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# The rate of ferrihydrite transformation to goethite via the Fe(II) pathway

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## ABSTRACT

In this study, we quantified the rate of ferrihydrite conversion to goethite via the Fe(II) pathway using synchrotron radiation-based energy dispersive X-ray diffraction (ED-XRD). Ferrihydrite transformation experiments were conducted in oxygen-free solutions at neutral pH with synthetic 2-line ferrihydrite reacting with 100 mM Fe(II). The kinetics of goethite crystallization was measured in situ at temperatures ranging from 21 to 90 °C. The results showed that in the presence of ferrous iron, the transformation of poorly ordered ferrihydrite into crystalline goethite is rapid and highly dependent on temperature. The time-resolved peak area data fitted using a Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetic model yielded rate constants of $4.0 \times 10^{-5}$, $1.3 \times 10^{-4}$, $3.3 \times 10^{-4}$, $2.27 \times 10^{-3}$, and $3.14 \times 10^{-3}$ 1/s at reaction temperatures of 21, 45, 60, 85, and 90 °C respectively. The activation energy for the transformation was determined to be 56 ± 4 kJ/mol. Comparison with the activation energy predicted for the phase conversion in the absence of ferrous iron indicates that Fe(II) acts as a catalyst that decreases the activation energy barrier by approximately 38 kJ/mol. The kinetic parameters derived from the experimental data suggest that goethite crystallization is controlled by a 1-D phase boundary growth mechanism with a constant nucleation rate occurring during the reaction.

**Keywords:** Crystal growth, goethite, geomicrobiology, ferrihydrite, kinetics, transformation

## INTRODUCTION

Ferrihydrite is a poorly ordered Fe oxyhydroxide mineral commonly found in soils, groundwater aquifers, lake sediments, and hot- and cold-spring deposits. Due to its poorly ordered and nanoparticulate (<10 nm) nature, ferrihydrite is thermodynamically unstable with respect to the crystalline Fe-oxyhydroxide phase goethite (Schwertmann 1999). In many soil and sedimentary systems, ferrihydrite conversion to goethite controls goethite occurrence and distribution (Cornell and Schwertmann 2003). The rate and mechanism of this transformation is dependent upon several physical and chemical factors, including temperature, pH, Eh, and $Fe(II)_{(aq)}$ concentration. Because ferrihydrite and goethite exhibit different crystal structures and particle sizes, this phase conversion can significantly modify mineral surface reactivity, e.g., sorption and redox properties. Identifying the reaction pathways and quantification of the rate of this transformation are essential to understanding the evolution of ferrihydrite, the formation of goethite, and their subsequent impact in low-temperature, near-surface environments.

The conversion of ferrihydrite to goethite occurs spontaneously in acidic and basic solutions through reconstructive transformation involving the dissolution of ferrihydrite and reprecipitation of goethite (Schwertmann and Murad 1983; Nagano et al. 1994). At circumneutral pH, ferrihydrite is highly insoluble and the conversion to goethite can only proceed in the presence of a catalyst such as $Fe(II)_{(aq)}$ (Tronc et al. 1992; Fredrickson et al. 1998; Benner et al. 2002; Glasauer et al. 2003; Hansel et al. 2003). Because $Fe(II)_{(aq)}$ is stable and accumulates in high concentration under anoxic non-sulfidic conditions, this transformation pathway can play an important role in the formation of goethite at redox transition zones. However, the rate of transformation is poorly constrained, largely due to a lack of in situ real-time data.

Synchrotron radiation-based energy dispersive X-ray diffraction (ED-XRD) allows an entire diffraction pattern to be collected on the contents of a reaction vessel in situ and on short time scales (seconds to minutes). This non-invasive technique can be used to characterize the changes in crystal structure during mineral crystallization and transformation reactions (e.g., Shaw et al. 2000; Cahill et al. 2000). In this study, we applied ED-XRD to investigate the conversion of 2-line ferrihydrite to goethite in oxygen-free solutions in the presence of $Fe(II)_{(aq)}$ at temperatures ranging from 21 to 90 °C. The experimental data provide important information about the transformation mechanism at circumneutral pH and can be used to quantify the rate of ferrihydrite transformation to goethite via the Fe(II) pathway.

## EXPERIMENTAL METHODS

Synthetic 2-line ferrihydrite was prepared by adding 40 g of $Fe(NO_3)_3 \cdot 9H_2O$ to 500 mL of distilled deionized water and slowly titrating the solution with 1 *M* NaOH until the solution pH reached 7.0 (Schwertmann and Cornell 2000). The precipitate was rinsed five times with distilled deionized water, then washed three times with deoxygenated water (doubly distilled, 18 MΩ water, boiled under constant flow of $O_2$-free $N_2$) and finally bubbled with $O_2$-free $N_2$ for 1 h to remove any $O_2$ dissolved in solution or sorbed to the mineral surfaces. After purging with $N_2$, the mineral suspension was immediately transferred into an anaerobic glove-box (95% $N_2$ + 5% $H_2$), and 10 mL aliquots of ferrihydrite suspension were placed into glass vials that contained a Teflon-coated magnetic stirrer. The glass vials were then sealed with butyl rubber stoppers and crimped. An aliquot of the starting suspension was

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filtered, dried, and characterized using standard powder XRD. The XRD pattern verified that the precipitate was pure 2-line ferrihydrite. An Fe(II) stock solution was prepared inside the anaerobic chamber by dissolving $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a deoxygenated 0.1 *M* HEPES buffer and titrating to pH 7.0 using oxygen-free 0.5 *M* NaOH. A range of ferrihydrite and Fe(II) concentrations were tested in off-line experiments to identify the $Fe(II)_{(aq)}/Fe(III)_{(s)}$ ratios that precipitated pure goethite and the $Fe(II)_{(aq)}/Fe(III)_{(s)}$ ratios that formed magnetite.

The in situ ferrihydrite-to-goethite transformation experiments were carried out at station 16.4 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory, U.K. The configuration and set-up of station 16.4 was described by Shaw et al. (2000). The ferrihydrite transformation experiments were conducted at temperatures from 21 to 90 °C and the reactions were followed for time periods up to 18 h. Heating was achieved by placing the vials inside an aluminium block fitted with four resistance cartridge heaters, and temperature was controlled by a thermocouple attached to the top. Two slots in the heater block allow the incoming X-ray beam to pass through the apparatus. The ferrihydrite-to-goethite phase conversion was initiated by injecting 5 mL of an Fe(II) solution into the sealed and stirring ferrihydrite-containing glass vials (final $m_{Fe(II)} = 100$ mM; ferrhydrite = 20 g/L). The solution injection was performed using an $N_2$ purged syringe and caution was taken to maintain oxygen-free conditions. The progress of the phase conversion was monitored by shining a polychromatic beam of X-rays through the reaction vessel and collecting the entire powder diffraction pattern of the cell contents simultaneously using three energy sensitive solid-state detectors set at fixed 2θ angles. The detectors were arranged in a vertical row with individual collimators at different diffraction angles to allow a wide range of *d*-spacings to be collected. Diffraction patterns were taken every 1–2 minutes. The interatomic spacing for a particular set of lattice planes can be calculated using a modified form of Bragg's law [$E = 6.199/d\sin\theta$)] from the energy [$E$(keV)] of a diffraction peak and the angle of the detector [θ]. At the end of each experiment, the final products were filtered, rinsed with deoxygenated water, and air-dried at room temperature and examined using conventional powder XRD and field emission gun scanning electron microscopy (FEG-SEM).

## RESULTS

In the off-line experiments, reddish ferrihydrite reacting with 100 mM Fe(II) at room temperature changed to yellow-colored goethite after 24 h of reaction time. The filtered and air-dried samples analyzed by SEM showed discrete acicular crystals, approximately 0.2 μm in length (Fig. 1). XRD patterns of the powder sample displayed six well-defined peaks at *d*-spaces of 4.18, 2.69, 2.45, 2.19, 1.72, and 1.56 Å, respectively, which correspond well with the peak positions for goethite (JCPDS card no. 29-713). No hematite or magnetite was detected in the reaction product. XRD patterns of control experiments performed in the absence of Fe(II) displayed no well-defined diffraction peaks, indicating that ferrihydrite was stable in the suspension at pH 7 over the time period of the experiment.

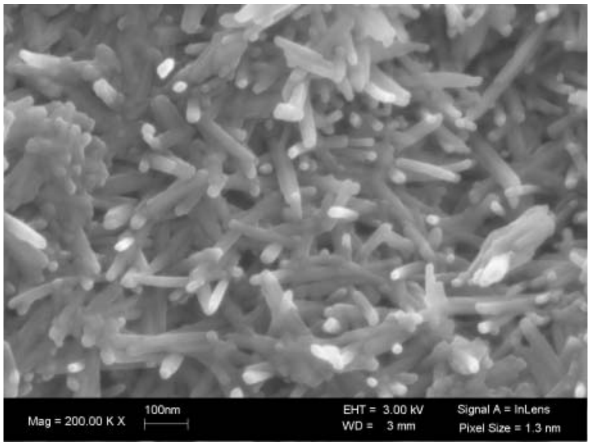

**FIGURE 1.** SEM image of acicular goethite crystals formed from ferrihydrite reacting with 100 mM of Fe(II) at pH 7 for 24 h.

The in situ time-resolved ED-XRD data showed that poorly ordered ferrihydrite transforms rapidly into crystalline goethite in the presence of ferrous iron (Fig. 2). Initially, the ED-XRD patterns displayed a broad hump between 30 to 100 keV with no Bragg peaks. The hump is produced by the diffuse scattering of the poorly ordered ferrihydrite and Fe(II) solution in the reaction vessel and also by the spectral intensity profile of the white beam (Clark 1996). As the reaction proceeded, a diffraction peak formed at 40.6 keV corresponding to the 4.18 Å *d*-spacing of the goethite {110} plane. Diffraction peaks were also observed at 63.1 keV (2.69 Å) and 69.3 keV (2.45 Å). Because of the resolution limits intrinsic to the ED-XRD technique, the low-intensity diffraction peaks were not detected.

To quantify the kinetics of the ferrihydrite to goethite transformation, the integrated peak area of the 4.18 Å peak was calculated by fitting the peak in each diffraction pattern with a pseudo-Voight function using the computer program XFIT (Cheary and Coelho 1992). The peak areas were converted to the degree of reaction parameter, α, which varies from 0 at the beginning of the reaction to 1 at the end when the peak area has stopped increasing (Fig. 3). The peak area data was fitted using a Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetic model (Avrami 1939, 1940; Johnson and Mehl 1939; O'Hare et al. 2000; Lupo et al. 2004) of the form:

$$\alpha = 1 - e^{-k(t-t_o)^m} \tag{1}$$

where α is the degree of reaction, *t* is time in seconds, $t_0$ is the induction time in seconds, *k* is the rate constant (1/s), and *m* is an value which relates to the reaction mechanism. The values of $t_0$, *k*, and *m* for each data set are given in Table 1.

The data presented in Figure 3 indicate that the change in diffraction peak area is rapid and highly dependent on tempera-

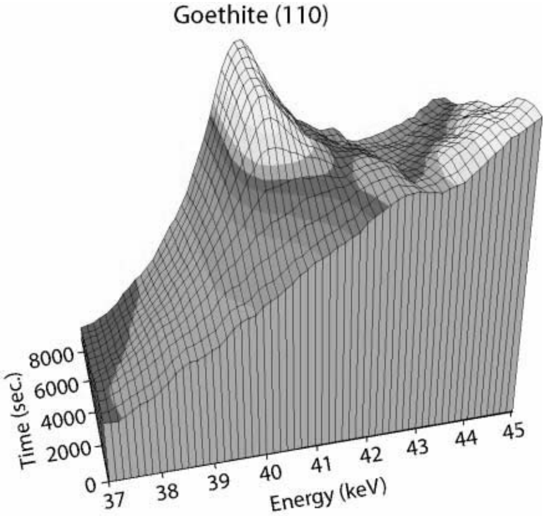

**FIGURE 2.** Three-dimensional representation of time-resolved ED-XRD patterns of the 4.18 Å peak showing the transformation of ferrihydrite to goethite in the presence of Fe(II) at 60 °C (ferrihydrite = 20 g/L; $m_{Fe(II)} = 100$ mM; pH = 7).

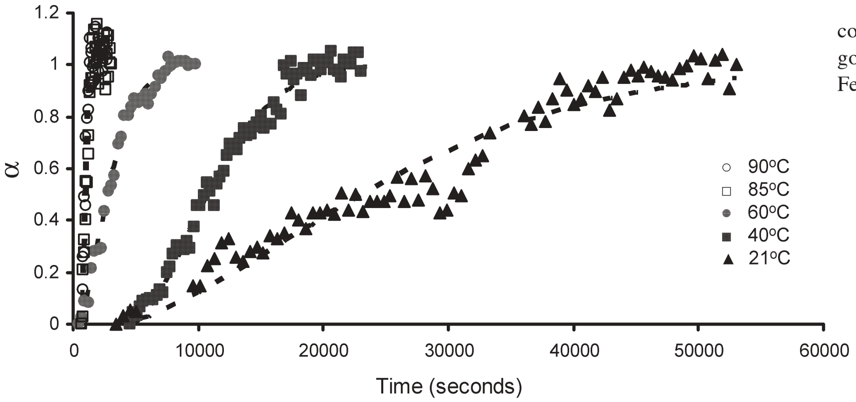

**FIGURE 3.** The degree of reaction (α) completed with time for the ferrihydrite to goethite transformation in the presence of Fe(II) at 21, 40, 60, 85, and 90 °C.

ture. The $k$ values for the ferrihydrite to goethite conversion increases markedly from 21 to 90 °C. At ambient temperature, the growth of the diffraction peaks occurred over the course of ~60 000 s (~16 h) yielding a rate constant of $4.0 \times 10^{-5}$/s. At 90 °C the transformation is significantly faster, with the reaction reaching completion in less than 1320 s (22 mins), resulting in a $k$ value of $3.14 \times 10^{-3}$/s.

The $t_0$ values for goethite formation are low, ranging from 700 to 4500 s, indicating that goethite nucleation is rapid. The results also show that $t_0$ values decrease with increasing temperature, as observed in other studies of goethite formation (e.g., Shaw et al. 2005). The rapid rate of induction is consistent with the nuclei forming directly from solution. This process is favored by the low solubility of goethite at pH 7 and the high rate of Fe ion diffusion in the solution to the site of nucleation.

The values of $m$ can be correlated with the nucleation rate, reaction mechanism, and geometry of the nuclei (Hulbert 1969). Two types of reaction mechanisms were considered. First, a phase-boundary (or surface) controlled mechanism, in which the reactions cannot proceed fast enough to attain equilibrium at the interface and the rate is determined by the available interface. The second was a diffusion-controlled (or transport-controlled) mechanism where the rate is controlled by the transport of reactant to the reaction zone. The geometry of the nuclei was also considered and established by examination of the crystal morphology of the reaction products.

Analysis of the experimental data indicates that the best fits are obtained with $m$ values of 1.55 to 1.81 (average = 1.66). Along with the acicular growth morphology of goethite crystals along its **c**-axis, the $m$ values suggests a 1-D phase-boundary controlled mechanism with a constant nucleation rate occurring during the reaction. Phase-boundary controlled crystallization reactions generally form crystals with well-defined crystallographic faces (Lasaga 1998). The goethite particles formed in the transformation experiments exhibit euhedral crystal shapes (Fig. 1), which is consistent with a phase-boundary controlled mechanism.

The apparent activation energy for goethite crystallization in the presence of Fe(II) can be calculated from the Arrhenius equation:

$$\ln k = \ln A_{\text{(cryst.)}} - \frac{E_{\text{a(cryst.)}}}{RT} \tag{2}$$

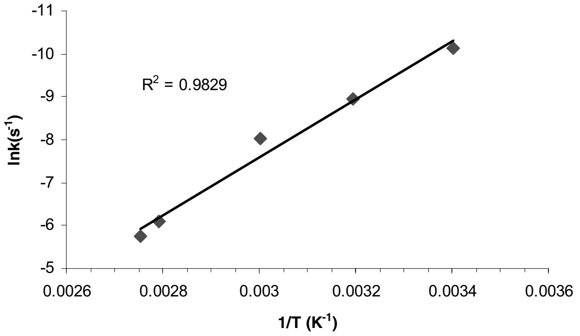

**FIGURE 4.** Arrhenius plot of the rate constants calculated from the 4.18 Å peak area growth at each temperature.

**TABLE 1.** Kinetic parameters derived from the JMAK model fit of data from the growth of the 4.18 Å Bragg peak during goethite formation

| Temperature (°C) | $k$ (1/s) | $t_0$ (seconds) | $m$ |
|---|---|---|---|
| 21 | $4.00\times10^{-5}$ ($\pm0.10\times10^{-5}$) | 3384 | 1.55±0.08 |
| 40 | $1.30\times10^{-4}$ ($\pm0.02\times10^{-4}$) | 4456 | 1.72±0.06 |
| 60 | $3.30\times10^{-4}$ ($\pm0.05\times10^{-4}$) | 402 | 1.56±0.06 |
| 85 | $2.27\times10^{-3}$ ($\pm0.09\times10^{-3}$) | 702 | 1.81±0.19 |
| 90 | $3.14\times10^{-3}$ ($\pm0.21\times10^{-3}$) | 720 | 1.62±0.26 |
| | | | average = 1.66 |

where $A$ is a pre-exponential factor (1/s), $E_a$ is the activation energy goethite crystallization (kJ/mol), R is the gas constant [8.314 J/(mol·K)], and $T$ is temperature (K). An Arrhenius plot of the rate constants calculated from the peak area growth at each temperature (ln k vs. $1/T$) yields a straight line (Fig. 4). This result suggests that a single mechanism dominates the crystallization process and that there are no changes in mechanism within temperature range studied. The slope of the fit yields an activation energy of 56 ± 4 kJ/mol and ln$A$ value 12.7 1/s. It is interesting to note that an activation energy of >34 kJ/mol is indicative of a phase-boundary controlled mechanism (Lasaga 1998), which is consistent with the $m$ values derived from the JMAK kinetic model.

## DISCUSSION

The conversion of ferrihydrite to goethite is a reconstructive transformation that requires the rearrangement of poorly ordered $FeO_3(OH)_3$ octahedral units to highly ordered edge-sharing octahedral double chains. This transformation involves extensive reassembly of the crystal structure, and can only proceed by a dissolution and reprecipitation mechanism. Because the conversion requires ferrihydrite to dissolve, the extent of goethite formation parallels the solubility of ferrihydrite, which is at a minimum between pH 7 to 8 (Cornell and Schwertmann 2003). At neutral pH, therefore the rate of ferrihydrite transformation to goethite is limited by the solubility of ferrihydrite. In the absence of ferrous iron, ferrihydrite will preferentially transform to crystalline hematite (Schwertmann and Murad 1983). The conversion from ferrihydrite to hematite is favored in this pH range (6 to 8), and proceeds via dehydration/dehydroxylation, which does not require ferrihydrite dissolution. However, the ferrihydrite-to-hematite transformation is kinetically slow and can require several months to reach completion. For example, the data reported by Schwertmann and Murad (1983) show a time to half conversion for ferrihydrite at pH 7 and room temperature of 112 days.

In contrast, our study demonstrates that in the presence of Fe(II), ferrihydrite readily transforms to goethite at ambient temperature and neutral pH, with a half conversion time of only 6.4 h. This acceleration in the transformation kinetics results from the ability of ferrous iron to reduce and dissolve ferrihydrite. Cornell and Schwertmann (2003) noted that aqueous Fe(II) can adsorb onto the surface of ferrihydrite and act as a reductant that transfers electrons to Fe(III) surface sites. The reduced structural Fe(II) atoms are unstable and desorb into solution. Simultaneously, the oxidized Fe(III) ions are insoluble and precipitate to form goethite. During goethite precipitation, ferrous iron remains readily extractable and is not incorporated into the goethite structure (Jeon et al. 2003). Because there is no net loss of Fe(II), the reductive dissolution process can continue until the ferrihydrite is dissolved completely. It is also noted that the precipitation of goethite forms discrete particles that do not pacify the reactivity of the ferrihydrite surfaces.

In the absence of Fe(II), the activation energy required for the ferrihydrite-to-goethite conversion at pH 7 can be estimated from transformation experiments conducted at higher pH conditions (Nagano et al. 1994; Shaw et al. 2005). The solubility of ferrihydrite increases with increasing pH, thereby allowing the activation energy for the ferrihydrite-goethite transformation to be measured at pH values greater than 11 (Fig. 5a). From a pH vs. $E_a$ plot, the predicted activation energy and ln*A* values at pH 7 for the ferrihydrite to goethite conversion is 94 kJ/mol and 21/s, respectively (Figs. 5b and 5c). These values are significantly higher than the $E_a$ and ln*A* values measured for ferrihydrite transformation in the presence of Fe(II) (56 kJ/mol and 12.7/s respectively). Comparison of the $E_a$ values indicates that Fe(II) acts as a catalyst that decreases the activation energy barrier by approximately 38 kJ/mol. Because the dissolution of ferrihydrite is the rate-limiting step in the overall reaction, this decrease in activation energy is attributed to the ability of ferrous iron to dissolve ferrihydrite.

In our ED-XRD experiments, no magnetite was detected during Fe(II) reaction with ferrihydrite. Previous studies have shown that magnetite can be formed by the sorption of Fe(II) onto ferrihydrite surfaces followed by a solid-state conversion from ferrihydrite to magnetite (Lovley et al. 1987; Tronc et al. 1992; Fredrickson et al. 1998; Benner et al. 2002; Hansel et al.

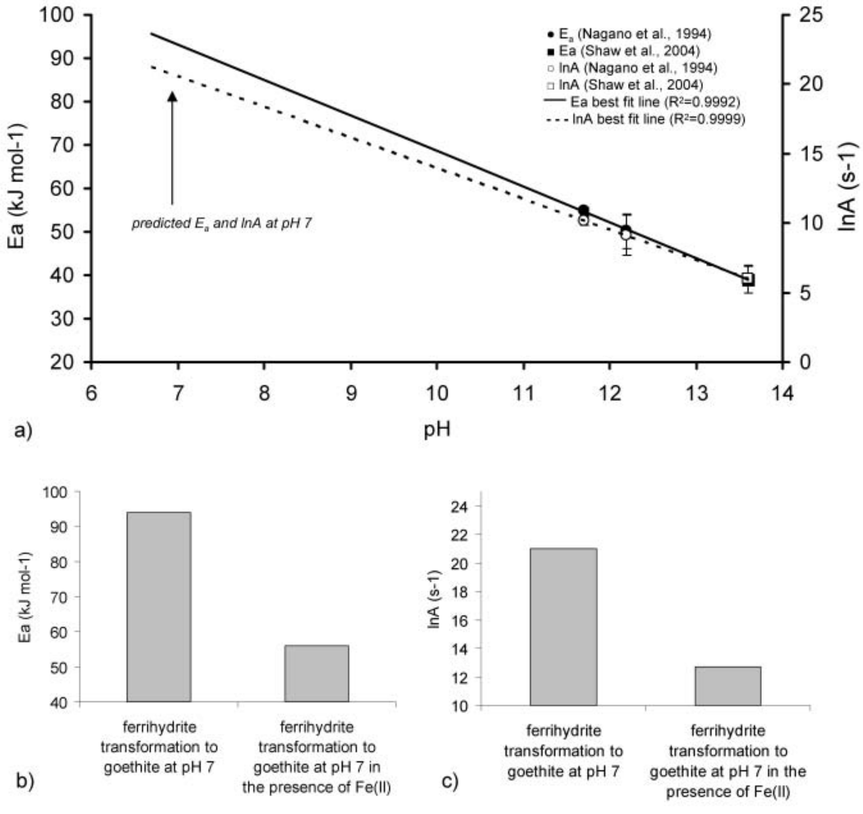

**FIGURE 5.** (**a**) The predicted activation energy for the ferrihydrite to goethite conversion in the absence of Fe(II); (**b**) comparison of $E_a$ values at pH 7; (**c**) comparison of ln*A* values at pH 7.

2003). However, the transformation to magnetite requires high $Fe(II)_{(aq)}/Fe(III)_{(s)}$ ratios and significantly longer reaction times. Our off-line experiments indicated that in a 24 h reaction period, magnetite can only be formed by a fifty fold increase in the $Fe(II)_{(aq)}/Fe(III)_{(s)}$ ratio. Nonetheless, magnetite potentially can be an important reaction end-product over longer periods of time. Goethite precipitation is more rapid than the solid-state conversion of ferrihydrite to magnetite, hence there may be an initial accumulation of goethite followed by a gradual transformation to magnetite at the expense of goethite (Hansel et al. 2003).

## CONCLUDING REMARKS

Goethite is a common iron oxyhydroxide mineral in geologic and aquatic settings, however, laboratory synthesis of goethite often require unrealistic environmental pH conditions (e.g., pH < 2 and > 11). The results of this study demonstrate that in the presence of Fe(II), the phase conversion of ferrihydrite to goethite at neutral pH is kinetically favorable. Quantification of the transformation kinetics indicates that goethite formation via the Fe(II) pathway readily out-competes the ferrihydrite to hematite conversion due to the large differences in reaction rates. This finding may explain why ferrihydrite is often associated with goethite in soils, whereas an association with hematite is rare.

## ACKNOWLEGDMENTS

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