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A Closer Look at Fe(II) Passivation of Goethite

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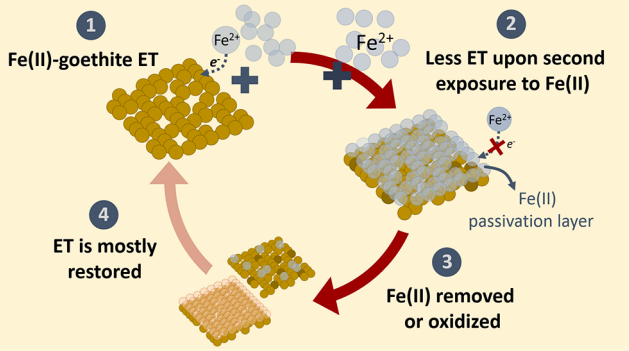
Supporting Information

ABSTRACT: Our understanding of how Fe(II) reacts with Fe(III) oxides has evolved based on evidence for electron transfer at the oxide−water interface and Fe(II)-catalyzed recrystallization. There is, however, some evidence that these, and other processes, such as microbial reduction, cease after continued contact with Fe(II) as the Fe oxide becomes "passivated". Here, we explore the mechanism of oxide passivation by measuring whether exposure to Fe(II) inhibits Fe(II)−goethite electron transfer, and whether this inhibition is reversible. To quantify the extent of electron transfer, we used selective isotope labeling with ^{57}Fe Mössbauer spectroscopy. We provide experimental evidence that pre-exposure to Fe(II) alters the products formed and inhibits the extent of electron transfer between goethite and Fe(II). We demonstrate that the goethite surface can accumulate a passivation layer of sorbed Fe(II) and that further electron transfer between Fe(II) and goethite is inhibited. Importantly, however, electron transfer can be partially restored upon removal of the layer of Fe(II) by extraction or oxidation. Our results suggest that in environments that are commonly subjected to transient geochemical fluctuations, electron transfer between Fe(II) and Fe oxides, and processes linked to it are likely to be relevant beyond just short time scales.



KEYWORDS: *Electron transfer, Fe(III) oxide, reductive dissolution, Fe oxide recrystallization, ETAE*

INTRODUCTION

Electron transfer between aqueous Fe(II) and Fe(III) oxides was invoked several decades ago to explain nonreversible adsorption of divalent metal ions on Fe oxides as well as Fe(II)-catalyzed reductive dissolution of Fe(III) oxides.[1−3] The last two decades have witnessed the accumulation of substantial experimental evidence, primarily based on bulk measurement techniques such as Mössbauer spectroscopy that demonstrate electron transfer occurs between Fe(II) and hematite, goethite, magnetite, ferrihydrite, and Fe-containing clay minerals over a wide range of conditions.[4−17]

Experimental confirmation of electron transfer between Fe(II) and Fe(III) oxides has significantly altered our conceptual understanding of environmental and geochemical processes involving Fe minerals. For example, contaminant reduction by Fe oxides in the presence of Fe(II) has been suggested to involve more than sorbed Fe(II) simply being a better reductant than aqueous Fe(II),[18] but rather that electron transfer between sorbed Fe(II) and the mineral creates a more thermodynamically stable iron oxide that makes the oxidation of Fe(II) more thermodynamically favorable. Secondary mineral transformation of metastable Fe oxides such as ferrihydrite to goethite or magnetite, and lepidocrocite to magnetite[19−25] are also now thought to involve an initial electron transfer step,[26,27] and electron transfer current density has been suggested to control mineral transformation.[28] Another significant and perhaps more controversial conceptual shift arising from experimental validation of Fe(II)−Fe(III) oxide electron transfer is the idea that Fe(II) catalyzes Fe oxide recrystallization of stable Fe oxide phases (often referred to as Fe atom exchange). Fe(II)-catalyzed Fe oxide recrystallization of stable iron oxides, such as goethite, was shown to occur in the absence of secondary mineral transformation and electron transfer is thought to play an initial first step here as well.[21,25]

Despite the suspected role of Fe(II)−Fe(III) oxide electron transfer in these processes, it is still unclear what controls Fe(II)−Fe(III) oxide electron transfer at the molecular or macroscopic scale. Recent computational molecular simulations and experiments with hydrothermally treated oxides,

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however, have provided some useful insights to Fe(II)−Fe(III) oxide electron transfer at the molecular scale. For example, density functional theory (DFT) calculations[29,30] as well as classical molecular dynamics (MD) simulations of atomically flat stoichiometric goethite (110) surfaces indicate that electron transfer from inner-sphere sorbed Fe(II) to adjacent lattice Fe(III) in goethite is, at best, a thermoneutral reaction with a large activation energy.[31] Both DFT calculations and MD simulations, however, also indicate that surface defects such as oxygen vacancies could substantially decrease this activation energy.[29] Experimental work with goethite also suggests that defects enable electron transfer.[32] Goethite synthesized by hydrolysis at low temperature revealed an Fe-deficient surface that was found to be more electron transfer-active with Fe(II) compared to more stoichiometric surfaces synthesized under hydrothermal conditions. It was thus proposed that the interfacial electron transfer mechanism entailed Fe(II) uptake into Fe vacancies followed by its oxidation and deposition into those sites, effectively healing the reactive surface defect content.[32,33]

While we have some insights into the factors controlling Fe(II)−Fe(III) oxide electron transfer at the molecular scale (e.g., defects), there are only indirect hints of macroscopic conditions that might be influencing the reactions between Fe(II) and Fe(III) oxides. For example, Fe(II) exposure substantially decreases rates of microbial respiration of Fe(III) oxides, such as goethite and hematite.[34−36] Sorption of Si onto lepidocrocite and schwertmannite have been suggested to inhibit atom exchange.[37] Further, Fe(II) concentrations above saturation have been reported to inhibit electron transfer between Fe(II) and hematite,[8] and the coating of goethite with 1,2-dioleoyl-*sn*-glycero-3-phosphatidic acid (DOPA) completely inhibited electron transfer. Finally, Fe(II)-catalyzed recrystallization of goethite was shown to diminish after increasingly delayed exposures to Fe(II), leading some to suggest that this process may only be relevant over short time scales.[38] Because Fe(II)−Fe(III) oxide electron transfer is a necessary step for microbial Fe respiration, as well as being considered integral to Fe(II)-catalyzed recrystallization,[32] it seems plausible that contact with Fe(II) alters the oxide surface in such a way that further electron transfer is inhibited.

To determine whether contact with Fe(II) alters the oxide surface in such a way that inhibits further electron transfer, we used Fe isotopes and Mössbauer spectroscopy to isolate what happened to Fe(II) reacted with goethite that had been previously reacted with Fe(II). Specifically we exposed goethite to aqueous ^{56}Fe(II) for various time periods and then evaluated the extent of electron transfer upon a second exposure to ^{57}Fe(II). We further evaluated how changes in the geochemical conditions would affect further electron transfer. Our findings indicate that exposure to Fe(II) inhibits electron transfer and that longer exposure time results in less electron transfer. Importantly, removing the sorbed Fe(II) by acid/buffer extraction or air oxidation mostly restores electron transfer.

METHODS

Oxide Synthesis. Synthesis procedures for goethite particles used in this study have been described previously.[33] Briefly, goethite was prepared from ^{56}Fe-enriched Fe metal ((Isoflex, 99.94% purity), ^{56}Fe goethite) by modifying the Schwertmann and Cornell method, using iron metal as the synthesis starting point instead of $Fe(NO_3)_3$.[39] The final mineral corresponded to the "as-synthesized goethite" of our most recent paper,[33] and it is similar to the microgoethite used in our previous work.[5,6,11,15,40,41] The Brunauer−Emmett−Teller (BET) specific surface area was determined by N_2 soprtion at 77 K and found to be ∼28−34 $m^2\ g^{-1}$. X-ray diffraction (XRD, Rigaku Mini FlexII) patterns showed that the material contains goethite and no other minerals.

Electron Transfer Experiments. All experiments were carried out in an anaerobic glovebox with N_2/H_2 atmosphere (93/7%), and all solutions were purged at least 2 h with N_2 prior to transfer into the glovebox. Fe(II) stock solutions were prepared inside the glovebox by reacting ^{57}Fe metal (Cambridge Isotope, 96.93% purity) or ^{56}Fe metal (Isoflex, 99.94%) with 1 M HCl overnight. The resulting solution was filtered to remove any residual Fe(0) and diluted with deionized (DI) water to the desired concentration (∼100 mM Fe(II), ∼0.1 M HCl).

Batch reactors were prepared by adding 10 mL of 25 mM KBr/25 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), pK_a 7.55[42]) buffer adjusted to pH 7.5 ± 0.05 to a 20 mL glass vial and adding Fe(II) stock to reach an initial Fe(II) concentration. The reaction was started by adding 20.0 ± 0.2 mg of ^{56}Fe goethite, and the reactors were placed on a end-over-end rotator in the absence of light. Samples of the suspension were filtered (0.2 μm), and the filtered solutions were acidified with trace metal grade HCl for subsequent Fe(II) and total Fe analysis using the 1,10-phenanthroline method.[43]

Respike Experiments. Reactors of ^{56}Fe goethite reacting with 1 mM ^{56}Fe(II) (or buffer alone) were prepared as described in the Electron Transfer Experiments section and kept in the end-over-end rotator for periods of time varying from 18 h (overnight) to 365 days. The reacted solids were then centrifuged (6000 rpm), the aqueous phase was poured off and the solids were resuspended in 10 mL of 1 mM ^{57}Fe(II). After overnight reaction with ^{57}Fe(II) the solids were filtered (0.2 μm) and analyzed with Mössbauer spectroscopy.

Respike Experiments on Extracted Samples. Another set of reactors was also pre-exposed to 1 mM ^{56}Fe(II) for different periods of time but further extracted before the respike. Specifically, the pre-exposed solids were centrifuged (6000 rpm), the aqueous phase was poured off, and the solids resuspended in 0.4 M HCl for 15 min or HEPES buffer at pH 5.3 for 1 h. The extracted solids were centrifuged again, the extractant was poured off, and the solids were then resuspended in 1 mM ^{57}Fe(II). After overnight reaction, the solids were analyzed with Mössbauer spectroscopy.

Oxidation Experiment. ^{56}Fe goethite was pre-exposed to 1 mM ^{56}Fe(II) for different periods of time. The reacted solids were then centrifuged (6000 rpm), the liquid fraction was poured off, and the solids were removed from the glovebox and air oxidized overnight. The solids were then brought inside the glovebox and allowed to degas. The solids were then resuspended in 1 mM ^{57}Fe(II). After overnight reaction, the suspensions were filtered, and the solids collected on 0.2 μm nitrocellulose filters were analyzed with Mössbauer spectroscopy.

One reactor was subjected to three cycles of oxidation. Specifically, ^{56}Fe goethite was pre-exposed to 1 mM ^{56}Fe(II) overnight, centrifuged, air oxidized overnight, brought inside the glovebox, and exposed again to 1 mM ^{56}Fe(II). The process was repeated until the solids were air oxidized three times. The solids were then brought inside the glovebox and

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allowed to degas. The solids were then resuspended in 1 mM ^{57}Fe(II). After overnight reaction the solids were analyzed with Mössbauer spectroscopy.

Mössbauer Spectroscopy. For Moössbauer spectroscopy, solids were collected on a 0.2 μm nitrocelullose filter and then sealed between two pieces of Kapton tape to avoid air oxidation. Mössbauer spectra were collected at 77 K on a spectrometer supplied by Web Research, Inc. (Edina, Minnesota, USA) and equipped with closed-cycle cryostat (CCS-850 System, Janis Research Co., Wilmington, Massachusetts, USA). We acquired spectra in transmission mode using a constant acceleration drive system and a ^{57}Co source. The velocity scale was calibrated using a 7-μm α-Fe(0) foil. We fit the spectra using the software Recoil (Ottawa, Canada).[44]

X-ray Absorption Spectroscopy (XAS)/X-ray Magnetic Circular Dichroism (XMCD). In an anaerobic glovebox to avoid air oxidation, goethite suspensions were deposited onto indium foil, dried, then pressed into the foil and the excess solid was removed. Silver paint was used to attach the indium foil to the copper sample manipulator for loading (under N_2) into the magnetic spectroscopy endstation on Beamline 6.3.1.1 at the Advanced Light Source (Berkeley, CA). Fe $L_{2,3}$-edge XAS was recorded at room temperature in total electron yield mode, with an effective probing depth of 50 Å. Fe $L_{2,3}$-edge XMCD spectra were obtained by measuring two XAS spectra with a fixed degree of circular polarization of ~0.7 and with opposing magnetization directions by reversing the 1.8 T applied field. The XAS spectra were normalized to incident beam intensity, and the XMCD spectrum was obtained as the difference between the two spectra.

RESULTS AND DISCUSSION

Effect of Fe(II) Exposure on Electron Transfer. To determine if reaction with Fe(II) inhibits Fe(II)−goethite electron transfer, we sequentially reacted goethite made from ^{56}Fe (Mössbauer- inactive) with Fe(II). Specifically, we exposed ^{56}Fe goethite to 1 mM ^{56}Fe(II) for one month before reacting it with 1 mM ^{57}Fe(II) (Mössbauer-active). In this way, we could isolate the second addition of Fe(II) as only these Fe atoms were visible to ^{57}Fe Mössbauer spectroscopy. Note that with this approach, we are characterizing what happens to the new Fe atoms sorbed to the goethite during the second Fe(II) exposure. When we compare the Mössbauer spectra of ^{57}Fe(II) reacted with ^{56}goethite aged in buffer alone with ^{56}goethite reacted with ^{56}Fe(II), we see marked differences in the spectra (Figure 1). For ^{56}goethite aged in buffer alone, the Mössbauer spectrum of the reacted solids showed formation of predominantly Fe(III) sextets that have Mössbauer parameters similar to goethite (Figure 1 and Table S1) (sextet 1 has CS = 0.48 mm s^{-1} and QS = −0.17 mm s^{-1}; sextet 2 has CS = 0.48 mm s^{-1} and QS = 0.07 mm s^{-1}).[11,33] The prevalence of the Fe(III) sextets indicates that most of the ^{57}Fe(II) that sorbed onto goethite was oxidized. These results are consistent with previous observations and confirm that electron transfer between Fe(II) and goethite induces growth of an Fe(III) layer similar to bulk goethite.[5,6,11,14,15,17,33,40,41]

In contrast, when goethite is exposed to 1 mM ^{56}Fe(II) for one month before reacting with ^{57}Fe(II), less than half of the spectral area is captured by (the goethite) Fe(III) sextets (Figure 1). The decreasing area of the sextets indicates that goethite is no longer the main product of the reaction with Fe(II). Less Fe(II), however, sorbs when goethite is exposed to

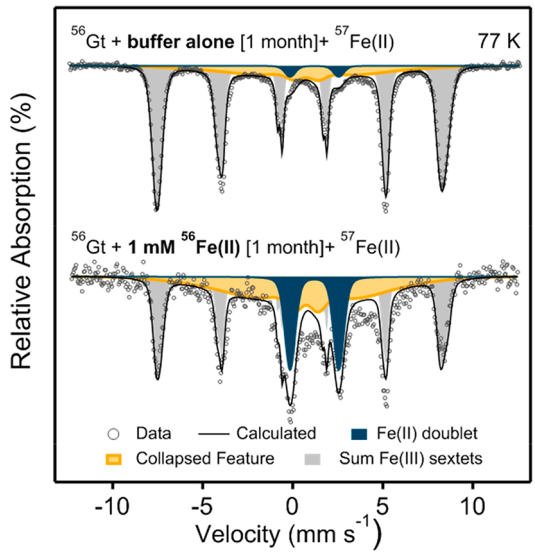

Figure 1. Mössbauer spectra of ^{56}goethite aged for one month in buffer alone and reacted with 1 mM ^{57}Fe(II) (top spectrum). ^{56}Goethite aged in 1 mM ^{56}Fe(II) for one month and reacted with 1 mM ^{57}Fe(II) (bottom spectrum).

^{56}Fe(II) before reacting it with ^{57}Fe(II) (30 compared to 139 μmol g^{-1} in Figure 1; see Table S1) (this can be seen in the higher noise to signal ratio in the sample first reacted with ^{56}Fe(II) in Figure 1). To confirm that the change in reaction products is not simply due to less ^{57}Fe(II) sorption, we reacted ^{56}Fe goethite with 0.05 mM ^{57}Fe(II) and compared the spectrum with a sample that was exposed to 1 mM ^{56}Fe(II) for one month before reacting it with 1 mM ^{57}Fe(II). Both samples sorbed similar amounts of ^{57}Fe(II) (25 and 30 μmoles g^{-1}), but only the sample that was previously exposed to ^{56}Fe(II) before reacting with ^{57}Fe(II) contained the large collapsed feature and Fe(II) doublet (Figure S1). The sample that was not exposed to Fe(II) contained only a small Fe(II) doublet and collapsed feature suggesting that the change in reaction products seen in Figure 1 is not due to less sorption of ^{57}Fe(II) but is a result of previous reaction with Fe(II). Data on Fe(II) sorption was based on the Fe(II) decrease in solution. Therefore, it is possible that in a second exposure ^{57}Fe(II) exchanged with ^{56}Fe(II) resulting in slightly higher ^{57}Fe(II) sorption than reported.

To investigate whether the length of time the goethite was reacted with Fe(II) influenced the products formed from oxidation of sorbed Fe(II) by goethite, we exposed ^{56}goethite to 1 mM ^{56}Fe(II) for different periods of time before reacting it with 1 mM ^{57}Fe(II). When goethite is exposed to buffer alone for 5 min and then reacted with ^{57}Fe(II) (Figure 2A), we see a Mössbauer spectrum predominantly captured by Fe(III) sextets, nearly identical to the goethite aged in buffer alone for one month. However, when we reacted goethite with ^{56}Fe(II) overnight before reacting it with ^{57}Fe(II), we see distinct changes in the Mössbauer spectrum with a larger Fe(II) doublet and a collapsed feature emerging. As goethite is exposed to ^{56}Fe(II) for longer times there is a clear trend of decreasing sextets area and increasing doublet area and collapsed feature. To quantify the changes in reaction products of ^{57}Fe(II) sorbed in the second Fe(II) exposure, we compared the percent area of the sextets, Fe(II) doublet, and collapsed feature as a function of how long the goethite was exposed to

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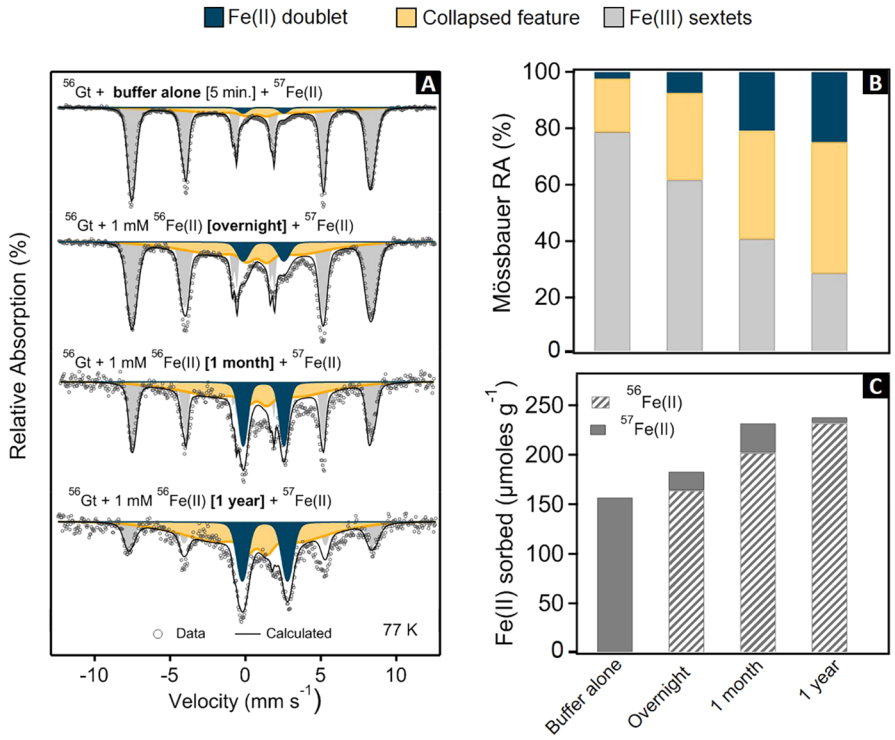

Figure 2. (A) Mössbauer spectra of ^{56}goethite reacted with 1 mM ^{57}Fe(II) after previous reaction with buffer alone for 5 min, with 1 mM ^{56}Fe(II) overnight, with 1 mM ^{56}Fe(II) for 1 month, and 1 mM ^{56}Fe(II) for 1 year. (B) Relative Mössbauer spectral area (RA) of Fe(III) sextets, Fe(II) doublet, and collapsed feature for panel A spectra. (C) Amount of ^{56}Fe(II) and ^{57}Fe(II) sorbed for samples in panel A.

^{56}Fe(II) (Figure 2B). The sextets (gray shading) decrease from 77% for goethite aged in buffer alone, to only 29% after a year of being exposed to ^{56}Fe(II). In contrast, the Fe(II) doublet (blue shading) increases with longer Fe(II) exposure times starting at only 2% for buffer alone and approaching 25% after a year of Fe(II) exposure. Similar to the Fe(II) doublet, the collapsed feature (yellow shading) increases as the Fe(II) exposure time increases (from 19% to 46% after one year).

The decreasing area of the sextets (i.e., goethite) and increasing area of the Fe(II) doublet and collapsed feature with longer Fe(II) exposure times indicates that goethite is no longer the main product of the reaction with Fe(II). The doublet is readily identified as Fe(II) based on the Mössbauer parameters (CS = 1.21 mm s^{-1}; QS = 2.7 mm s^{-1}). Large Fe(II) doublets have been previously observed when reacting goethite with Fe(II), but only in the presence of Shewanella medium (after filter sterilization) or high concentrations of organic matter.[15,45] The only observation we know of where the Fe(II) doublet comprised 100% of the spectral area, and therefore no Fe(II)−goethite electron transfer occurred, was when an 18-C chain phospholipid was sorbed to goethite prior to reaction with Fe(II).[11] The increase in doublet area with increased exposure time to Fe(II) indicates that a smaller fraction of the sorbed Fe(II) is oxidized in the second Fe(II) addition compared to first Fe(II) addition. We emphasize that we are not comparing the mass of Fe(II) that was found on goethite surface (i.e., percentage of Fe(II) doublet × μmoles of Fe(II) sorbed), but instead characterizing the fate of the new Fe atoms that sorbed onto goethite (or were exchanged with sorbed ^{56}Fe(II)).

Whereas the Fe(II) doublet is readily identified as Fe(II), the collapsed feature is more challenging to interpret. To probe its composition, we collected the 4 K Mössbauer spectrum to see if the collapsed feature ordered. If the collapsed feature was a superparamagnetic Fe(III) phase, it should order to a sextet as the temperature is lowered,[46] yet it does not order even at 4 K (Figure S2). Others have observed some Fe-containing natural soils with collapsed features that did not order at 4.2 K;[47] however, these samples likely contained natural organic matter (NOM) and/or cation substitutions such as Al, which are known to lower the ordering temperature.[48] We further probed the collapsed feature by oxidizing it by exposing it to air for one month. Air oxidation of goethite reacted with Fe(II) removed both the collapsed feature and Fe(II) doublet (Figure S3), similar to what we observed in our previous work.[33] We suspect that loss of the collapsed feature upon air exposure, as well as not ordering even at 4 K (in the absence of NOM and cation substitution), indicates that collapsed feature likely contains some Fe(II) and that the increasing area of the collapsed feature suggests additional inhibition of electron transfer beyond what was observed by the increasing Fe(II) doublet.

While our Mössbauer results provide clear evidence that previous exposure to Fe(II) alters both the products formed and the extent of electron transfer between Fe(II) and goethite, we also wanted to evaluate whether the amount of Fe(II) that sorbs or aging of goethite played a role. We first considered whether the amount of Fe(II) sorbed (in the first addition) influences the products formed and extent of electron transfer. As shown in Figure 2C, the amount of ^{56}Fe(II) sorbed in the first Fe(II) exposure increases with increasing exposure time (from 165 μmol g^{-1} for overnight to 202 for one year) suggesting it may influence the products formed. To test this, we reacted ^{56}goethite with a 10-fold lower ^{56}Fe(II) concentration (0.1 compared to 1 mM) and then reacted the goethite with 1 mM ^{57}Fe(II). As expected,

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substantially less sorption occurred with the lower Fe(II) concentration (48 μmol g^{-1}) compared to the higher Fe(II) concentration (202 μmol g^{-1}) (Figure 3A). We observed more sextet area (56%) for the goethite that sorbed a smaller amount of Fe(II) than for goethite that sorbed a higher amount of Fe(II) (41%) (Figures 3A and S4) indicating that more Fe(II) sorption does indeed cause a small shift (~15%) in products and extent of electron transfer. The 4-fold increase in Fe(II) sorption, however, led to only an ~15% decrease in sextet's area suggesting that, while the amount of Fe(II) sorbs has some effect, it is not responsible for the close to 50% decrease observed when goethite is prereacted with Fe(II) for overnight compared to one year (Figure 2B).

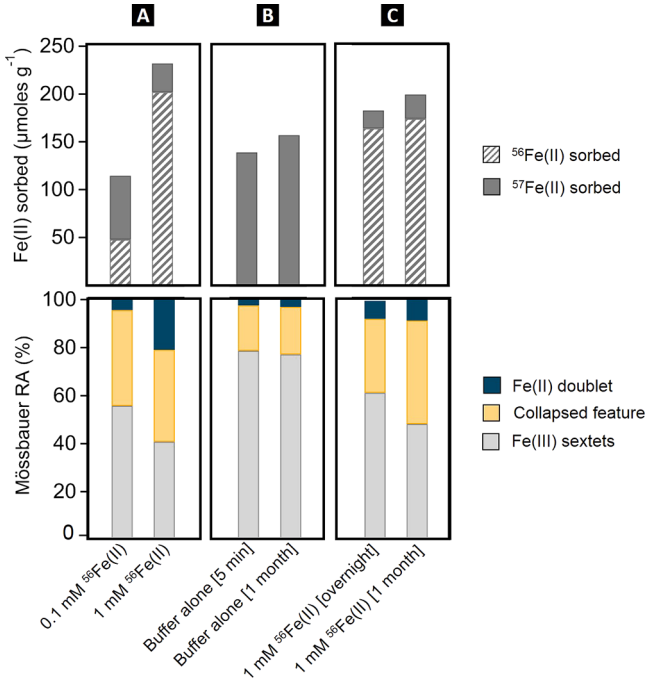

Figure 3. Sorbed Fe(II) data and relative Mössbauer spectral area (RA) of Fe(III) sextets, Fe(II) doublet, and collapsed feature for samples (A) comparing low and high ^{56}Fe(II) sorption, (B) aging time in buffer alone, and (C) aging time in 1 mM ^{56}Fe(II). Mössbauer spectra for this data are provided in Figure S4.

Next we considered whether the change in products and extent of electron transfer happened simply due to goethite aging (with and without Fe(II)) rather than the reaction with Fe(II). To test if aging in the absence of Fe(II) leads to inhibition of electron transfer we aged ^{56}goethite in buffer alone for 5 min and for 1 month and then reacted it with 1 mM ^{57}Fe(II). We observed a negligible difference in the spectra of goethite aged for 5 min or for 1 month indicates that aging of goethite in buffer alone has little effect (Figure 3B). We also investigated aging goethite in the presence of Fe(II) by comparing goethite samples that sorbed similar amounts of ^{56}Fe(II) and ^{57}Fe(II) but that reacted with ^{56}Fe(II) for different times (overnight and 1 month). Goethite that was aged with ^{56}Fe(II) for one month had smaller Fe(III) sextets than goethite that was exposed overnight (48% compared to 61%) (Figure 3C). Our findings suggest that the sorbed Fe(II) or new layer of goethite matures over time and becomes less able to accept electrons. In summary, our results suggest that aging of goethite in buffer alone (in the absence of Fe(II)) does not measurably affect Fe(II)−goethite electron transfer products or extent. In contrast, we found that the amount of Fe(II) that sorbs onto goethite in the first exposure and the aging of goethite (in the presence of Fe(II)) result in some

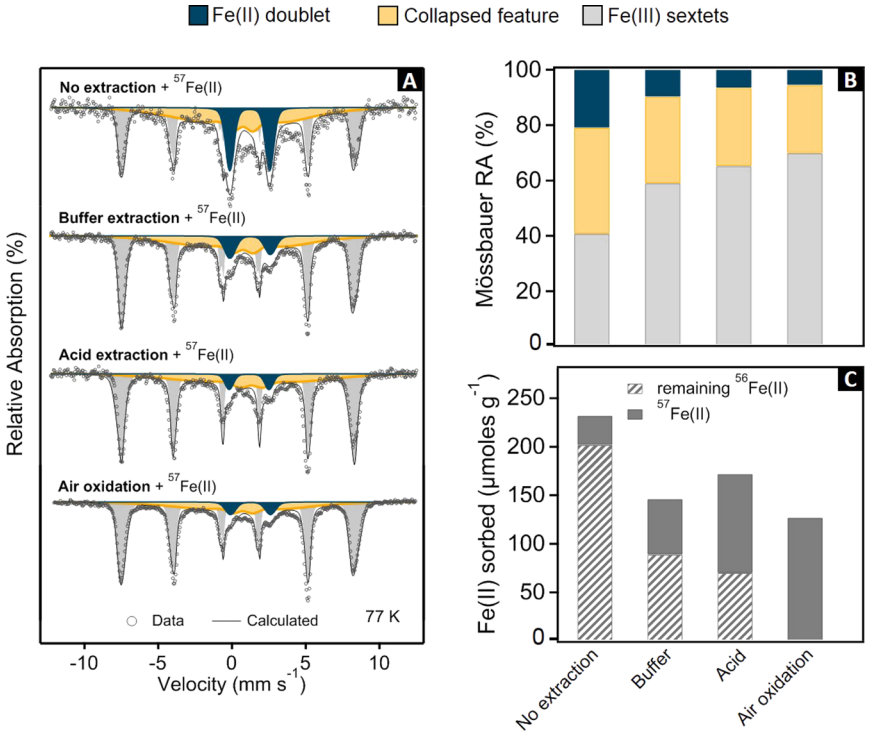

Figure 4. (A) Mössbauer spectra of ^{56}goethite reacted with 1 mM ^{57}Fe(II) after previous reaction with 1 mM ^{56}Fe(II) [1 month], before and after buffer extraction, acid extraction, and air oxidation. (B) Relative Mössbauer spectral area (RA) of Fe(III) sextets, Fe(II) doublet, and collapsed feature for panel A samples. (C) Amount of ^{56}Fe(II) and ^{57}Fe(II) sorbed for samples in panel A.

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change in reaction products and inhibition of electron transfer. Neither amount of Fe(II) sorbed or aging of goethite (Figure 3), however, has as large effect on the reaction products as the length of time that goethite is reacted with Fe(II) (Figure 2B).

Can We Restore Electron Transfer? The dominant role of Fe(II) in changing the reaction products and inhibiting the extent of Fe(II)−goethite electron transfer raises the question of whether it is restored when Fe(II) is removed. Fe(II) desorption and oxidation are likely to occur during geochemical fluctuations arising from changes in pH, Fe(II) concentrations, or redox conditions.[49] To test whether electron transfer could be restored by removing Fe(II), we chemically extracted or oxidized the Fe(II) and further reacted the solids with ^{57}Fe(II). More specifically, we reacted ^{56}goethite with ^{56}Fe(II) for one month and extracted the solids with HEPES buffer, which removed 47% of the ^{56}Fe(II) initially sorbed (Figure 4C). The extracted goethite was then reacted with 1 mM ^{57}Fe(II) overnight. Removing the Fe(II) with a buffer extraction resulted in significantly smaller Fe(II) doublet and collapsed feature, suggesting buffer extraction partially restores electron transfer (Figure 4A,B). We also tested a stronger extraction with 0.4 M HCl that recovered 64% of the Fe(II) initially sorbed (Figure 4C). Acid extraction resulted in even smaller Fe(II) doublets and collapsed feature indicating that electron transfer was restored even more than with the buffer extraction (Figure 4A,B).

In addition to pH fluctuations, soils can also experience changes in redox conditions during water table fluctuations[50,51] that may remove Fe(II) by oxidation, rather than dissolution. To test if oxidation of Fe(II) affects subsequent Fe(II)−goethite products and electron transfer, we exposed ^{56}goethite to 1 mM ^{56}Fe(II) for one month and then exposed the solids to the ambient air. After overnight exposure to air, the solids were resuspended in 1 mM ^{57}Fe(II) in an anaerobic glovebox. Air oxidized the Fe(II) and resulted in a smaller doublet and collapsed feature indicating that oxidation substantially restored electron transfer (Figure 4A,B). Interestingly, oxidation of the goethite/Fe(II) also results in more ^{57}Fe(II) sorption compared to the nonoxidized samples (Figure 4C).

Taken together, the results from acid/buffer extraction and air oxidation suggest that when goethite is exposed to Fe(II), a layer of sorbed Fe(II) forms and passivates the surface giving rise to a change in reaction products and inhibition of further electron transfer. Note that Fe(II) comes from both the Fe(II) that sorbed but did not oxidize, as well as the Fe(III) in goethite that was reduced (see discussion in SI, Figure S5).[41] As shown in Figure 4, when the Fe(II) is removed either by extraction or oxidation, Fe(II)−goethite electron transfer is partially restored. Interestingly, when we extracted and oxidized goethite exposed to Fe(II) for a shorter period of time (overnight instead of a month), more Fe(II) was removed (Table S1), and electron transfer was restored even more (Figure S6). This suggests that in addition to passivation of the goethite surface by Fe(II), there is also some maturing of the layer of sorbed Fe(II) that makes it more difficult to restore the electron transfer by removing the Fe(II) after longer exposure times.

How Does Fe(II) Inhibit Electron Transfer? Our Mössbauer data clearly demonstrates that exposure to Fe(II) partially inhibits further Fe(II)−goethite electron transfer and that removing or oxidizing the Fe(II) can restore some electron transfer. To probe how Fe(II) changes the surface compositional characteristics of goethite and inhibits electron transfer, we used Fe *L*-edge XMCD. In stoichiometric goethite, two spin antiparallel Fe magnetic sublattices yield an antiferromagnetic structure, and thus, no net magnetic moment would be observed. As we have previously shown though, goethite chemically synthesized in the laboratory shows a weak magnetic moment comprising predominantly the site occupied by octahedral Fe(III) (Figure 5a).[33] We

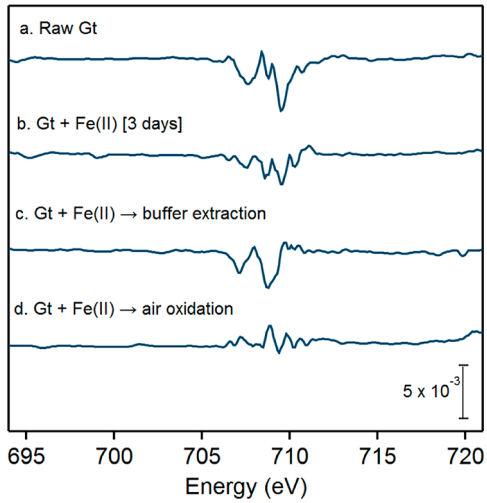

Figure 5. Fe *L*-edge XMCD of (a) raw goethite, (b) goethite after reaction with Fe(II) for 3 days, and (c) goethite reacted with Fe(II) overnight and further subjected to buffer extraction or (d) air oxidation.

previously attributed the weak magnetic moment in as-synthesized goethite to defects arising from both Fe vacancies and excess OH.[33] After reaction with Fe(II), however, the magnetic response is significantly decreased, and the XMCD signal is within the noise (Figure 5b). We previously suggested that the decreased magnetic response is consistent with annealing of defects, possibly by Fe(II) insertion into and subsequent oxidation within vacant cationic sites. Less defects in goethite after reaction with Fe(II) (as evidenced by the lack of magnetic response in the Fe(II)-reacted goethite) is therefore one possible explanation for product change and inhibition of electron transfer inhibition observed after reaction with Fe(II).

To evaluate whether removing the Fe(II) restores the magnetic moment (as it restores the electron transfer in Figure 4), we reacted goethite overnight with Fe(II) and then extracted the solids with HEPES buffer (Figure 5c). Extracting the Fe(II) with buffer restored the goethite magnetic moment of goethite. This is consistent with the idea that defects enable electron transfer as our Mössbauer data showed that extracting the Fe(II) with a buffer wash restored electron transfer. However, since the removal of the sorbed Fe(II) restored the magnetic response, it suggests that during this short exposure the Fe(II) was occupying but not necessarily permanently annealing some of the Fe vacancies. Furthermore, our Mössbauer data also showed that the longer goethite reacted with Fe(II), the harder it is to desorb the Fe(II) and restore electron transfer. Perhaps the longer reaction time and observed maturing of the Fe(II) layer indicates that with longer time some of the Fe(II) is indeed more permanently annealing some defects.

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If instead of removing the Fe(II) with a buffer, we air-oxidize the goethite reacted with Fe(II), the magnetic moment is not restored (Figure 5d). This finding surprised us as our previous work[33] as well as our data here with Fe(II) and the buffer extraction suggest that removing the vacancies (and therefore the magnetic moment) would lead to less electron transfer. Instead, our data shows that air oxidation restores electron transfer even though the magnetic moment is reduced to noise suggesting no defects are present (Figure 5d). Likely, this is due to an important difference in extraction versus oxidation as the buffer extraction removes Fe(II), whereas the air oxidation does not remove the Fe(II), but instead rapidly oxidizes it to Fe(III). We further tried to anneal the goethite by exposing it to multiple Fe(II) exposure/oxidation cycles to see if it might inhibit electron transfer by presumably removing defects but found no change in products or extent of electron transfer (Figure S7). Maybe the type of annealing of defects provided by hydrothermal treatment in our previous work[33] is more effective at annealing defects than the oxidation of sorbed Fe(II). Fast oxidation by O_2 may form a layer of short-range-ordered Fe(III) minerals[49] that perhaps allows electron transfer but is sufficiently disordered such that it does not contribute a net magnetic moment.

■ ENVIRONMENTAL IMPLICATIONS

The collective experimental and modeling work on electron transfer and Fe(II)-catalyzed recrystallization has employed innovative techniques and methodologies to provide useful insights on the Fe(II)/goethite system. Mössbauer spectroscopy demonstrated Fe(II)−Fe(III) oxide electron transfer under many conditions[4−17] and inductively coupled plasma-mass spectrometry demonstrated atom mixing between the oxide and the aqueous phase.[40,41] Computational molecular simulations, such as density functional theory (DFT) calculations as well as classical molecular dynamics (MD) simulations of atomically flat stoichiometric goethite (110) surfaces, however, indicated that electron transfer from inner-sphere sorbed Fe(II) to adjacent lattice Fe(III) in goethite is, at best, a thermoneutral reaction with a large activation energy.[29−31] Importantly, however, both DFT calculations and MD simulations, also indicate that atomic-scale surface defects such as vacancies could substantially decrease this activation energy,[29,32] and our previous experimental work using surface-sensitive XMCD and Mössbauer spectroscopy showed that such defects enable electron transfer.[33] Recently, atom probe tomography provided an expanded view into microstructural complexity of the active Fe(II)-catalyzed atom exchange interface and showed that oxidative adsorption and growth on goethite is spatially heterogeneous and that it can access interior surface area via surface-exposed pores and intergranular boundaries, prospectively by diffusive transport.[52]

Each of these various approaches brings unique strengths to unravel the reaction mechanism in the Fe(II)/goethite system. In this work, the use of Mössbauer spectroscopy, a bulk measurement, allows us to probe the active atom exchange interface irrespective of their location at external or interior interfaces. Our experimental design with sequential isotope exposures (^{56}Gt + ^{56}Fe(II) + ^{57}Fe(II)) and different exposure times allowed us to track the fraction of new Fe atoms that sorbed onto and reacted with goethite as a function of the length of the previous exposure. Our results show that exposure to Fe(II) changes the reaction products formed and inhibits the extent of electron transfer between goethite and Fe(II). The experimental work appears to converge on a conceptual model that suggests the goethite surface accumulates a passivating layer of Fe(II) that influences the reaction products that form and the extent of electron transfer upon further exposure to Fe(II). Furthermore, the longer the goethite is exposed to Fe(II), the more electron transfer is inhibited. Electron transfer, however, can be partially restored upon removal of the layer of Fe(II) or upon fast oxidation of sorbed Fe(II).

Our results help explain previous observations of Fe(II) inhibition of microbial Fe(III)−oxide respiration and Fe(II)-catalyzed recrystallization.[34−36,38] Our initial hypothesis was that reaction with Fe(II) would anneal surface defects and inhibit electron transfer consistent with computational calculations that suggested that defects are necessary to enable electron transfer.[29,30] The present observations, however, further suggest that, while defects may play a role in electron transfer, passivation by Fe(II) as well as maturing of the Fe(II) layer seem to be the most important factors influencing the extent of electron transfer. The exact nature of the maturing is unclear, although there is some indication that annealing of defects might be occurring.

We further demonstrated that the electron transfer inhibition can be reversed and restored by the removal of the Fe(II) at the surface of goethite. However, the longer Fe(II) reacts with goethite, the harder it was to remove the Fe(II) and to restore electron transfer. In the environment, geochemical fluctuations associated with naturally dynamic or seasonal variability in hydrogeological conditions, for example, in hyporheic zones, can frequently modify pore-fluid pH, Fe(II) concentrations, and dissolved oxygen concentrations.[51,53] Because such fluctuations strongly affect sorbed Fe(II) loading, our data suggests that in natural environments Fe(II)−goethite electron transfer and processes linked to it (such as microbial Fe(II) reduction and Fe(II)-catalyzed recrystallization)[34−36,38] are likely relevant beyond just short time scales. The frequency with which soil and sediments undergo alternating geochemical conditions will likely determine the extent to which Fe(II)−goethite electron transfer impacts Fe and linked geochemical cycles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.9b00224.

Details and discussion on Mössbauer fitting, discussion on the origin of the sorbed Fe(II), and additional figures of wet extractions (PDF)

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Notes

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■ REFERENCES

(1) Zhang, Y.; Charlet, L.; Schindler, P. W. Adsorption of Protons, Fe(II) and Al(III) on Lepidocrocite (γ-FeOOH). *Colloids Surf.* **1992**, *63* (3), 259−268.

(2) Wehrli, B.; Sulzberger, B.; Stumm, W. Redox Processes Catalyzed by Hydrous Oxide Surfaces. *Chem. Geol.* **1989**, *78* (3), 167−179.

(3) Coughlin, B. R.; Stone, A. T. Nonreversible Adsorption of Divalent Metal Ions (Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Pb^{II}) onto Goethite: Effects of Acidification, Fe^{II} Addition, and Picolinic Acid Addition. *Environ. Sci. Technol.* **1995**, *29* (9), 2445−2455.

(4) Tanwar, K. S.; Petitto, S. C.; Ghose, S. K.; Eng, P. J.; Trainor, T. P. Structural Study of Fe(II) Adsorption on Hematite($1\bar{1}02$). *Geochim. Cosmochim. Acta* **2008**, *72* (14), 3311−3325.

(5) Williams, A. G. B.; Scherer, M. M. Spectroscopic Evidence for Fe(II)-Fe(III) Electron Transfer at the Iron Oxide-Water Interface. *Environ. Sci. Technol.* **2004**, *38* (18), 4782−4790.

(6) Cwiertny, D. M.; Handler, R. M.; Schaefer, M. V.; Grassian, V. H.; Scherer, M. M. Interpreting Nanoscale Size-Effects in Aggregated Fe-oxide Suspensions: Reaction of Fe(II) with Goethite. *Geochim. Cosmochim. Acta* **2008**, *72* (5), 1365−1380.

(7) Gorski, C. A.; Scherer, M. M. Influence of Magnetite Stoichiometry on Fe^{II} Uptake and Nitrobenzene Reduction. *Environ. Sci. Technol.* **2009**, *43* (10), 3675−3680.

(8) Larese-Casanova, P.; Scherer, M. M. Fe(II) Sorption on Hematite: New Insights Based on Spectroscopic Measurements. *Environ. Sci. Technol.* **2007**, *41* (2), 471−477.

(9) Neumann, A.; Olson, T. L.; Scherer, M. M. Spectroscopic Evidence for Fe(II)−Fe(III) Electron Transfer at Clay Mineral Edge and Basal Sites. *Environ. Sci. Technol.* **2013**, *47* (13), 6969−6977.

(10) Latta, D. E.; Neumann, A.; Premaratne, W. A. P. J.; Scherer, M. M. Fe(II)−Fe(III) Electron Transfer in a Clay Mineral with Low Fe Content. *ACS Earth Space Chem.* **2017**, *1* (4), 197−208.

(11) Latta, D. E.; Bachman, J. E.; Scherer, M. M. Fe Electron Transfer and Atom Exchange in Goethite: Influence of Al-Substitution and Anion Sorption. *Environ. Sci. Technol.* **2012**, *46* (19), 10614−10623.

(12) Yanina, S. V.; Rosso, K. M. Linked Reactivity at Mineral-Water Interfaces Through Bulk Crystal Conduction. *Science* **2008**, *320* (5873), 218−222.

(13) Schaefer, M. V.; Gorski, C. A.; Scherer, M. M. Spectroscopic Evidence for Interfacial Fe(II)-Fe(III) Electron Transfer in a Clay Mineral. *Environ. Sci. Technol.* **2011**, *45* (2), 540−545.

(14) Amstaetter, K.; Borch, T.; Larese-Casanova, P.; Kappler, A. Redox Transformation of Arsenic by Fe(II)-Activated Goethite (α-FeOOH). *Environ. Sci. Technol.* **2010**, *44* (1), 102−108.

(15) Pasakarnis, T.; McCormick, M. L.; Parkin, G. F.; Thompson, A.; Scherer, M. M. Fe^{II} aq−Fe^{III} oxide Electron Transfer and Fe Exchange: Effect of Organic Carbon. *Environ. Chem.* **2015**, *12* (1), 52−63.

(16) Rosso, K. M.; Yanina, S. V.; Gorski, C. A.; Larese-Casanova, P.; Scherer, M. M. Connecting Observations of Hematite (α-Fe_2O_3) Growth Catalyzed by Fe(II). *Environ. Sci. Technol.* **2010**, *44* (1), 61−67.

(17) Silvester, E.; Charlet, L.; Tournassat, C.; Géhin, A.; Grenèche, J.-M.; Liger, E. Redox Potential Measurements and Mössbauer Spectrometry of Fe^{II} Adsorbed onto Fe^{III} (oxyhydr)oxides. *Geochim. Cosmochim. Acta* **2005**, *69* (20), 4801−4815.

(18) Stewart, S. M.; Hofstetter, T. B.; Joshi, P.; Gorski, C. A. Linking Thermodynamics to Pollutant Reduction Kinetics by Fe^{2+} Bound to Iron Oxides. *Environ. Sci. Technol.* **2018**, *52* (10), 5600−5609.

(19) Hansel, C. M.; Benner, S. G.; Fendorf, S. Competing Fe(II)-Induced Mineralization Pathways of Ferrihydrite. *Environ. Sci. Technol.* **2005**, *39* (18), 7147−7153.

(20) Zhou, Z.; Latta, D. E.; Noor, N.; Thompson, A.; Borch, T.; Scherer, M. M. Fe(II)-Catalyzed Transformation of Organic Matter−Ferrihydrite Coprecipitates: A Closer Look Using Fe Isotopes. *Environ. Sci. Technol.* **2018**, *52* (19), 11142−11150.

(21) ThomasArrigo, L. K.; Byrne, J. M.; Kappler, A.; Kretzschmar, R. Impact of Organic Matter on Iron(II)-Catalyzed Mineral Transformations in Ferrihydrite−Organic Matter Coprecipitates. *Environ. Sci. Technol.* **2018**, *52* (21), 12316−12326.

(22) Tamaura, Y.; Ito, K.; Katsura, T. Transformation of γ-FeO(OH) to Fe_3O_4 by Adsorption of Iron (II) Ion on γ-FeO(OH). *J. Chem. Soc., Dalton Trans.* **1983**, No. 2, 189−194.

(23) Han, R.; Liu, T.; Li, F.; Li, X.; Chen, D.; Wu, Y. Dependence of Secondary Mineral Formation on Fe(II) Production from Ferrihydrite Reduction by Shewanella oneidensis MR-1. *ACS Earth Space Chem.* **2018**, *2* (4), 399−409.

(24) Perez, J. P. H.; Tobler, D. J.; Thomas, A. N.; Freeman, H. M.; Dideriksen, K.; Radnik, J.; Benning, L. G. Adsorption and Reduction of Arsenate during the Fe^{2+}-Induced Transformation of Ferrihydrite. *ACS Earth Space Chem.* **2019**, *3* (6), 884−894.

(25) Zhou, Z.; Latta, D. E.; Noor, N.; Thompson, A.; Borch, T.; Scherer, M. M. Fe (II)-Catalyzed Transformation of Organic Matter−Ferrihydrite Coprecipitates: A Closer Look Using Fe Isotopes. *Environ. Sci. Technol.* **2018**, *52* (19), 11142−11150.

(26) Jolivet, J.; Belleville, P.; Tronc, E.; Livage, J. Influence of Fe(II) on the Formation of the Spinel Iron Oxide in Alkaline Medium. *Clays Clay Miner.* **1992**, *40*, 531−531.

(27) Tronc, E.; Belleville, P.; Jolivet, J. P.; Livage, J. Transformation of Ferric Hydroxide into Spinel by Iron(II) Adsorption. *Langmuir* **1992**, *8* (1), 313−319.

(28) Yang, L.; Steefel, C. I.; Marcus, M. A.; Bargar, J. R. Kinetics of Fe(II)-Catalyzed Transformation of 6-line Ferrihydrite under Anaerobic Flow Conditions. *Environ. Sci. Technol.* **2010**, *44* (14), 5469−5475.

(29) Alexandrov, V.; Rosso, K. M. Ab Initio Modeling of Fe(II) Adsorption and Interfacial Electron Transfer at Goethite (a-FeOOH) Surfaces. *Phys. Chem. Chem. Phys.* **2015**, *17* (22), 14518−14531.

(30) Russell, B.; Payne, M.; Ciacchi, L. C. Density Functional Theory Study of Fe(II) Adsorption and Oxidation on Goethite Surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *79* (16), 165101.

(31) Zarzycki, P.; Kerisit, S.; Rosso, K. M. Molecular Dynamics Study of Fe(II) Adsorption, Electron Exchange, and Mobility at Goethite (α-FeOOH) Surfaces. *J. Phys. Chem. C* **2015**, *119* (6), 3111−3123.

DOI: 10.1021/acsearthspacechem.9b00224
ACS Earth Space Chem. XXXX, XXX, XXX−XXX

(32) Zarzycki, P.; Rosso, K. M. Energetics and the Role of Defects in Fe (II)-Catalyzed Goethite Recrystallization from Molecular Simulations. *ACS Earth and Space Chemistry* **2019**, *3* (2), 262−272.
(33) Notini, L.; Latta, D. E.; Neumann, A.; Pearce, C. I.; Sassi, M.; N'Diaye, A. T.; Rosso, K. M.; Scherer, M. M. The Role of Defects in Fe(II)−Goethite Electron Transfer. *Environ. Sci. Technol.* **2018**, *52* (5), 2751−2759.
(34) Roden, E. E. Geochemical and Microbiological Controls on Dissimilatory Iron Reduction. *C. R. Geosci.* **2006**, *338* (6), 456−467.
(35) Roden, E. E.; Urrutia, M. M. Influence of Biogenic Fe(II) on Bacterial Crystalline Fe(III) Oxide Reduction. *Geomicrobiol. J.* **2002**, *19* (2), 209−251.
(36) Roden, E. E.; Zachara, J. M. Microbial Reduction of Crystalline Iron(III) Oxides: Influence of Oxide Surface Area and Potential for Cell Growth. *Environ. Sci. Technol.* **1996**, *30* (5), 1618−1628.
(37) Jones, A. M.; Collins, R. N.; Rose, J.; Waite, T. D. The Effect of Silica and Natural Organic Matter on the Fe(II)-Catalysed Transformation and Reactivity of Fe(III) Minerals. *Geochim. Cosmochim. Acta* **2009**, *73* (15), 4409−4422.
(38) Joshi, P.; Fantle, M. S.; Larese-Casanova, P.; Gorski, C. A. Susceptibility of Goethite to Fe^{2+}-Catalyzed Recrystallization over Time. *Environ. Sci. Technol.* **2017**, *51* (20), 11681−11691.
(39) Schwertmann, U.; Cornell, R. M. Goethite. In *Iron Oxides in the Laboratory*; Wiley-VCH Verlag GmbH: 2007; pp 67−92.
(40) Handler, R. M.; Beard, B. L.; Johnson, C. M.; Scherer, M. M. Atom Exchange between Aqueous Fe(II) and Goethite: An Fe Isotope Tracer Study. *Environ. Sci. Technol.* **2009**, *43* (4), 1102−1107.
(41) Handler, R. M.; Frierdich, 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. Fe(II)-Catalyzed Recrystallization of Goethite Revisited. *Environ. Sci. Technol.* **2014**, *48* (19), 11302−11311.
(42) Good, N. E.; Winget, G. D.; Winter, W.; Connolly, T. N.; Izawa, S.; Singh, R. M. M. Hydrogen Ion Buffers for Biological Research. *Biochemistry* **1966**, *5* (2), 467−477.
(43) Tamura, H.; Goto, K.; Yotsuyanagi, T.; Nagayama, M. Spectrophotometric Determination of Iron(II) with 1,10-Phenanthroline in the Presence of Large Amounts of Iron(III). *Talanta* **1974**, *21* (4), 314−318.
(44) Rancourt, D. G.; Ping, J. Y. Voigt-Based Methods for Arbitrary-Shape Static Hyperfine Parameter Distributions in Mössbauer Spectroscopy. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1991**, *58* (1), 85−97.
(45) Chen, C.; Thompson, A. Ferrous Iron Oxidation under Varying pO_2 Levels: The Effect of Fe(III)/Al(III) Oxide Minerals and Organic Matter. *Environ. Sci. Technol.* **2018**, *52* (2), 597−606.
(46) van der Zee, C.; Roberts, D. R.; Rancourt, D. G.; Slomp, C. P. Nanogoethite is the Dominant Reactive Oxyhydroxide Phase in Lake and Marine Sediments. *Geology* **2003**, *31* (11), 993−996.
(47) Thompson, A.; Rancourt, D. G.; Chadwick, O. A.; Chorover, J. Iron Solid-Phase Differentiation along a Redox Gradient in Basaltic Soils. *Geochim. Cosmochim. Acta* **2011**, *75* (1), 119−133.
(48) Murad, E.; Cashion, J. *Mössbauer Spectroscopy of Environmental Materials and Their Industrial Utilization*; Springer Science & Business Media: 2011.
(49) Thompson, A.; Chadwick, O. A.; Rancourt, D. G.; Chorover, J. Iron-Oxide Crystallinity Increases During Soil Redox Cscillations. *Geochim. Cosmochim. Acta* **2006**, *70* (7), 1710−1727.
(50) Liptzin, D.; Silver, W. L.; Detto, M. Temporal Dynamics in Soil Oxygen and Greenhouse Gases in Two Humid Tropical Forests. *Ecosystems* **2011**, *14* (2), 171−182.
(51) Silver, W. L.; Lugo, A. E.; Keller, M. Soil Oxygen Availability and Biogeochemistry Along Rainfall and Topographic Gradients in Upland Wet Tropical Forest Soils. *Biogeochemistry* **1999**, *44* (3), 301−328.
(52) Taylor, S. D.; Liu, J.; Zhang, X.; Arey, B. W.; Kovarik, L.; Schreiber, D. K.; Perea, D. E.; Rosso, K. M. Visualizing the iron atom exchange front in the Fe (II)-catalyzed recrystallization of goethite by atom probe tomography. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116* (8), 2866−2874.
(53) Schuur, E. A.; Matson, P. A. Net Primary Productivity and Nutrient Cycling Across a Mesic to Wet Precipitation Gradient in Hawaiian Montane Forest. *Oecologia* **2001**, *128* (3), 431−442.

DOI: 10.1021/acsearthspacechem.9b00224
ACS Earth Space Chem. XXXX, XXX, XXX−XXX