Low temperature, non-stoichiometric oxygen-isotope exchange coupled to Fe(II)-goethite interactions

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ABSTRACT

The oxygen isotope composition of natural iron oxide minerals has been widely used as a paleoclimate proxy. Interpretation of their stable isotope compositions, however, requires accurate knowledge of isotopic fractionation factors and an understanding of their isotopic exchange kinetics, the latter of which informs us how diagenetic processes may alter their isotopic compositions. Prior work has demonstrated that crystalline iron oxides do not significantly exchange oxygen isotopes with pure water at low temperature, which has restricted studies of isotopic fractionation factors to precipitation experiments or theoretical calculations. Using a double three-isotope method (^{18}O - ^{17}O - ^{16}O and ^{57}Fe - ^{56}Fe - ^{54}Fe) we compare oxygen and iron isotope exchange kinetics, and demonstrate, for the first time, that oxygen-isotope exchange between structural oxygen in crystalline goethite and water occurs in the presence of aqueous Fe(II) ($\text{Fe(II)}_{\text{aq}}$) at ambient temperature (i.e., 22-50 °C). The three-isotope method was used to extrapolate partial exchange results to infer the equilibrium, mass-dependent isotope fractionations between goethite and water. In addition, this was combined with a reversal approach to equilibrium by reacting goethite in two unique waters that vary in composition by about 16‰ in $^{18}\text{O}/^{16}\text{O}$ ratios. Our results show that interactions between $\text{Fe(II)}_{\text{aq}}$ and goethite catalyzes oxygen-isotope exchange between the mineral and bulk fluid; no exchange (within error) is observed when goethite is suspended in ^{17}O -enriched water in the absence of $\text{Fe(II)}_{\text{aq}}$. In contrast, Fe(II)-catalyzed oxygen-isotope exchange is accompanied by significant changes in $^{18}\text{O}/^{16}\text{O}$ ratios. Despite significant oxygen exchange, however, we observed disproportionate amounts of iron versus oxygen exchange, where iron-isotope exchange in goethite was roughly three times that of oxygen. This disparity provides novel insight into the reactivity of oxide minerals in aqueous solutions, but presents a challenge for utilizing such an approach to

determine equilibrium isotope fractionation factors. Despite the uncertainty from extrapolation, there is consistency in goethite-water fractionation factors for our reversal approach to equilibrium, with final weighted average fractionation factors of $\Delta^{18}\text{O}_{\text{Gth-water}} = 3.0 (\pm 2.5\text{‰})$ and $0.2 (\pm 0.9\text{‰})$ at 22 °C and $1.9 (\pm 1.5\text{‰})$ and $-1.6 (\pm 0.8\text{‰})$ at 50 °C for nano-particulate and micron-sized goethite, respectively (errors at 2σ level). This variability of $\Delta^{18}\text{O}_{\text{Gth-water}}$ with particle size may reflect differences in the grain boundaries of goethite and ratios of surface area to volume. Reaction of ferrihydrite with $\text{Fe(II)}_{\text{aq}}$ in two distinct waters resulted in a quantitative conversion to goethite and complete oxygen-isotope exchange in each case, and similar fractionation factors were observed for experiments using the two waters. Comparison of our results with previous studies of oxygen isotope fractionation between goethite and water suggests that particle size may be a contributing factor to the disparity among experimental studies.

1. INTRODUCTION

Oxygen isotope compositions in ferric iron (oxyhydr)oxide minerals (iron oxides hereon) are potentially important proxies for paleoclimate (Bao et al., 1999; Bao et al., 2000; Girard et al., 2000; Girard et al., 2002; Girard et al., 1997; Hren et al., 2006; Poage et al., 2000; Sjöström et al., 2004; Tabor and Yapp, 2005; Yapp, 1987; Yapp, 1991; Yapp, 1993; Yapp, 1998; Yapp, 2000; Yapp, 2008), as they may record the temperature and composition of mineral formation water. Meaningful interpretation of oxygen isotope compositions in the rock record, however, requires that temperature-dependent mineral-water oxygen isotope equilibrium fractionation factors are accurately known, or at least that fractionations measured in the laboratory predict those in nature, and that no secondary diagenetic processes have overprinted the original isotopic composition of the mineral. Reported oxygen isotope fractionation factors for the goethite-water system vary by about 8‰ in $\delta^{18}\text{O}$ at 25 °C (Bao and Koch, 1999; Müller, 1995; Yapp, 1990; Yapp, 2007; Zheng, 1998), a substantial range that makes it unclear what the equilibrium fractionation factor is, and impedes the utility of oxygen isotope measurements for naturally occurring minerals.

Disparate reported goethite-water oxygen isotope equilibrium fractionation factors may arise from the different synthesis approaches used to measure the mineral-water fractionations (Bao and Koch, 1999; Müller, 1995; Yapp, 1990), which can be prone to method-specific kinetic effects and thus may not reflect true equilibrium. In addition, the sources of disagreements between experimental and theoretical approaches remains unclear (Zheng, 1998). Other method-specific synthesis conditions, such as pH, Cl^- concentration in fluid, and Al content in goethite, have been proposed as important variables that affect measured goethite-water oxygen isotope fractionations (Yapp, 2007; Yapp, 2012). To date, no direct measurement of the goethite-water

oxygen isotope equilibrium fractionation factor via isotopic exchange reactions has been possible because of limited oxygen-isotope exchange at surface environmental temperatures (Yapp, 2001). Under reducing conditions, however, microbially-mediated dissolution-reprecipitation may alter the oxygen isotope values of natural goethite as noted by Yapp, 2001. This bears on the “survivability” of oxygen isotope signatures in natural iron oxide minerals when $\text{Fe(II)}_{\text{aq}}$ is present, and also offers a novel approach to experimentally measure mineral-water oxygen isotope equilibrium fractionation factors at low temperature.

Biogeochemical iron cycling is common in sedimentary environments, including that which occurs during microbial iron reduction, resulting in secondary abiotic reactions between $\text{Fe(II)}_{\text{aq}}$ and Fe(III) -oxide minerals. These secondary reactions have been proposed to involve Fe(II) sorption and electron transfer to the mineral surface, electron conduction across the surface or through the bulk structure, coupled to the reductive dissolution of Fe(III) at an adjacent or spatially separated surface site, ultimately resulting in atom exchange between Fe(II) in solution and the oxide surface (Handler et al., 2009; Pedersen et al., 2005; Rosso et al., 2010; Williams and Scherer, 2004; Yanina and Rosso, 2008). The catalytic role of Fe(II) allows continued iron oxide recrystallization under steady-state conditions in terms of $\text{Fe(II)}_{\text{aq}}$ concentration and goethite solid phase identity and microscopic characteristics (Handler et al., 2009; Handler et al., 2014). These electron-transfer atom-exchange (ETAE) reactions between $\text{Fe(II)}_{\text{aq}}$ and Fe(III) -oxide minerals provide an exceptional opportunity to measure iron and oxygen-isotope exchange dynamics and fractionations.

Numerous reports of iron isotope fractionation during Fe(II) - Fe(III) ETAE reactions have been reported (Icopini et al., 2004; Jang et al., 2008; Mikutta et al., 2009; Wu et al., 2010), and enriched ^{57}Fe tracers have been recently employed to directly quantify, rather than infer, isotopic

exchange between iron components. For the Fe(II)-goethite system, near-complete (~90%) exchange between Fe(II)_{aq} and the Fe(III)-oxide has been observed (Handler et al., 2009; Handler et al., 2014), thus facilitating the ability to apply the “three-isotope” method to simultaneously measure isotopic exchange, via an enriched ⁵⁷Fe tracer, and natural mass-dependent fractionation in ⁵⁶Fe/⁵⁴Fe to obtain equilibrium isotope fractionation factors at low temperature (Beard et al., 2010; Frierdich et al., 2014a). The extensive iron-atom exchange that occurs between Fe(II)_{aq} and Fe(III)-oxide minerals, therefore, provides strong motivation to re-explore oxygen-isotope exchange for oxide-water systems.

Here, we investigate whether interaction between Fe(II)_{aq} and goethite catalyzes oxygen-isotope exchange between the mineral and water at low temperature. We concentrate our efforts on the mineral goethite due to i) its widespread natural occurrence, ii) previous investigations involving its reactions with Fe(II), demonstrating high extents of Fe exchange, and iii) because it is the most utilized iron oxide in oxygen isotope paleoclimate studies. We employ two isotopic tracers (⁵⁷Fe-enriched Fe(II)_{aq} and ¹⁷O-enriched water) to simultaneously track iron and oxygen exchange. The three-isotope method (¹⁸O-¹⁷O-¹⁶O) is used to monitor mass-dependent isotope fractionations in ¹⁸O/¹⁶O ratios, with the amounts of exchange constrained by variations in ¹⁷O/¹⁶O between goethite and water. Furthermore, a reversal approach was used to constrain equilibrium by reacting goethite that has natural oxygen-isotope compositions with two ¹⁷O-enriched waters that had ¹⁸O/¹⁶O ratios both higher and lower than that expected to be in equilibrium with goethite. Lastly, the results of our exchange experiments are compared with a goethite synthesis experiment, where ferrihydrite was converted to goethite via Fe(II)_{aq}-catalysis with both oxygen exchange and fractionation constrained during conversion and continued

reaction, using waters with two distinct oxygen isotope compositions to approach equilibrium from two directions.

2. METHODS

2.1. Water and Reagent Preparation.

The experimental design is based on reacting goethite that has natural abundance oxygen and iron isotope compositions with ^{57}Fe -enriched $\text{Fe(II)}_{\text{aq}}$ solutions that contain ^{17}O -labeled water. Changes in $^{57}\text{Fe}/^{56}\text{Fe}$ and $^{17}\text{O}/^{16}\text{O}$ ratios track the amount of isotopic exchange, whereas mass-dependent isotope fractionation for oxygen is determined by monitoring the $^{18}\text{O}/^{16}\text{O}$ ratios. Experiments were performed in two isotopically distinct waters (differing in $^{18}\text{O}/^{16}\text{O}$ by $\sim 16\text{‰}$), to confirm discrete isotope exchange trajectories, essentially a “reversal” approach to equilibrium. The starting waters were purified municipal tap water ($\geq 18.2 \text{ M}\Omega \text{ cm}$) from Houston, Texas and Fairbanks, Alaska, USA. These locations were chosen because of a reported $\sim 20\text{‰}$ spread in the $\delta^{18}\text{O}$ of the regions’ water (Bowen et al., 2007; O'Brien and Wooller, 2007). Waters were subsequently enriched by mixing them with ^{17}O -enriched H_2O (Isotec-Sigma-Aldrich, 90.7% ^{17}O); here on, the final ^{17}O -enriched waters are referred to simply as “water”. Goethite of two particle sizes, nanorods and microrods (Cwiertny et al., 2008), were utilized to test if oxygen-isotope exchange and fractionation depends upon surface area and particle size. These two types of goethite are the same as those described in Friedrich et al. (2014a) and have specific surface areas of 119 and $43 \text{ m}^2 \text{ g}^{-1}$ and dimensions of $\sim 100 \times 10 \times 10 \text{ nm}$ and $\sim 1000 \times 100 \times 100 \text{ nm}$ for nano- and microgoethite, respectively; these are respectively defined as n-Gth and μ -Gth. Mineral syntheses were performed in Iowa City, IA, USA, where the annual average precipitation has $\delta^{18}\text{O} \sim -8\text{‰}$ VSMOW (Bowen et al., 2007). Goethite materials produced from

Iowa water should have oxygen isotope compositions that, at equilibrium, have an oxygen isotope composition intermediate to goethite in oxygen isotope equilibrium with the Houston and Fairbanks water. Two ^{57}Fe -enriched aqueous Fe(II) solutions were prepared by diluting ~pure ^{57}Fe (II) (derived from dissolution of $^{57}\text{Fe}^0$, CHEMGAS-97.82%, in 1 M HCl) with 0.1 M reagent-grade FeCl_2 of natural isotopic abundance dissolved in Houston and Fairbanks water.

2.2. Exchange Experiments

The experimental protocol in this study involved the use of $\text{Fe(II)}_{\text{aq}}$ at circum-neutral pH and thus extreme care was taken to eliminate external Fe(II) oxidation by O_2 . All reactions were conducted inside an anaerobic chamber (Coy Laboratory Products, 3% H_2 -97% Ar) with an O_2 content maintained at < 1 ppm by continual atmospheric circulation over Pd catalysts. Prior to use, Houston and Fairbanks waters were deoxygenated by sparging with N_2 for 15 minutes followed by an additional 30 minutes of sparging inside the anaerobic chamber using its atmosphere after it passed through a secondary O_2/CO_2 trap consisting of a 15% pyrogallol-50% KOH aqueous solution. Goethite, labware, and chemical reagents were placed inside the chamber for >48 hours before use.

Pre-weighed portions of goethite (20 ± 0.2 mg) were combined with 8.8 mL of either Houston or Fairbanks water in 15 mL polypropylene centrifuge tubes with plug caps. The reactors were buffered, for ionic strength and pH, by adding an additional 1 mL of 250 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) and 250 mM KBr, which was pre-adjusted to pH 7.6 with KOH. Buffer solutions at 22 °C were prepared with both ^{17}O -enriched Houston and Fairbanks water. Note that oxygen derived from HEPES comprises less than 0.2% of all of the oxygen atoms in the final reactors and thus has a negligible effect on the measured oxygen isotope composition of the starting ^{17}O -enriched waters. Reactions were initiated by

adding 0.1 mL of a 0.1 M ^{57}Fe -enriched $\text{Fe(II)}_{\text{aq}}$ solution. The acidity of the Fe(II) solution caused the pH to decrease to 7.5 where it remained (± 0.1) for the length of the reaction. After initiating the experiment, the reactors were wrapped in Al foil and placed on an end-over-end rotator to keep the goethite suspension mixed in the absence of light.

Aqueous speciation calculations (Friedrich et al., 2014a), using the PHREEQC geochemical modeling interface (Parkhurst and Appelo, 1999), indicate that for all experiments $\text{Fe(H}_2\text{O)}_6^{2+}$ comprised a minimum of 97% of all aqueous Fe species. The total Fe aqueous ion complexes were a maximum of $\sim 0.01\%$ of all waters in the experiments. These calculations indicate that oxygen isotope “salt effects” (Hu and Clayton, 2003) were completely negligible under all experimental conditions in this study.

Elevated temperature experiments were also conducted to determine if isotopic fractionation between water and goethite follows a $1/T^2$ relation consistent with temperature dependent synthesis experiments (Bao and Koch, 1999; Yapp, 2007). A $1/T^2$ relation is consistent with, although does not prove, equilibrium isotope fractionation. We immediately found that conducting exchange experiments with $\text{Fe(II)}_{\text{aq}}$ at elevated temperatures is experimentally challenging because a constant, elevated temperature must be maintained in addition to anoxic conditions and suspension mixing. These conditions were achieved by running elevated temperature experiments in the same 15 mL tubes as our prior experiments except that solution temperature control and mixing was done by an Eppendorf Thermomixer R with an eight hole 15 mL dry thermoblock. Prior to initiating reactions, water, containing HEPES/KBr buffer, was preheated to 50°C . Reactions were then initiated by introducing 0.1 mL of a 0.1 M ^{57}Fe -enriched Fe(II) solution. Elevated temperature experiments were conducted at pH 6.8

instead of 7.5 as Fe(II) reaction with the solid at elevated pH results in loss of Fe(II)_{aq} and the formation of magnetite (Friedrich et al., 2014a).

Reactors were sacrificed at specified time intervals for sampling of Fe(II)_{aq} and goethite for iron and oxygen isotope analysis. The reactor suspension was filtered (0.2 µm), using a Swinnex filter holder assembly for solid recovery, into a clean 15 mL centrifuge tube. This aqueous component was acidified to 0.4 M HCl and saved for chemical and iron isotope analysis. An additional 5 mL of ¹⁷O-spiked Houston or Fairbanks water was passed through the filter assembly to wash residual HEPES, KBr, and sorbed Fe(II) from the solid; the wash fluid was discarded. The filter containing the washed goethite was then removed from the filter assembly and placed in a glass vial, dried in a vacuum desiccator inside the anaerobic chamber where it was stored until oxygen isotope analysis. Iron concentrations were measured by the Fe(II) selective reagent *Ferrozine*® (Stookey, 1970). Total iron was determined following the reduction of Fe(III) by hydroxylamine hydrochloride. Only Fe(II) was detected in the aqueous component. Additional iron fractions (e.g., sorbed, solid) were also sub-sampled to constrain the Fe mass balance; see the Supplementary Information (SI) (Tables S1, S2) and our prior work (Friedrich et al., 2014a).

2.3. Ferrihydrite Conversion Experiments

In addition to the exchange experiments described above, we performed synthesis experiments from ferrihydrite, which was converted to goethite by reaction with Fe(II)_{aq}. Ferrihydrite was precipitated outside the anaerobic chamber by titrating a ferric nitrate solution to pH 7 using NaOH (Schwertmann and Cornell, 2000). The resulting slurry was partitioned into two bottles and then centrifuged, the supernatant was decanted, and the solid was re-suspended in water. This was repeated 5 times with the last re-suspension in water occurring inside the

anaerobic chamber with Fairbanks and Houston water. Ferrihydrite was used as a suspension rather than dried to a powder to prevent irreversible aggregation and loss of reactivity (Raiswell et al., 2010). All reactions utilizing ferrihydrite were initiated within one week of the suspension preparation, as wet-aging may result in gradual re-crystallization (Raiswell et al., 2010). Reactions were initiated and sampled at 22 °C as discussed above (Section 2.2.) except 2 g/L of ferrihydrite was reacted with 1 mM Fe(II)_{aq} solutions for 14 d at pH 6.8; the lower pH was chosen to prevent magnetite nucleation (Friedrich et al., 2014b).

2.4. Isotopic Analyses and Data Presentation

2.4.1. Iron Isotopes

The iron isotope composition of Fe(II)_{aq} was determined by measuring ⁵⁷Fe/⁵⁶Fe ratios on a Micromass *Isoprobe* at the University of Wisconsin-Madison following previously described methods (Beard et al., 2010). These compositions are presented in the standard delta (δ) notation in units of per mil (‰):

$$\delta^{57}\text{Fe}/^{56}\text{Fe} = [({}^{57}\text{Fe}/^{56}\text{Fe})_{\text{sample}} / ({}^{57}\text{Fe}/^{56}\text{Fe})_{\text{standard}} - 1] * 1000 \quad (1)$$

(⁵⁷Fe/⁵⁶Fe)_{standard} is the average ratio of igneous rocks (Beard et al., 2003). The measured isotope composition of the IRMM-014 Fe isotope standard was $\delta^{57}\text{Fe}/^{56}\text{Fe} = -0.04 \pm 0.17 \text{ ‰}$ (2σ; n=51).

Prior to iron isotope analyses, all samples were purified by anion-exchange chromatography to remove potentially interfering matrix components (i.e., HEPES, KBr, HCl). As discussed previously, the purification steps do not affect the iron isotope compositions (Friedrich et al., 2014a; Friedrich et al., 2014b). External precision based on the average standard deviation of replicate analyses of identical samples processed through the entire analytical procedure was 0.26‰ in $\delta^{57}\text{Fe}/^{56}\text{Fe}$ (2σ; n=19).

2.4.2. Oxygen Isotopes

Oxygen isotope ratios of goethite were measured in the Stable Isotope Laboratory at the University of Wisconsin-Madison by laser fluorination and gas-source mass spectrometry. Solids were removed from the anaerobic chamber, packed (2-4 mg) into the hollow ends of Ni pins, and placed into an outer vacuum chamber overnight prior to analysis (Spicuzza et al., 1998). The mass of goethite in each pin was recorded (± 0.1 mg) for oxygen recovery calculations. Samples were moved individually into an inner chamber for fluorination. Oxygen was extracted from goethite by laser heating the solid in a BrF_5 atmosphere. Molecular oxygen was cryogenically separated from residual BrF_5 and reaction products, and then converted to CO_2 by reduction on an electrical-resistance-heated graphite rod. Oxygen yields were then measured manometrically (± 0.1 μmole), and the CO_2 was passed into a dual-inlet triple-collector Finnigan MAT-251 isotope ratio mass spectrometer (IRMS).

For $^{18}\text{O}/^{16}\text{O}$ ratios, oxygen isotope compositions are presented in standard δ notation

$$\delta^{18}\text{O} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}} - 1] * 1000 \quad (2)$$

and $(^{18}\text{O}/^{16}\text{O})_{\text{standard}}$ is the isotope ratio for VSMOW. The average measured $\delta^{18}\text{O}$ value of the UWG-2 (Gore Mountain garnet) oxygen isotope standard was $\delta^{18}\text{O} = 5.77 \pm 0.22\text{‰}$ (2σ ; $n=49$), consistent with the long term average value of 5.8‰ for the UW Stable Isotope Lab (Valley et al., 1995).

Determination of the extent of oxygen-isotope exchange, as evidenced by the incorporation of the tracer isotope (^{17}O) into the goethite in this study, was accomplished using a novel approach. It is important to note that for quantifying the effective amount of exchange, the measurement of absolute $\delta^{17}\text{O}$ values is not required, only a way to precisely measure the relative amount of ^{17}O exchanged. To accomplish this, we utilized a high level of ^{17}O enrichment in the experimental waters. Since the normal procedure for calculation of $\delta^{13}\text{C}$ in CO_2 analyzed

by gas-source mass spectrometry assumes a mass-dependent relation of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, any deviation in the $^{17}\text{O}/^{16}\text{O}$ ratio from the terrestrial mass-dependent fractionation line will change the $\delta^{13}\text{C}$ value calculated by the mass spectrometer software. The ^{17}O concentrations used in this study were high enough to alter the calculated values of $\delta^{13}\text{C}$ by up to 6‰ during analysis of CO_2 derived by fluorination of experimental goethite samples. This 6‰ shift corresponds roughly to an enrichment of 90‰ in $\delta^{17}\text{O}$; a 1‰ enrichment in $\delta^{17}\text{O}$ corresponds to a calculated $\delta^{13}\text{C}$ increase of 0.066‰. See the Supplementary Information for details on the calculation of $\delta^{13}\text{C}$ values, which we define as “ $\delta^{13}\text{C}_{\text{Calc}}$ ”, for use in calculating the extent of oxygen exchange.

Because a >1000 molar excess of oxygen is contained in the water relative to the Fe(III)-oxide for each experimental run, only the solid was monitored for temporal changes in oxygen isotope composition; the initial oxygen isotope composition of the ^{17}O -enriched water was determined for mass-balance constraints to calculate the fraction of oxygen-isotope exchange and to determine the $\delta^{18}\text{O}$ value of each water (see section 2.5 below and Table 1). The external precision in $\delta^{18}\text{O}$, based on replicate analyses for select samples, for $\mu\text{-Gth}$ was 0.22‰ (2σ ; $n=15$) and 0.24‰ (2σ ; $n=11$) for $n\text{-Gth}$. The external precision for $\delta^{13}\text{C}_{\text{Calc}}$ values was ± 0.10 ‰ (2σ ; $n=11$) and ± 0.08 ‰ (2σ ; $n=15$) for $n\text{-Gth}$ and $\mu\text{-Gth}$, respectively. Oxygen yields were quantitative for microgoethite ($96\pm 2\%$), but slightly poorer and more variable for nanogoethite ($91\pm 4\%$) (Table 2); the poorer yields and precision for nanogoethite are attributed to its tendency to sputter from the Ni pins during laser heating.

2.5. Isotopic Exchange Calculations

A critical aspect of this study is to quantify the relative amounts of iron and oxygen in goethite that exchange with the fluid component (i.e., $\text{Fe(II)}_{\text{aq}}$ and H_2O). A common way to infer

isotopic exchange is to monitor the fractional movement of an isotope ratio of one component towards the equilibrium value (Criss, 1999) as defined below:

$$F = \frac{\delta_t - \delta_i}{\delta_{eq} - \delta_i} \quad (3)$$

where δ_t is the isotopic composition of one reacting component at time t , δ_i is the initial isotopic composition of that component, and δ_{eq} is the isotopic composition for the entire system at equilibrium (i.e., reactor mass balance plus equilibrium fractionation between reacting components) after complete mixing has occurred. Eq 3 is valid for quantifying the relative approach of a system to isotopic equilibrium, and has been employed successfully for experimental calibrations of isotopic fractionation (Friedrich et al., 2014a; Friedrich et al., 2014b; Graham, 1981; Guilbaud et al., 2010; Li et al., 2011; Northrop and Clayton, 1966; Wu et al., 2011). Furthermore, F is a useful kinetic parameter for assessing the equilibration time of mineral-fluid systems (Cole et al., 1983; Criss, 1999; Criss et al., 1987; Gregory and Criss, 1986). Although F is related to isotopic exchange, and commonly referred to as the fraction of isotopic exchange (Cole and Ohmoto, 1986), it does not provide an assessment of the number of atoms that have exchanged for a component at any given time.

Consider a two component system where each exists in non-equal proportions. As an example, Fe(II)_{aq} and Fe(III) in goethite in this study comprise ~5 and 95% of the total iron atoms, respectively. For this situation, Fe(II)_{aq} would need to “turnover” a minimum of ~20 times for the iron in goethite to completely exchange, just once, with the fluid. Clearly, F cannot be a direct measure of the number of atoms that have exchanged since for an ideal two-component system the F of the fluid is equal to the F of the mineral at any given time (Criss et al., 1987). Hence, we use a mass-balance approach to derive equations to quantify the number of atoms in a mineral that exchange with a fluid species, as previously described for the exchange

between Fe(II)_{aq} and goethite (Handler et al., 2014; Mikutta et al., 2009). The following equations are applicable to both iron exchange between Fe(II)_{aq} and goethite or oxygen exchange between goethite and water.

Briefly, we initially define a mass-balance equation:

$$\delta_{sys} \times N_{sys} = \delta_{aq}^i \times N_{aq} + \delta_{Gth}^i \times N_{Gth}^{ex} \quad (4)$$

where δ_{sys} , δ_{aq}^i , and δ_{Gth}^i is the isotopic composition of the entire system, initial isotopic composition of the aqueous component, and initial isotopic composition of goethite, respectively. N_{sys} , N_{aq} , and N_{Gth}^{ex} is the total moles of iron or oxygen for the system, moles of Fe(II) or water in the system, and moles of Fe(III) or oxygen in goethite that has exchanged, at least once, with the aqueous component, respectively. Importantly, the “system” described here refers to the components that have participated in exchange and are at equilibrium after mixing. At this condition, $\delta_{sys} = \delta_{Gth}^{ex} = \delta_{aq}^t$ and $N_{sys} = N_{aq} + N_{Gth}^{ex}$; δ_{aq}^t is the measured isotopic composition of the aqueous component for time >0 and δ_{Gth}^{ex} is the isotopic composition of goethite that has exchanged, at least once, with the aqueous component. Substitution of δ_{aq}^t for δ_{sys} and $N_{aq} + N_{Gth}^{ex}$ for N_{sys} into eq 4 and solving for δ_{aq}^t yields:

$$\delta_{aq}^t = \frac{N_{Fe(II)}}{(N_{Fe(II)} + N_{Gth}^{ex})} \times \delta_{aq}^i + \frac{N_{Gth}^{ex}}{(N_{Fe(II)} + N_{Gth}^{ex})} \times \delta_{Gth}^i \quad (5)$$

Eq 5 predicts how the isotopic composition of the aqueous component changes with progressive exchange with Gth, and this can be modified to produce the % of iron or oxygen atoms in Gth that has exchanged with the aqueous component:

$$\frac{N_{Gth}^{ex}}{N_{Gth}^{Tot}} \times 100 = \% \text{ Gth Exchange} = \frac{N_{aq} \times (\delta_{aq}^i - \delta_{aq}^t)}{N_{Gth}^{Tot} \times (\delta_{aq}^t - \delta_{Gth}^i)} \times 100 \quad (6)$$

Since a >1000 molar excess of oxygen is contained in the water relative to the oxide, eq 6 is not particularly useful for quantifying oxygen exchange in goethite, as the composition of the

fluid will not significantly change. For iron, however, the Fe(II)_{aq}:Gth molar ratio is about 1:20 and thus eq 6 is essential.

Mass-dependent isotope fractionation between Fe(II)_{aq} and Gth during exchange may affect calculations made by eq 6 because the process is no longer one of pure mixing. The degree of isotopic fractionation, and its effect on calculations via eq 6, depends on the level of the enrichment of the tracer relative to the fractionation factor between the aqueous component (H₂O or Fe(II)_{aq}) and goethite, and the ratio of $N_{aq}:N_{Gth}^{Tot}$. Because the equilibrium iron isotope fractionation factor between Fe(II)_{aq} and goethite is known (Beard et al., 2010; Frierdich et al., 2014a), a correction can be made:

$$\frac{N_{Gth}^{ex}}{N_{Gth}^{Tot}} \times 100 = \% \text{ Gth Fe Exchange} = \frac{N_{aq} \times [\delta_{aq}^i - (\delta_{aq}^t - w)]}{N_{Gth}^{Tot} \times [(\delta_{aq}^t - w) - \delta_{Gth}^i]} \times 100 \quad (7)$$

and

$$w = F \times \Delta \times \left(1 - \frac{N_{aq}}{N_{Gth}^{Tot} + N_{aq}} \right) \quad (8)$$

where Δ is the Fe(II)_{aq}-Gth equilibrium isotope fractionation factor in terms of $\delta^{57/56}\text{Fe}$ values (‰); $\Delta^{57/56}\text{Fe}_{\text{Fe(II)aq-Gth}}$ for nano- or microgoethite is equal to -0.61 or -0.52‰, respectively (Beard et al., 2010; Frierdich et al., 2014a). The last term adjusts Δ to the iron mole fraction of Fe(II) for the system.

Note that the model provided here allows us to quantify only the “minimum” amount of exchange that has occurred as additional “hidden” reactions (e.g., $^{56}\text{Fe(II)}_{aq}$ exchange for $^{56}\text{FeOOH}$) are likely to have transpired, but these hidden reactions do not change the isotopic composition of any component and thus cannot be tracked experimentally.

The isotopic composition of Gth as a function of exchange can also be derived from a mass-balance equation in order to quantify oxygen (or iron) isotope exchange (see Supplementary Information for derivation), which simplifies to:

$$\frac{N_{Gth}^{ex}}{N_{Gth}^{Tot}} \times 100 = \% \text{ Gth O Exchange} = \frac{\delta_{Gth}^t - \delta_{Gth}^i}{\delta_{aq}^t - \delta_{Gth}^i} \times 100 \cong \frac{\delta_{Gth}^t - \delta_{Gth}^i}{\delta_{aq}^i - \delta_{Gth}^i} \times 100 \quad (9)$$

The temporal oxygen isotope composition of water (δ_{aq}^t) is effectively constant because oxygen in the water represents a >1000 molar excess relative to oxygen in the solid goethite. Hence, δ_{aq}^t is equal to the initial composition of the fluid (δ_{aq}^i). Interestingly, eq 9 simplifies to a form identical to F (eq 3) and can thus also be used for an assessment of the relative approach to isotopic equilibrium. Also note that Gth-water oxygen isotope fractionation has an insignificant effect (equivalent to ~1% or less exchange at our enrichments) on calculated oxygen exchange values in this study, even if the Gth-water oxygen isotope fractionation factor is assumed to be equal to ~ +3‰ in $\delta^{17}\text{O}$ (Yapp, 2007), which is the largest fractionation factor reported. Note that for a one per mil change in $\delta^{17}\text{O}$, the corresponding shift in measured $\delta^{13}\text{C}_{calc}$ is only ~ 0.07‰ and within the range of our measurement error as noted above in section 2.4.2.

3. RESULTS

3.1. Fe(II)-Catalyzed Oxygen-Isotope Exchange between Goethite and Water

Reaction of goethite with Fe(II)_{aq} results in iron-atom exchange between Fe(III) in the mineral and Fe(II) in solution, with no change in solid phase identity or microscopic characteristics (Friedrich et al., 2014a; Friedrich et al., 2012; Handler et al., 2009; Handler et al., 2014; Latta et al., 2012; Pedersen et al., 2005). As expected, similar amounts of iron exchange were observed in this study as evident by the temporal decrease of $^{57}\text{Fe}/^{56}\text{Fe}$ ratios in the Fe(II)_{aq} component (Table 2); these large changes can only occur if structural Fe(III) in goethite, which

had a natural iron isotope composition in our experiments, is reduced to Fe(II) and released to solution. The current conceptual model for this exchange is that it occurs in an approximately 1:1 manner; one iron added to goethite causes another iron to be released (Handler et al., 2009; Handler et al., 2014). Such recrystallization of goethite must involve the breaking and making of Fe-O bonds, increasing the lability of lattice atoms and, thus, exchange of structural oxygen with water is expected.

Goethite suspended in ^{17}O -enriched water containing $\text{Fe(II)}_{\text{aq}}$ does indeed show a significant shift in $\delta^{13}\text{C}_{\text{Calc}}$ over time (Table 2), which demonstrates uptake of ^{17}O from the fluid (Figure 1). Control experiments in which goethite was suspended in Fe(II)-free, ^{17}O -enriched water for 30 days show minimal change (none within error) in their oxygen isotope composition relative to the starting mineral (red symbols, Figure 1A), a result that may be expected based on the limited solubility of goethite at pH 7.5. In the experiments using ^{17}O -enriched water containing $\text{Fe(II)}_{\text{aq}}$, the rate of ^{17}O uptake by goethite, however, rapidly decreases and appears to approach a steady-state composition that is far from complete exchange with the enriched water (Figure 1B). Calculations (eq 9) indicate that the shift in $\delta^{13}\text{C}_{\text{Calc}}$ corresponds to about 20% oxygen-isotope exchange after 51 days of reaction for both nano- and microgoethite.

Comparison of the amount of iron versus oxygen exchange reveals a surprising disparity. Iron-isotope exchange is much more extensive than oxygen-isotope exchange (Figure 2), a result that was unanticipated because either oxygen or iron-isotope exchange in iron oxides should break Fe-O bonds. For larger fractions of iron-atom exchange, beyond that which would solely involve surface atoms and which would be anticipated to require access of the exchange front into particle interiors, one might expect the relative amount of Fe:O exchange to approach a value of 1:1. In contrast, the data suggest 1:0.31 at 50 d. No difference in the extent of iron or

oxygen exchange is observed for n-Gth vs. μ -Gth particles, despite a three-fold difference in specific surface area. This suggests that oxygen exchange is not dependent merely on available goethite surface area exposed. However, interpretation of the similar amounts of exchange, despite differences in specific surface area, is complicated by the fact that both materials are highly aggregated at pH 7.5. As noted in prior work, aggregation may decrease “reactive” surface area of nano-particulate goethite (Cwiertny et al., 2008; Handler et al., 2014; Rubasinghege et al., 2012; Stemig et al., 2014).

In an effort to increase the fraction of oxygen-isotope exchange, reactions were also conducted at elevated temperature (50 °C). This temperature increase enhanced the amount of iron exchange for nanogoethite but not for microgoethite (Figure 2B). These differences in iron exchange at 50 °C are difficult to interpret because Fe(II) recovery for the μ -Gth reaction was low (i.e., ~30%, SI Table S1), suggesting a secondary process occurred in the 50 °C μ -Gth experiments such as Fe(II) precipitation and passivation or minor magnetite formation, as discussed in our prior work (Friedrich et al., 2014a). The amount of additional oxygen-isotope exchange relative to reactions at 22 °C for both goethite materials was minimal, i.e., Δ ~5-10% (Figures 2, 3). Control experiments that contained goethite in ^{17}O -enriched water at 50 °C without Fe(II)_{aq} produced ~5% exchange relative to ~1% for the Fe(II)-free control at 22 °C (red symbols, Figure 3), indicating that the minor additional oxygen exchange during Fe(II)_{aq}-goethite reactions at 50 °C may reflect background recrystallization that becomes more important at higher temperatures. In Section 4 we discuss the origins for the differences in iron and oxygen-isotope exchange.

3.2. Mineral-Water Oxygen Isotope Fractionation

Extensive experimental studies of Fe(II)_{aq}-goethite interactions have shown that iron-isotope exchange occurs without significant changes in crystal morphology or total mass, suggesting a balanced dissolution/recrystallization mechanism (Beard et al., 2010; Frierdich et al., 2014a; Handler et al., 2009; Handler et al., 2014). Because Fe(II)-catalyzed recrystallization of goethite results in mineral-water oxygen-isotope exchange, albeit less than anticipated, changes in the ¹⁸O/¹⁶O ratios of the solid may in part reflect mass-dependent oxygen isotope fractionation. Indeed, temporal variations in δ¹⁸O values for goethite were significant during reactions with Fe(II)_{aq} (Figure 4). For both sizes of goethite, ¹⁸O/¹⁶O ratios either increased or decreased depending on whether the reaction occurred in Houston or Fairbanks water, respectively. The opposite trajectories of δ¹⁸O values in goethite suggest that the initial composition of the solid is above the equilibrium value in the lower-δ¹⁸O Fairbanks water and below equilibrium in the higher-δ¹⁸O Houston water. The temporal fractionation trajectories, where the % exchange is calculated based on ¹⁷O and ⁵⁷Fe tracers (see above), are similar for nano- and microgoethite, and have a form similar to that observed for oxygen-isotope exchange (i.e., rapid initial change followed by a plateau at longer times), suggesting that apparent isotopic fractionation is directly proportional to the amount of exchange with water. The corresponding fractionation-exchange trajectories are linear for all of the exchange experiments conducted in this study (Figure 5), indicating that there was no apparent change in the instantaneous isotope fractionation factor.

The linear fractionation vs. exchange trajectories of goethite provide the possibility to extrapolate δ¹⁸O values to 100% exchange to estimate the goethite-water oxygen isotope equilibrium fractionation factor. The accuracy and precision of extrapolated values depends on data quality and the extent of extrapolation. Unfortunately, only ~15-25% of oxygen in goethite

underwent exchange and thus the errors associated with final extrapolated values are in the per mil range for most samples (Figure 5, Table 3). Even so, there is excellent agreement between the mineral-water oxygen isotope fractionation factor determined for microgoethite reacted in Houston and Fairbanks water, where final estimated $^{18}\text{O}/^{16}\text{O}$ fractionations lie within 0.1‰, despite the fact that these values were obtained using waters that differed by ~16‰, resulting in steep trajectories that approached equilibrium from opposite directions (Table 3). The congruency of these two results suggests that the final extrapolated values are close to the equilibrium values.

The fractionation factors for nanogoethite are more variable and have larger errors for reactions in each water, relative to those obtained for microgoethite. For both reactions with nanogoethite, however, the extrapolated oxygen isotope fractionation factors are substantially larger than for microgoethite. Combination of the fractionation factors obtained from both waters for each mineral yields a weighted average for $\Delta^{18}\text{O}_{\text{Gth-water}}$ of $3.0 \pm 2.5\text{‰}$ (2σ) and $0.2 \pm 0.9\text{‰}$ (2σ) at 22 °C for nanogoethite and microgoethite, respectively.

Reactions at 50 °C have smaller goethite-water fractionation factors for both particle sizes, and are consistent with a $1/T^2$ dependence. As was the case for the lower-temperature experiments, there is good agreement between oxygen isotope fractionation factors obtained using a reversal approach to equilibrium (Figure 5), and, as observed for reactions at 22 °C, there appears to be a particle-size affect where nanogoethite and microgoethite produce distinctly different extrapolated values for $\Delta^{18}\text{O}_{\text{Gth-water}}$ of $1.9 \pm 1.5\text{‰}$ (2σ) and $-1.6 \pm 0.8\text{‰}$ (2σ), respectively. A similar particle-size effect on measured $^{56}\text{Fe}/^{54}\text{Fe}$ fractionations has been observed for nano- versus microgoethite for similar exchange experiments (Beard et al., 2010; Frierdich et al., 2014a). To our knowledge, however, a similar effect on oxygen isotope

fractionation for iron oxide-fluid systems has not been observed. The significance of these results is discussed in detail in Section 4.1.

3.3. Fe(II)-catalyzed Transformation of Ferrihydrite

Goethite was synthesized by reaction of $\text{Fe(II)}_{\text{aq}}$ with ferrihydrite to test how phase transformations may affect oxygen-isotope exchange and fractionation with water, and whether such an approach yields a meaningful estimate for the equilibrium oxygen isotope fractionation factor. Reaction of $\text{Fe(II)}_{\text{aq}}$ with ferrihydrite results in a rapid transformation to lepidocrocite and goethite, which is followed by a gradual conversion to goethite as the single solid phase (SI Figure S1), a result consistent with recent work (Boland et al., 2014). Mineral phase evolution is accompanied by particle morphological changes consistent with those of lepidocrocite and goethite (SI Figure S2). In contrast to the exchange experiments discussed earlier, extensive oxygen-isotope exchange between the solid and fluid occurred during ferrihydrite transformation to goethite (Figure 6). Similarly, a substantial shift in the $\delta^{18}\text{O}$ values for goethite occurred, and final values approached $-17.09 \pm 0.16\text{‰}$ and $-1.16 \pm 0.08\text{‰}$ (2σ) for reactions in Fairbanks and Houston water, respectively. Corresponding oxygen isotope fractionation factors for these two different starting waters differ by $\sim 0.6\text{‰}$ (Table 3), despite their drastically different fractionation trajectories (Figure 6B). Again, the congruency between these values suggest that they may be near-equilibrium values; the combined oxygen isotope fractionation factor for these experiments is $\Delta^{18}\text{O}_{\text{Gth-Water}} = 1.6 \pm 0.2\text{‰}$ (2σ) at 22 °C . Note that the particle size (SI Figure S2) and measured fractionation of goethite formed from the transformation of ferrihydrite are intermediate to the results obtained for nanogoethite and microgoethite.

4. DISCUSSION

4.1. Equilibrium Goethite-Water Oxygen Isotope Fractionations

The current study is the first, to our knowledge, to directly measure goethite-water oxygen isotope fractionation by direct exchange experiments at room temperature. The ^{17}O -enriched tracer experiments demonstrate that oxygen isotope compositions of iron oxides may be perturbed during biogeochemical iron cycling through aqueous Fe(II) -oxide interactions, but may be relatively inert in the absence of $\text{Fe(II)}_{\text{aq}}$. This bears on the use of oxygen isotope compositions in natural goethite minerals as proxies for paleoclimate. Furthermore, comparison of the extrapolated fractionation factors obtained in this study with those of prior synthesis approaches reveals a relation between goethite particle size and mineral-water oxygen isotope fractionation.

Prior synthesis experiments yield goethite-water fractionation factors that range by about 10‰ at 22 °C (Bao and Koch, 1999; Müller, 1995; Xu et al., 2002; Yapp, 2007). The results from these works do not randomly span the entire range of fractionation factors but rather lie at the extremities of ~ -2 to 0‰ and $+6$ to $+8$ ‰, which appear to correlate with syntheses conducted at high and low pH, respectively, as highlighted by Yapp (2007). A model to describe the bimodal nature of these results suggests that fractionations during high pH (~ 14) syntheses are kinetically controlled, whereas low pH (~ 1 -2) experiments are inferred to have approached equilibrium (Yapp, 2007). The pH model developed in Yapp (2007) proposes that intermediate goethite-water fractionations (i.e., between the current reported extremities) may occur at circumneutral pH during synthesis experiments. The extrapolated goethite-water fractionations determined in the present work do, in fact, lie between the values reported by Bao and Koch, 1999 and Yapp, 2007, and were conducted at pH 7.5 (Figure 7).

Several distinctions exist, however, between the current study and previous work. The mechanism of isotopic fractionation in our work is likely different than that of a synthesis approach, where our work involved true exchange reactions. Furthermore, the exchange experiments with nano- and microgoethite, both of which were conducted at pH 7.5, yield significantly different fractionations that imply pH is not the only cause for the discrepancy between our exchange work and synthesis approaches. Interestingly, goethite-water fractionations observed for nanogoethite are similar to those of Yapp (2007), whereas for microgoethite our measured fractionations are consistent with Bao and Koch (1999). Of importance is the fact that the particle size of goethite synthesized at pH extremes also have distinct differences, where synthesis at low pH (e.g., Yapp, 2007) produces goethite nanoparticulates, and synthesis at high pH (e.g., Bao and Koch, 1999) tends to produce micron-sized particles (Schwertmann and Cornell, 2000). Thus, the unique fractionations that we see between nano- and microgoethite with water, but their apparent similarity with prior works that employed goethite of similar size, suggests that much of the disagreement for reported equilibrium fractionation factors in the goethite-water system arises from the fact that materials of drastically different size are created during synthesis experiments under pH extremes. As noted above, a similar particle size effect on the fractionation of iron isotopes has been reported for goethite (Beard et al., 2010; Frierdich et al., 2014a).

The thermodynamic properties of nanoparticulate iron oxides are known to differ from their larger counterparts as a result of a larger proportion of their atoms occurring at the mineral surface which comprise unique energetic properties relative to the bulk crystalline solid (Navrotsky et al., 2008). Beard et al. (2010) and Frierdich et al. (2014a) interpreted iron isotope fractionations for goethite that varied with crystal size to reflect the distinct isotopic properties of

surface-bound iron relative to iron in the bulk crystal. Indeed, the proportion of atoms at the surface of n-Gth and μ -Gth is about 20% and 7%, respectively (see Handler et al., 2014 for calculations), which accounts for a substantial fraction of the total atoms in the mineral. Following this reasoning, the isotopic properties of oxygen near the surface of goethite could also exhibit unique fractionations as a result of a bonding environment that differs from that of the interior of the bulk crystal. Molecular dynamics simulations (Boily, 2012) and synchrotron-based X-ray surface diffraction and crystal truncation rod analysis (Ghose et al., 2010) show that goethite surface Fe-O bonds exhibit a substantial amount of relaxation relative to the bulk mineral, which could change their thermodynamic, and hence isotopic, properties.

4.2. Mechanism for Non-Stoichiometric Iron and Oxygen Exchange in Goethite.

The experiments discussed above unexpectedly show that a greater amount of iron in goethite exchanges with $\text{Fe(II)}_{\text{aq}}$ relative to oxygen in goethite with oxygen in water. This discovery requires explanation, as the exchange of either iron or oxygen necessitates the breaking and formation of Fe-O bonds. We propose that this behavior arises from differences in the exchange rate of various possible oxygen functional groups on the crystal surface relative to water oxygens ligating aqueous Fe(II). Fe(II) docking to or release from the surface can be presumed to be facilitated by oxygen ligand exchange reactions that interconvert:

where x and y distinguish oxygen ligand species due to local coordination to other $\text{Fe}^{2+/3+}$ and/or H^+ ions. In either direction of this interconversion, i.e., during growth of the goethite by addition of a new lattice iron atom or during dissolution by removal of an iron atom, the ligand exchange rate of O_x is implied to be slower than that of O_y . Simply put, the more labile O_y , which represents oxygen in water, does not readily incorporate into goethite during Fe(II) adsorption or

oxidative growth (moving left to right in eq 10) and is not removed from the mineral during Fe(II) desorption or Fe(III) reductive dissolution (moving right to left in eq 10). On this basis we can speculate electron-transfer atom-exchange (ETAE) mechanisms that are consistent with non-stoichiometric Fe:O isotopic exchange, where iron exchange can approach 100%, but oxygen exchange between goethite and water is more limited.

Two types of oxygen species are present in the goethite bulk, one is an OH⁻ that bridges shared edges of iron octahedra and one is a bare O²⁻ that bridges corners of iron octahedra. At goethite surfaces, broken symmetry creates a wider variety of lattice oxygen speciation than what would be present in the interior, including singly (η^1 -OH₂), doubly (μ_2 -OH), or triply (μ_3 -OH and μ_3 -O) coordinated oxygens with structural Fe(III) (Casey, 2001). These differences in oxygen speciation strongly affect their exchange rate with water oxygens. ¹⁷O-NMR methods, for example, have been used to measure exchange rates between cation-coordinated water molecules with the bulk fluid (Richens, 2005), and yield a relatively fast exchange rate constant of 4.4×10^6 exchanges s⁻¹ for [Fe(H₂O)₆]²⁺ (Ducommun et al., 1980), and 6.8×10^4 exchanges s⁻¹ for [Fe(H₂O)₆]³⁺ (Swaddle and Merbach, 1981). Singly coordinated water molecules (η^1 -OH₂) on the goethite surface (i.e., >Fe^{III}-OH₂ functional groups) are likewise relatively labile, exhibiting a rate constant of $\sim 10^6$ exchanges s⁻¹, based on ¹⁷O-NMR of aqueous iron-containing clusters (Balogh et al., 2007; Panasci et al., 2012). Consequently, η^1 -OH₂ groups associated with Fe(II)_{aq}, sorbed Fe(II), and >Fe^{III}-OH₂ should all readily exchange oxygen isotopes and equilibrate with the bulk fluid rapidly. Because the fluid contains a >1000 molar excess of oxygen relative to the mineral, and because mass-dependent fractionation will be minor relative to the enrichment of the ¹⁷O isotope tracer, these groups should thus have essentially the same isotopic composition as the fluid with respect to any slower reaction involving these species.

The exchange rates of doubly and triply coordinated surface oxygen functional groups for goethite are not accurately known, but because of numerous bonds to lattice Fe^{III} , these should be much slower to exchange than singly coordinated oxygen species. Indeed, ^{17}O -NMR and ^{18}O -enriched tracer techniques have shown that multiply coordinated surface oxygen groups on aqueous Al oxide clusters and bayerite ($\alpha\text{-Al}(\text{OH})_3$), respectively, are orders of magnitude slower (e.g., 10^{-4} to 10^{-8} exchanges s^{-1}) than for $\eta^1\text{-OH}_2$ groups (Casey et al., 2001; Rosenqvist and Casey, 2004). Furthermore, these oxygen atoms should be less strongly affected by redox-state changes in the underlying structural iron atoms to which they are bonded because the associated local charge redistribution is shared across bridging bonds (Hillier and Wydrzynski, 2008). Thus, on the time scale of $\text{Fe}(\text{II})_{\text{aq}}$ -goethite iron exchange, doubly and triply coordinated functional groups on goethite can be considered inert to a close approximation. We propose that the extreme differences in reactivity of these various oxygen groups in the $\text{Fe}(\text{II})_{\text{aq}}$ -goethite-water system causes the disparity in iron versus oxygen-isotope exchange that we observe during $\text{Fe}(\text{II})$ -catalyzed goethite recrystallization.

Consider the following simple conceptual model for the mass and charge balanced ETAE process for goethite. For the oxidative addition of Fe:

and after electron migration within the goethite to a different surface iron site, for the subsequent reductive dissolution of iron:

where the subscripts w and s indicate that iron or oxygen species are isotopically equilibrated with the water or solid phases, respectively, and $>\text{OH}^-_s$ is a highly Fe^{III} -coordinated (slow-exchanging) oxygen species associated with the solid. As written, this increases the

stoichiometric Fe:O isotopic exchange rate expectation of 1:2 to 1:1, because the $>\text{OH}^-_s$ species never resides in the fluid phase. As written these reactions also illustrate a process for non-stoichiometric iron and oxygen exchange in terms of a stoichiometric FeOOH growth/dissolution fundamental unit. The reactions do not, however, represent a step-wise mechanism, which of course will include less frequent exchange of bridging oxygens with water oxygens, likely through a transient water addition reaction intermediate (Casey, 2001).

We can extend such a model more specifically to a representative low-index surface of goethite, such as a (110) surface (Figure 8). Here, two goethite surface octahedral sites of a double-chain termination are considered, where one is a vacancy and the other is occupied by an Fe(III). Singly coordinated groups on the periphery of these sites should readily exchange with the bulk fluid (Balogh et al., 2007; Panasci et al., 2012), and thus maintain the isotopic signature of the fluid (Figure 8A). When Fe(II) sorbs on the vacant surface site, the solid should retain its doubly coordinated oxygen atoms because they are recalcitrant to exchange; they generally maintain the isotopic signature of the goethite. During Fe(II) adsorption at the vacant site, $\eta^1\text{-OH}_2$ groups associated with the incoming Fe(II) and the vacant site will compete for incorporation as bridging ligand (i.e., conversion to a slow exchanging lattice oxygen species) for the adsorbing Fe(II) but generally maintain the isotopic signature of the fluid during incorporation. Because such sites nominally comprise the most energetically favorable sites for charge uptake under normal environmental conditions (Boily, 2012) we speculate that this specific process of converting labile singly coordinated oxygen species to doubly or higher coordination as part of the lattice comprises the incorporation mechanism of fluid oxygen into goethite upon iron addition (Figure 8B). The adsorbed Fe(II) is inferred to transfer an electron to the underlying Fe(III) in goethite, based on experimental studies (Cwiertny et al., 2008; Silvester

et al., 2005; Williams and Scherer, 2004), and to be capable of migrating to a different surface iron site on a goethite crystallite, thus comprising simultaneous Fe(II) oxidative adsorption and reduction of a structural Fe(III) to Fe(II) (Figure 8C). This newly formed Fe(II) atom then detaches, entering solution, taking with it some of its oxygen atoms (Figure 8D). The iron detachment step should remove primarily singly coordinated oxygen, already expected to be in isotopic equilibrium with the bulk fluid, whereas the more highly bonded oxygen atoms remain with the mineral. Accounting for the total number of fluid and goethite oxygen atoms before and after one Fe(II)_{aq}-goethite iron exchange in our specific example in Figure 8 reveals no net oxygen exchange coupled to one iron exchange. Although other possible sites of Fe(II) sorption and Fe(III) reduction/detachment may result in stoichiometric or, hypothetically, even an excess of oxygen uptake from the fluid, iron on the goethite surface with the most singly coordinated oxygen atoms will be the most likely to detach, as discussed in Casey et al. (2001). Simply put, iron-isotope exchange will preferentially occur for goethite surface iron atoms that have the most singly coordinated oxygen groups, which already are in oxygen isotope equilibrium with the fluid, thus resulting in an overall less than stoichiometric Fe:O exchange of isotopes because the kinetically less labile multi-coordinated goethite surface oxygen atoms will be less likely to interact with the fluid.

It is unclear at present if our model of differential reactivity for oxygen and iron atoms on the goethite surface can be fully reconciled with the evidence that essentially complete turnover of iron atoms in goethite can be attained via Fe(II)_{aq}-goethite interactions (Handler et al., 2009; Handler et al., 2014). Handler et al. (2009) proposed a "redox-driven conveyor belt" model, inspired by the evidence for electron conduction through iron oxides (Yanina and Rosso, 2008) and the observation that no significant changes occurred in the morphology, dimensions, and size

distribution of goethite crystallites despite near-complete iron-isotope exchange. Because, for complete exchange, the "redox-driven conveyor belt" model infers complete dissolution on one end of a goethite crystal and precipitation on the opposite side of the crystal, oxygen and iron-isotope exchange may be expected to occur in stoichiometric proportions. If, on the other hand, dissolution and re-precipitation occurs in close proximity (Figure 8), the non-stoichiometric nature of the model proposed above can be maintained, but it becomes harder to envision how complete iron-isotope exchange may ultimately occur. Regardless of the spatial proximity of dissolution and re-precipitation, the greater tendency of goethite to retain its oxygen atoms during exchange (eq 10) may provide the simplest explanation for the non-stoichiometric exchange of iron and oxygen.

Differential diffusion of iron and oxygen is another possible mechanism that warrants discussion. Diffusion coefficients have been determined for iron (Hallström et al., 2011) and oxygen (Giletti and Hess, 1988) in magnetite, but only at high temperatures. Indeed, iron and oxygen isotope evidence from magnetite grains in banded iron formations suggest that diffusion of both iron and oxygen occurs over micron-length scales during metamorphism (Hyslop et al., 2008; Li et al., 2013). Unfortunately, diffusion coefficients for iron and oxygen in goethite are unknown and cannot be measured experimentally at high-temperature because dehydration and transformation of goethite to hematite occurs at 250 °C (Gualtieri and Venturelli, 1999). Although distortion of Fe-O bonds at the grain boundary, crystal defects, and perhaps Fe(II)-Fe(III) electron-exchange reactions may enhance the mobility of atoms in the goethite crystal structure, the low-temperatures and short timescales of our experiments are likely insufficient for significant iron and oxygen diffusion at the micrometer-scale. Given the lack of any direct measurements of low or high temperature goethite diffusion coefficients, it is difficult to evaluate

the potential role of diffusion at the nm-scale as a mechanism contributing to the greater isotopic exchange of iron versus oxygen in the grain-boundary regions, which might impact n-Gth more than μ -Gth.

5. CONCLUSIONS

Using a double, three-isotope approach (^{18}O - ^{17}O - ^{16}O and ^{57}Fe - ^{56}Fe - ^{54}Fe), we have shown that interaction between $\text{Fe(II)}_{\text{aq}}$ and goethite results in both iron and oxygen-isotope exchange and mass-dependent fractionation between structural iron and oxygen in the mineral and water. Unexpectedly, iron and oxygen-isotope exchange is incongruent, where iron preferentially exchanges in stoichiometric excess by a factor of approximately three. The excess iron exchange (or under-exchange for oxygen) may result from the tendency of goethite Fe(III) that has an excess of singly coordinated oxygen (i.e., bound water or $\eta^1\text{-OH}_2$) to preferentially detach during Fe(II)-Fe(III) electron-transfer reactions, which results in a preferential loss of the ^{17}O tracer relative to goethite oxygen that is multiply coordinated. It is not clear, however, how such surface conditions are extended through the entire crystal, as is apparently required to completely exchange all iron in goethite under some experimental conditions. Alternatively, we cannot rule out nm-scale diffusion of iron through disordered grain-boundary domains that may contribute to more complete exchange of iron vs. oxygen.

We find that goethite grains that have dramatically different particle sizes undergo similar amounts of iron and oxygen exchange, but have unique inferred equilibrium oxygen isotope fractionations, a result we have observed previously for iron isotopes that has been interpreted to reflect different isotopic properties for surface and interior iron atoms (Beard et al., 2010; Frierdich et al., 2014a). The apparent oxygen isotope fractionations that we measure for nano-

and microgoethite (n-Gth and μ -Gth) appear to exhibit equilibrium fractionations that are consistent with Yapp (2007) and Bao and Koch (1999), respectively. Prior discrepancies regarding equilibrium oxygen isotope fractionation factors obtained from synthesis experiments may be, at least in part, a result of the nanometer- versus micron-sized particles that tend to form during low and high pH synthesis experiments, respectively. In addition to exchange experiments, goethite synthesis experiments where reaction of ferrihydrite with $\text{Fe(II)}_{\text{aq}}$ resulted in the rapid conversion to goethite produced particle sizes that are intermediate between those of the nano- and microgoethite used in the exchange experiments; the final mineral-water fractionations were also intermediate between the exchange results obtained for nano- and microgoethite (although identical within error at the 2σ level). Because this work shows that oxygen isotopes may exchange between goethite and water in the presence of Fe(II) , it is essential to consider past iron cycling and diagenesis of natural goethite when assessing the fidelity of its oxygen isotope composition in terms of paleoclimate interpretations.

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Table 1. Initial oxygen and iron isotope composition of the ^{17}O -enriched water, goethite, and aqueous Fe(II) solutions used for exchange experiments.

Component	$\delta^{13}\text{C}_{\text{calc}}$ (‰) ^a	$\delta^{18}\text{O}$ (‰)	$\delta^{57/56}\text{Fe}$ (‰) ^b
Water: FB-1	-21.51	-19.08	NA
Water: FB-2	-23.53	-19.32	NA
Water: H-1	-22.07	-2.65	NA
Water: H-2	-23.52	-2.60	NA
$\mu\text{-Gth}$	-27.80 ± 0.03	-9.31 ± 0.23	0.01 ± 0.04
$n\text{-Gth}$	-27.81 ± 0.08	-7.81 ± 0.29	-0.17 ± 0.04
$\text{Fe(II)}_{\text{aq}}\text{-FB}$	NA	NA	104.66 ± 0.16
$\text{Fe(II)}_{\text{aq}}\text{-H}$	NA	NA	105.04 ± 0.29
Ferrihydrite	-27.72	-0.36	-0.14 ± 0.07

^a Constants used in eq 9 (i.e., $\delta_{\text{aq}}^{\text{i}}$ and $\delta_{\text{Gth}}^{\text{i}}$) for the calculation of oxygen-isotope exchange. Note that a 0.066‰ shift in $\delta^{13}\text{C}_{\text{calc}}$ corresponds to a 1‰ enrichment in absolute $\delta^{17}\text{O}$.

^b Constants used in eq 7 for the calculation of iron-isotope exchange.

949 **Table 2.** Temporal iron and oxygen isotope compositions for Fe(II)_{aq} and goethite, respectively.

Time (d)	Aqueous Fe(II)				Goethite							
	$\delta^{57/56}\text{Fe}$ (‰)		% Gth Fe Ex ^a		O Yield (%)		$\delta^{13}\text{C}_{\text{Calc}}$ (‰)		% Gth O Ex ^b		$\delta^{18}\text{O}$ (‰) VSMOW	
	FB	H	FB	H	FB	H	FB	H	FB	H	FB	H
n-Gth 22°C^d												
0	104.66	105.04	0.0	0.0	94	94	-27.81	-27.81	0	0	-7.81	-7.81
0.007	99.70	100.51	0.2	0.2	88	71	-27.65	-27.68	2.5	2.4	-7.46	-7.13
1	36.30	-	8.2	8.2	92	92	-27.42	-	6.2	-	-8.18	-
3	24.15	24.04	14.4	14.5	94	86	-27.38	-27.35	6.8	8.7	-8.80	-6.96
7	18.80	17.03	19.5	22.0	95	90	-27.22	-27.24	9.4	10.7	-8.86	-6.67
14	12.95	12.49	29.7	31.0	43	91	-27.07	-27.13	11.7	12.8	-9.65	-6.54
30	8.36	8.69	46.9	45.3	93	92	-26.91	-26.94	14.3	16.4	-9.64	-6.30
51	6.17	5.77	63.1	67.6	91	95	-26.70	-26.81	17.6	18.8	-8.85	-6.76
Blk30	NA ^c	NA	NA	NA	88	-	-27.74	-	1.1	-	-8.16	-
n-Gth 50°C^e												
0	104.66	105.04	0.0	0.0	94	94	-27.81	-27.81	0	0	-7.81	-7.81
0.007	82.12	80.85	1.2	1.3	89	91	-27.72	-27.68	2.1	3.2	-7.83	-7.34
1	16.51	16.60	22.7	22.6	92	91	-27.38	-27.41	10.0	9.9	-8.26	-7.03
3	10.37	8.94	38.1	43.9	92	96	-27.19	-27.17	14.5	15.9	-8.98	-6.49
8	6.07	6.18	65.3	63.2	85	90	-27.07	-27.06	17.2	18.6	-9.35	-6.63
15	5.44	4.94	71.3	77.9	91	92	-27.01	-26.97	18.6	20.8	-9.68	-6.54
30	4.32	4.21	88.0	90.1	92	94	-26.81	-26.80	23.3	25.1	-10.19	-6.32
Blk30	NA	NA	NA	NA	92	89	-27.58	-27.62	5.4	4.7	-8.26	-7.78
μ-Gth 22°C^d												
0	104.66	105.04	0.0	0.0	93	93	-27.80	-27.80	0	0	-9.31	-9.31
0.007	74.71	74.08	1.8	1.8	100	10	-27.59	-26.56	3.3	4.5	-9.71	-8.89
0.25	45.39	44.15	5.8	6.0	98	97	-27.47	-27.48	5.2	6.0	-9.93	-8.93
1	30.75	30.09	10.5	10.9	98	95	-27.34	-27.37	7.3	8.1	-10.15	-8.79
2	23.20	21.58	15.3	16.8	95	10	-27.25	-27.33	8.7	8.9	-10.27	-8.75
4	16.89	16.31	22.5	23.4	98	93	-27.12	-27.17	10.8	11.9	-10.67	-8.51
8	13.11	12.72	30.0	31.0	98	10	-27.01	-27.07	12.6	13.8	-10.45	-8.27
15	11.12	10.64	35.8	37.6	97	97	-26.88	-26.94	14.6	16.2	-10.79	-8.33
30	9.00	8.70	44.8	46.4	95	95	-26.83	-27.02	15.4	14.7	-10.51	-8.57
51	6.21	6.21	65.2	65.3	99	97	-26.54	-26.65	20.0	21.7	-11.15	-7.97
Blk30	NA	NA	NA	NA	94	96	-27.71	-27.74	1.4	1.1	-9.61	-9.51
μ-Gth 50°C^e												
0	104.66	105.04	0.0	0.0	93	93	-27.80	-27.80	0	0	-9.31	-9.31
0.007	67.39	68.17	2.5	2.4	95	98	-27.58	-27.59	4.2	5.2	-9.84	-9.25
1	21.21	20.80	17.1	17.6	93	93	-27.30	-27.32	11.7	11.9	-10.52	-9.08
3	13.35	12.68	29.4	31.1	97	97	-27.16	-27.12	15.0	16.9	-10.94	-8.68
8	9.97	9.76	40.3	41.3	96	95	-27.02	-27.02	18.2	19.4	-11.28	-8.47
15	9.99	9.49	40.2	42.5	97	94	-27.00	-26.98	18.7	20.4	-11.41	-8.45
30	7.97	8.02	50.9	50.6	97	97	-26.93	-26.90	20.3	22.4	-11.58	-8.25
Blk30	NA	NA	NA	NA	-	10	-27.60	-27.56	4.7	6.0	-9.92	-8.93
Fh Conversion^e												
0	104.66	105.04	0.0	0.0	62	62	-27.72	-27.72	0.0	0.0	-0.36	-0.36
1	5.85	5.59	70.6	74.1	96	91	-23.97	-23.83	89.3	92.6	-14.24	0.73
3	4.86	4.98	84.6	83.1	93	89	-23.81	-23.78	93.1	93.8	-15.78	-0.40
7	5.57	5.62	74.1	73.6	92	70	-23.70	-23.75	95.7	94.5	-17.20	-1.22
14	5.30	5.37	77.8	77.1	98	93	-23.78	-23.64	93.8	97.1	-16.97	-1.10
Blk14	NA	NA	NA	NA	48	50	-26.36	-26.47	32.4	29.8	-2.14	5.80

^a Calculated from eq 7. ^b Calculated from eq 9. ^c Not applicable since no Fe(II) was present. ^d $\delta^{13}\text{C}_{\text{Calc}}$ of starting FB and H water (i.e., δ_{aq}^0 in eq 9) is -21.51 and -22.07‰, respectively. ^e Experiments employed a separately enriched batch of FB and H water having initial $\delta^{13}\text{C}_{\text{Calc}}$ values (i.e., δ_{aq}^i in eq 9) of -23.53 and -23.52‰, respectively.

Table 3. Extrapolated oxygen isotope values of goethite after reaction with Fe(II)_{aq} in ¹⁷O-enriched Fairbanks (FB) or Houston (H) water and calculated mineral-water fractionation factors. δ¹⁸O compositions of FB and H waters are -19.20 ± 0.34 and -2.63 ± 0.07 (2σ), respectively. Note that the different levels of ¹⁷O enrichment, as illustrated by δ¹³C_{Calc} (Table 1), have a minimal effect on δ¹⁸O.

	n-Gth		μ-Gth		Fh Conversion	
	FB	H	FB	H	FB	H
22 °C						
δ ¹⁸ O ^a	-17.92 ± 2.04 ^b	1.10 ± 1.41	-18.97 ± 0.71	-2.52 ± 0.51	-17.09 ± 0.16	-1.16 ± 0.08
Δ ¹⁸ O _{Gth-Water}	1.28 ± 2.07	3.72 ± 1.41	0.23 ± 0.79	0.11 ± 0.52	2.11 ± 0.16	1.47 ± 0.08
Weighted Average	3.0 ± 2.5 ^c		0.2 ± 0.9		1.6 ± 0.2	
50 °C						
δ ¹⁸ O ^a	-16.93 ± 1.31	-0.74 ± 0.55	-20.31 ± 0.35	-4.97 ± 0.60	NA ^d	NA
Δ ¹⁸ O _{Gth-Water}	2.27 ± 1.35	1.89 ± 0.56	-1.11 ± 0.49	-2.34 ± 0.61	NA	NA
Weighted Average	1.9 ± 1.5		-1.6 ± 0.8		NA	

^a Reported δ¹⁸O values (VSMOW) for n-Gth and μ-Gth exchange experiments are from extrapolations to complete exchange (see Figure 5). Values for Fh conversion experiments (i.e., Fe(II)-catalyzed transformation of ferrihydrite to goethite) represent mean of last two time points (see Figure 6 and Table 2).

^b All errors reported at the 2σ level.

^c Errors for weighted average values are the square root of the sum of the square of the errors.

^d Not applicable as Fh conversion experiment was not performed at 50 °C.

FIGURE CAPTIONS

Figure 1. (A) Isotopic shift in $\delta^{13}\text{C}_{\text{Calc}}$ of nano- and microgoethite during reaction with $\text{Fe(II)}_{\text{aq}}$ in ^{17}O -spiked Fairbanks water at 22 °C. Also shown are controls for both goethite minerals suspended in Fe(II) -free ^{17}O -spiked Fairbanks water (red symbol). Black horizontal line represents the mean value of replicate measurements ($n=10$) for natural abundance goethite starting materials; standard deviation shown as dashed line. **(B)** Temporal isotope composition of goethite materials shown in panel A in comparison with the composition of Fairbanks water. Water is represented as a horizontal line since its composition does not significantly change during exchange with goethite due to a >1000 mole excess of oxygen in the fluid relative to the solid. At 100% exchange, the $\delta^{13}\text{C}_{\text{Calc}}$ of the solid would be equal to the water plus/minus mass-dependent isotope fractionation. Note that fractionation has an insignificant effect ($\sim 1\%$ exchange) on $\delta^{13}\text{C}_{\text{Calc}}$ values in this study due to the large ^{17}O -enrichment (see text in Section 2).

Figure 2. Fraction of goethite iron exchange between $\text{Fe(II)}_{\text{aq}}$ and goethite, and fraction of goethite oxygen-isotope exchange between goethite and water calculated from eqs 7 and 9 from enriched ^{57}Fe and ^{17}O tracers (expressed as $\delta^{13}\text{C}_{\text{Calc}}$), respectively. Data for nanogoethite (n-Gth) and microgoethite (μ -Gth) shown for reactions at both 22 °C and 50 °C. Only reactions in Fairbanks water are plotted for clarity.

Figure 3. Comparison of oxygen-isotope exchange between goethite and Fairbanks water at 22 °C and 50 °C. Fraction of goethite oxygen-isotope exchange calculated from eq 9 from enriched ^{17}O tracer (expressed as $\delta^{13}\text{C}_{\text{Calc}}$).

Figure 4. Oxygen isotope ratios during reaction of nanogoethite (n-Gth) and microgoethite (μ-Gth) with aqueous Fe(II) in Houston (H) and Fairbanks (FB) water at 22 °C and 50 °C.

Figure 5. Values of $\delta^{18}\text{O}$ in nanogoethite (n-Gth), microgoethite (μ-Gth) and water at 22 °C and 50 °C. The fractionation of goethite vs. water evolves towards equilibrium at higher percentages of exchange. Waters do not change in their $\delta^{18}\text{O}$ values due to mass balance. $^{18}\text{O}/^{16}\text{O}$ variations, used to infer the equilibrium mass-dependent oxygen isotope fractionation, used two isotopically distinct waters (Houston, H; Fairbanks, FB) to confirm discrete isotope exchange trajectories, essentially a “reversal” approach to equilibrium; 2σ errors for projected exchange trajectories shown as dashed lines. At 100% exchange, the difference in isotopic composition of the mineral and fluid represents the fractionation factor. Fraction of goethite oxygen-isotope exchange calculated from eq 9 from enriched ^{17}O tracer (expressed as $\delta^{13}\text{C}_{\text{Calc}}$).

Figure 6. (A) Oxygen-isotope exchange vs. time and **(B)** $\delta^{18}\text{O}$ of iron oxide solid and water during Fe(II)-activated recrystallization of ferrihydrite. Solid phase is ferrihydrite at $t=0$ and does not recrystallize in Fe(II)-free reaction. In the presence of Fe(II), ferrihydrite transforms to lepidocrocite followed by goethite (See SI Figure S1,S2). Reaction conditions: 2 g/L solid, 25 mM HEPES (pH 6.8), 25 mM KBr, 1 mM Fe(II). Fraction of goethite oxygen-isotope exchange calculated from eq 9 from enriched ^{17}O tracer (expressed as $\delta^{13}\text{C}_{\text{Calc}}$).

Figure 7. Temperature dependent $^{18}\text{O}/^{16}\text{O}$ fractionation factor for the goethite-water system as determined for exchange experiments between $\text{Fe(II)}_{\text{aq}}$ and nanogoethite and microgoethite, and the Fe(II) -catalyzed ferrihydrite (Fh) conversion experiment (blue symbols, this study). Temperature dependent curves derived from synthesis experiments and associated error (dashed lines) for low (Yapp, 2007) and high (Bao and Koch, 1999) pH synthesis experiments shown for comparison.

Figure 8. Possible mechanism for incongruent goethite oxygen and iron-isotope exchange between water and $\text{Fe(II)}_{\text{aq}}$, respectively. **(A)** The goethite surface contains a variety of oxygen sites, including singly-coordinated water molecules ($\eta^1\text{-OH}_2$), doubly-coordinated hydroxyl groups ($\mu_2\text{-OH}$), and triply-coordinated hydroxyl ($\mu_3\text{-OH}$) and oxo ($\mu_3\text{-O}$) groups. For simplicity, these are indicated as a 1, 2, or 3 for the coordination environment of oxygen; hydroxyl and oxo groups are not distinguished. Note that singly coordinated groups readily exchange with the fluid and are thus denoted as blue spheres, whereas double and triple coordinated groups exchange slowly and are denoted as red spheres. Only the oxygen atoms associated with a vacant site and adjacent Fe(III) octahedron are considered for this conceptualization. **(B)** Fe(II) sorption occurs in a vacant site. **(C)** Electron transfer to an adjacent Fe(III) . **(D)** Desorption of the newly formed Fe(II) removes two oxygen atoms that isotopically equilibrated with the fluid composition. In this conceptualization, there is a net decrease in the amount of singly coordinated oxygen groups but no net change in the amount of fluid oxygen atoms associated with the solid during a single iron exchange $[\text{V} + \text{Fe} + 5(\eta^1) + 1(\mu_2) + 2(\mu_3) \rightarrow \text{Fe} + \text{V} + 3(\eta^1) + 4(\mu_2) + 1(\mu_3)]$; “V” represents a vacancy, note eq is not charge balanced].

Figure 1)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8