

**THREE ISOTOPE METHOD DETERMINATION OF THE EQUILIBRIUM FE ISOTOPE FRACTIONATION BETWEEN AQUEOUS Fe(II) AND GOETHITE.** B. L. Beard<sup>1,2</sup> and R. Handler<sup>3</sup>, M. M. Scherer<sup>3</sup>, L. Wu<sup>1,2</sup>, A. D. Czaja<sup>1,2</sup>, A. Heimann<sup>1,2</sup>, C. M. Johnson<sup>1,2</sup> <sup>1</sup>Department of Geosciences, 1215 W. Dayton Street, University of Wisconsin, Madison, WI 53706, USA, <sup>2</sup>NASA Astrobiology Institute, University of Wisconsin, <sup>3</sup>Dept of Civil and Environmental Engineering, The University of Iowa, 4126 Seamans Center for the Engineering Arts and Sciences, Iowa City, IA 52242 (e-mail: beardb@geology.wisc.edu)

**Introduction:** The interaction of aqueous Fe(II) (Fe(II)<sub>aq</sub>) and iron oxide/hydroxides is a dynamic process that can include: sorption of Fe(II)<sub>aq</sub> onto the oxide surface, exchange of electrons between Fe(II) and Fe(III), loss of Fe(II) to the iron oxide via transport of electrons in the substrate, production of more stable oxides through phase transformations, and coupled electron and atom exchange. Goethite is the most common crystalline iron oxide phase in lacustrine and marine sediments and therefore we have investigated the degree of Fe isotope exchange and Fe isotope fractionation between Fe(II)<sub>aq</sub> and goethite. Understanding the degree of reactivity between Fe(II)<sub>aq</sub> and goethite and the isotopic fractionation involved in these reactions is important in use of the Fe isotope system to identify abiologic and biologic processes.

**Experimental Design:** Experiments used a <sup>57</sup>Fe tracer to determine the degree of isotope exchange between Fe(II)<sub>aq</sub> and goethite by analysis of <sup>57</sup>Fe/<sup>56</sup>Fe ratios; the <sup>56</sup>Fe/<sup>54</sup>Fe ratio was also analyzed to constrain the mass dependent Fe isotope fractionations. Experiments used an enriched <sup>57</sup>Fe(II)<sub>aq</sub> solution ( $\delta^{57}\text{Fe}/^{56}\text{Fe} \sim +840\text{‰}$ ;  $\delta^{56}\text{Fe} \sim 0\text{‰}$  and goethite with normal Fe isotope compositions that were allowed to react for up to 30 days. Two types of goethite were used, a microrod goethite (590nm by 42nm; N<sub>2</sub> BET surface area 40m<sup>2</sup>/g) and a nanorod goethite (81nm by 11nm; N<sub>2</sub> BET surface area 110m<sup>2</sup>/g). The details of the experimental setup are described in [1]. Five samples were taken from each reactor under anaerobic conditions: an aqueous Fe sample collected by centrifugation, decanting, and filtration, and 4 serial partial dissolutions of the solids. Experiments were triplicated.

**Results:** After the initial sorption of Fe(II)<sub>aq</sub> onto the goethite the Fe(II)<sub>aq</sub> concentration did not vary, indicating steady-state conditions. The <sup>57</sup>Fe/<sup>56</sup>Fe of all of the components at the end of the experiment approached the Fe isotope composition dictated by mass balance which robustly demonstrates that there is near complete atom exchange between Fe(II)<sub>aq</sub> and goethite and thus we believe that these experiments represent equilibrium isotope exchange. Based on the differences in Fe isotope composition and oxidation state in the aqueous Fe and serial extractions that were measured, we identify at least 4 components that experi-

enced Fe isotope exchange. These components include Fe(II)<sub>aq</sub>, Fe(II)<sub>sorb</sub>, Fe(III)<sub>surface</sub>, and bulk goethite. The Fe(II)<sub>aq</sub>, Fe(II)<sub>sorb</sub> and bulk goethite components reflect nearly pure compositions in the aqueous Fe, extract 1, and extract 4 samples, respectively. The Fe(III)<sub>surface</sub> component may be characterized using extract 2 after minor (<0.06 ‰) correction for Fe(II) that reflects small extents of carryover of sorbed Fe(II).

The <sup>56</sup>Fe values for the Fe(III)<sub>surface</sub> component, at complete exchange are higher than those of the bulk goethite, which implies that the Fe atom bonding environments of these components differ. Based on mass balance calculations the Fe(III)<sub>surface</sub> component sampled in extracts 2 and 3 may reflect 4.2% of the total Fe in the nanorods, and 0.8% of the total Fe in the microrods. Assuming rhombohedra geometry, ~20% of the Fe atoms in the nanorods should be surface atoms, and ~4% of the Fe atoms in the microrods should be surface atoms; therefore, the Fe(III)<sub>surface</sub> component sampled in extracts 2 and 3 seems likely to reflect only a small proportion of the total surface Fe(III) atoms of the goethite.

The Fe isotope fractionations between Fe(II)<sub>aq</sub> and the other components are shown in figure 1. There is no resolvable difference in the  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(II)sorb}}$  frac-

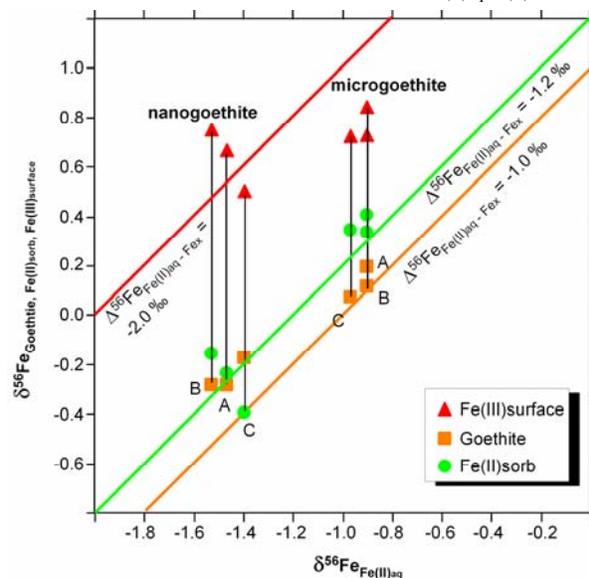


Figure 1: Plot of measured  $\delta^{56}\text{Fe}$  values of solid extracts after 30 days of equilibration of Fe(II)<sub>aq</sub> with goethite versus the measured Fe isotope composition of Fe(II)<sub>aq</sub>.

tionation factor between the nano and microrod experiments, and the pooled  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(II)sorb}}$  average of all the experiments is  $-1.24 \pm 0.14\%$ . The equilibrium  $\text{Fe(II)}_{\text{aq}} - \text{Fe(II)}_{\text{sorb}}$  fractionation factor measured here is significantly different than all estimates from previous studies, which ranged from  $-0.3$  to  $-3.7\%$  [2-6]. There are, however, measurable differences in the isotopic fractionation factors for other components between the nano and microrod experiments, where the  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-goethite}}$  and the  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(III)surface}}$  fractionations are higher in the nanorod experiments (Fig. 1). This difference is most pronounced for the  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(III)surface}}$  fractionation factor. We suggest that these differences are largely controlled by surface area effects. Extract 2 is the best representative of the  $\text{Fe(III)}_{\text{surface}}$  component, and its characteristics include a high  $\delta^{56}\text{Fe}$  value relative to all other components. The origin of the high  $\delta^{56}\text{Fe}$  values for the  $\text{Fe(III)}_{\text{surface}}$  component is most likely due to differences in bonding of Fe at the surface of the goethite as compared to Fe that is in the interior of the goethite. Possible differences in isotopic properties could include the decrease in number of bonds to structural oxygen as compared to the interior of goethite, or energetic changes due to crystal defects, edges, or corners on the surface, or specific crystal faces.  $\text{Fe(III)}_{\text{surface}}$  may reflect a variety of isotopic compositions due to these effects, as indicated by the different  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(III)surface}}$  fractionations measured for the nanorod and microrod experiments (Fig. 1). We suggest that the less negative  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(III)surface}}$  fractionation factor measured for the microrod goethite is a result of a lower proportion of surface Fe that has high  $\delta^{56}\text{Fe}$  values relative to bulk Fe, as compared to the nanorod experiments.

The Fe isotope effects due to differences in bonding of Fe on the surface of goethite will be most pronounced on the nanorod experiment, and we suggest that differential surface effects may explain the small (0.2%) difference in the measured  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-goethite}}$  fractionation factor between the nanorod experiments and the microrod experiments (Fig. 1). Because the nanorod goethite has a higher surface area relative to the microrod goethite, the slightly more negative  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-goethite}}$  fractionation factor for the nanorods is interpreted to reflect the greater proportion of surface Fe that has high  $\delta^{56}\text{Fe}$  values, which is consistent with the  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(III)surface}}$  fractionations. Therefore, the best estimate for the equilibrium  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-goethite}}$  fractionation is the microrod experiments, which has less  $\text{Fe(III)}_{\text{surface}}$  effects.

**Implications:** This experiment, coupled with other experiments from our laboratory [7-9] allow calculation of equilibrium fractionation factors for the system

$\text{Fe(II)-Fe(III)-siderite-hematite-goethite}$ . These experimentally determined fractionation factors between aqueous Fe species and between minerals agree well with several empirically determined fractionation factors based on *ab initio* calculations or spectroscopic data [10-13]. Combined aqueous Fe mineral fractionations determined by empirical methods do not compare well with the experimentally determined fractionation factors and may indicate that some type of scaling is necessary for empirically determined reduced partition function ratios.

The ease with which Fe isotopes exchange via redox cycling between  $\text{Fe(II)}_{\text{aq}}$  and goethite bears on the application of Fe isotopes for tracing abiologic and biologic processes in nature. For example, oxidation of  $\text{Fe(II)}_{\text{aq}}$ , followed by precipitation of ferric oxide/hydroxides has been modeled as a Rayleigh process, where relatively large  $\text{Fe(II)}_{\text{aq}}$ -ferric oxide fractionations are predicted at high extents of oxidation; if isotopic re-equilibration is fairly extensive, as shown here, this would tend to decrease the apparent  $\text{Fe(II)}_{\text{aq}}$  - ferric oxide fractionations that occur toward the end of a Rayleigh process. In other systems, where pore fluid  $\text{Fe(II)}_{\text{aq}}$  may interact with ferric oxide/hydroxides, the isotopic response due to exchange will depend upon the molar proportions of  $\text{Fe(II)}_{\text{aq}}$  and ferric oxide/hydroxide. At low proportions of  $\text{Fe(II)}_{\text{aq}}$  to ferric oxide/hydroxides, the largest shifts in Fe isotope compositions will occur in the  $\text{Fe(II)}_{\text{aq}}$  component; in contrast, under conditions of extensive flow of  $\text{Fe(II)}_{\text{aq}}$  through a ferric oxide/hydroxide matrix, the Fe isotope compositions of  $\text{Fe(II)}_{\text{aq}}$  will initially shift but then recover to be equal to the  $\delta^{56}\text{Fe}$  value of the input  $\text{Fe(II)}_{\text{aq}}$  [6]. Our results bear importantly on proposals that Fe isotopes may be an indicator of DIR in natural systems; the continued exposure of new surface atoms that occurs during DIR, and the associated relatively large magnitude  $\text{Fe(II)}_{\text{aq}} - \text{Fe(III)}_{\text{surface}}$  fractionation determined in the current study, supports the interpretation that DIR is the most efficient process for producing large quantities of low- $\delta^{56}\text{Fe}$   $\text{Fe(II)}_{\text{aq}}$ .

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