under anaerobic flow conditions. *Environ. Sci. Technol.* 44, 5469–5475. doi:10.1021/es1007565
- Yee, N., 2006. The rate of ferrihydrite transformation to goethite via the Fe(II) pathway. *Amer. Mineral.* 91, 92–96. doi:10.2138/am.2006.1860