

# Demonstration of significant abiotic iron isotope fractionation in nature

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## ABSTRACT

Field and laboratory studies reveal that the mineral ferrihydrite, formed as a result of abiotic oxidation of aqueous ferrous to ferric Fe, contains Fe that is isotopically heavy relative to coexisting aqueous Fe. Because the electron transfer step of the oxidation process at pH >5 is essentially irreversible and should favor the lighter Fe isotopes in the ferric iron product, this result suggests that relatively heavy Fe isotopes are preferentially partitioned into the readily oxidized Fe(II)(OH)<sub>x(aq)</sub> species or their transition complexes prior to oxidation. The apparent Fe isotope fractionation factor,  $\alpha_{\text{ferrihydrite-water}}$ , depends primarily on the relative abundances of the Fe(II)<sub>(aq)</sub> species. This study demonstrates that abiotic processes can fractionate the Fe isotopes to the same extent as biotic processes, and thus Fe isotopes on their own do not provide an effective biosignature.

**Keywords:** iron, isotope geochemistry, inorganic origin, oxidation, aqueous speciation.

## INTRODUCTION

Iron (Fe) has four stable isotopes (<sup>54</sup>Fe, <sup>56</sup>Fe, <sup>57</sup>Fe, and <sup>58</sup>Fe), and thus there is the potential for isotopic variability to develop in nature through either abiotic or biotic mechanisms. For example, molecular vibration theory predicts that Fe isotopes may be fractionated during both equilibrium and irreversible (i.e., disequilibrium) abiotic reactions between minerals and fluids due to the relative stability of the heavier isotopes in more tightly bound minerals and aqueous species (Bigeleisen and Mayer, 1947; Urey, 1947; Polyakov, 1997). On the other hand, microbes can use Fe during both dissimilatory and assimilatory redox processes as either an electron donor or acceptor (Lovley et al., 1991, 1996; Leblanc et al., 1996; Mandernack et al., 1999). The microbes may selectively process and "fractionate" the relatively weakly bonded lighter Fe isotopes in order to maximize chemical energy, as is common for microbial processing of other bioreactive elements, such as carbon, nitrogen, sulfur, and oxygen (Hubner, 1986; Fogel and Cifuentes, 1993).

It has been proposed that microbially mediated Fe isotope fractionation, on the order of 1‰ to 2‰ in terms of the <sup>56</sup>Fe/<sup>54</sup>Fe ratio, is of greater magnitude than the fractionation resulting from abiotic processes in nature (Beard and Johnson, 1999; Beard et al., 1999). This proposal was based on the comparison of the ~1.3‰ fractionation of the <sup>56</sup>Fe/<sup>54</sup>Fe ratio observed during dissimilatory reduction of Fe in the Fe-oxyhydroxide mineral ferrihydrite by *Shewanella* algae under laboratory conditions with the near-uniform isotope composition of Fe (range of <0.4‰) in terrestrial and lunar igneous rocks. If this hypothesis is true, then Fe isotopes might be used as an effective biosignature in both the search for evidence of ancient life (Beard et al., 1999) and in remote sensing of microbially mediated processes such

as subsurface degradation of organic contaminants (Bullen and McMahon, 1998). However, recent laboratory experiments have demonstrated that Fe dissolved in acid media can be abiotically fractionated on an anion resin exchange column by more than 6‰ in terms of the <sup>56</sup>Fe/<sup>54</sup>Fe ratio (Anbar et al., 2000). Although the relevance of these latter experiments to natural systems is debatable, their results clearly indicate a need to assess the importance of abiotic Fe isotope fractionation in nature.

Here we report the first conclusive evidence for significant abiotic Fe isotope fractionation in a natural aqueous system. We investigated Fe isotope fractionation between the mineral ferrihydrite and aqueous Fe under both field and laboratory conditions. Ferrihydrite is the predominant iron oxyhydroxide mineral to form in aquatic systems at pH >4 and precipitates as a result of oxidation of aqueous ferrous Fe, or Fe(II) to ferric Fe, or Fe(III) through both abiotic and biotic mechanisms (Childs et al., 1982; Casanova et al., 1999). Rates of abiotic Fe(II) oxidation in aqueous systems are well known (Millero, 1985) and can be compared to rates observed in natural systems to determine the relative importance of the abiotic mechanism. For this study, we sampled ferrihydrite and coexisting water along a stream that is fed by an Fe-rich groundwater spring. In addition, abiotic laboratory experiments were designed to simulate the natural ferrihydrite precipitation process. We measured the Fe isotope compositions of both solid and aqueous samples by using thermal ionization mass spectrometry with a "double-spike" tracer amendment approach.<sup>1</sup> Fe isotope compositions are reported here in terms of

<sup>1</sup>GSA Data Repository item 2001083, Field, experimental, and mass spectrometry techniques and data, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at [www.geosociety.org/pubs/ft2001.htm](http://www.geosociety.org/pubs/ft2001.htm).

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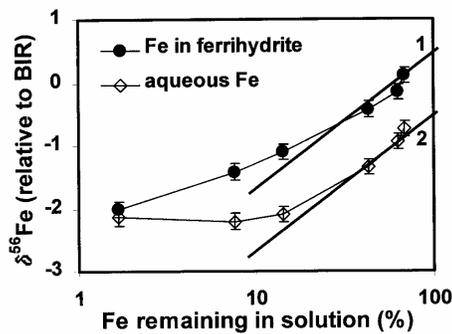


Figure 1. Values of  $\delta^{56}\text{Fe}$  of ferrihydrate and coexisting aqueous Fe samples from Tongariro field site. Note log scale on horizontal axis. Fe percentage remaining in solution calculated on basis of Fe/B ratio in sample relative to that in spring water, assuming conservative behavior for boron. Model lines describe Rayleigh fractionation process, fractionation factor  $\alpha = 1.009$ . Line 1—instantaneous solid composition; line 2—instantaneous liquid composition. BIR is USGS standard basalt.

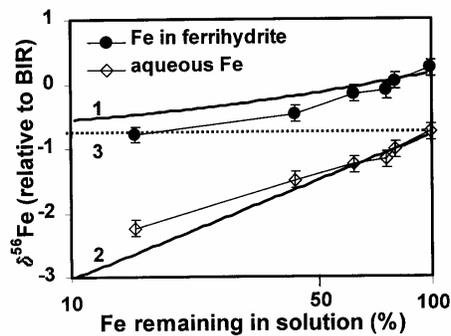


Figure 2. Values of  $\delta^{56}\text{Fe}$  of ferrihydrate and coexisting aqueous Fe samples collected during batch experiment. Model lines (solid) describe Rayleigh fractionation process, fractionation factor  $\alpha = 1.001$ . Line 1—accumulated solid composition, line 2—instantaneous liquid composition, line 3—Fe isotope composition of  $\text{Fe(II)Cl}_2$  reagent. BIR is USGS standard basalt.

$\delta^{56}\text{Fe}$ , the per mil deviation of  $^{56}\text{Fe}/^{54}\text{Fe}$  of the sample from that of BIR-1, an Icelandic basalt.

#### FIELD SETTING AND RESULTS FOR NATURAL SAMPLES

The field site is on the lower western flank of Mount Ruapehu, a composite volcano in Tongariro National Park, New Zealand. The ferrihydrate deposits and water chemistry have previously been well characterized (Henmi et al., 1980; Childs et al., 1982) and together comprise a coherent reaction flow path. At this site,  $\text{O}_2$ -poor, moderately acidic (pH  $\sim 5.8$ ), and Fe-rich (30 ppm)  $\text{CO}_2$ -charged groundwater issues as a spring (total dissolved solids [TDS]  $\sim 1000$  ppm) from an andesitic ash flow deposit into a dilute stream (pH  $\sim 7.8$ , TDS  $\sim 100$  ppm). Chemically, the spring water is Na-Ca-Mg- $\text{SO}_4$ - $\text{HCO}_3$ -Cl type. Oxygen and hydrogen isotope data indicate that the spring water is meteoric in origin, derived from a high-elevation catchment on the volcano. Carbon isotope data indicate a volcanic source for the dissolved  $\text{CO}_2$ . Cation ratios indicate that dissolved solids are derived from acid dissolution of the andesite. At the spring and downstream, the water mixes with the dilute stream water and rapidly loses  $\text{CO}_2$  and oxygenates, causing ferrihydrate to precipitate progressively on the stream bed.

The rate of abiotic oxidation of aqueous Fe(II) to intermediate-Fe(III) complexes is first order with respect to Fe(II) concentration and oxygen partial pressure, and it is second order with respect to solution pH (Millero, 1985). The Fe(II) concentrations of the stream water samples are closely predicted by a simple finite-difference model of abiotic oxidation that uses published oxidation rate constants (Millero, 1985) and measured stream flow and assumes progressive downstream oxygenation of the stream water as well as increasing pH constrained by sample pH. Therefore, although Fe-oxidizing bacteria are likely to be present in the stream water and bed, their influence on the Fe(II) oxidation rate is apparently minor, and it is reasonable to assume that the oxidation process is overall abiotically controlled.

Fe isotope compositions of ferrihydrate and coexisting aqueous Fe samples are plotted in Figure 1 as a function of the percentage of spring-water-derived Fe remaining. Along the first 600 m of downstream reach (i.e., where  $>10\%$  Fe remains in solution),  $\delta^{56}\text{Fe}$  of ferrihydrate is  $\sim 0.9\%$  greater than that of coexisting aqueous Fe. As

shown in Figure 1, a Rayleigh fractionation model using a solid-liquid fractionation factor of 1.0009 provides a reasonable fit to the data for this part of the reaction flow path. Farther downstream the isotopic contrast between Fe in ferrihydrate and aqueous Fe decreases, becoming negligible 1600 m downstream from the spring. The relatively constant isotope composition of aqueous Fe in this downstream reach may result from either a decreased fractionation factor or isotopic back reaction of the aqueous Fe, relatively heavy colloidal Fe being transported from farther upstream or passed through the filter during sample collection.

#### LABORATORY EXPERIMENTS AND RESULTS FOR SYNTHETIC SAMPLES

Batch and steady-state ferrihydrate precipitation experiments were conducted by oxidizing a ferrous chloride solution in a  $\text{CO}_2$ - $\text{HCO}_3^-$ -buffered pH-stat reactor. In the batch experiment conducted at pH = 5.9, incremental samples of suspended ferrihydrate and coexisting solution were collected by extracting a small sample of the reactor contents through a filter as the amount of dissolved Fe(II) decreased from 99% to 15% of the starting concentration in response to Fe(II) oxidation. The results shown in Figure 2 reveal that  $\delta^{56}\text{Fe}$  of ferrihydrate is consistently greater than that of the coexisting aqueous Fe. A Rayleigh fractionation model using a solid-liquid fractionation factor of 1.001 provides a reasonable fit to the data for samples taken while the percentage of Fe remaining in solution was greater than 50%. The divergence of the data for aqueous Fe from model values at lower dissolved Fe concentrations may result from isotopic back reaction between late-stage solutions and early-formed ferrihydrate. The trend for  $\delta^{56}\text{Fe}$  of accumulated ferrihydrate toward lesser values than that of the starting material implies chemical isolation of some early-formed ferrihydrate, perhaps as cores of larger grains or as a coating on the reactor walls.

A series of steady-state experiments conducted at pH = 5.4–6.2 utilized a flow-through reactor design that minimized potential isotopic back reaction between the solid and aqueous phases. Upon reaching the condition of constant Fe(II)-Fe(III) aqueous concentrations, samples of suspended ferrihydrate and coexisting solution were collected through a filter for analysis. Initial aqueous Fe(II) concentrations and injection rates of water and Fe(II)Cl<sub>2</sub> solution were identical in each

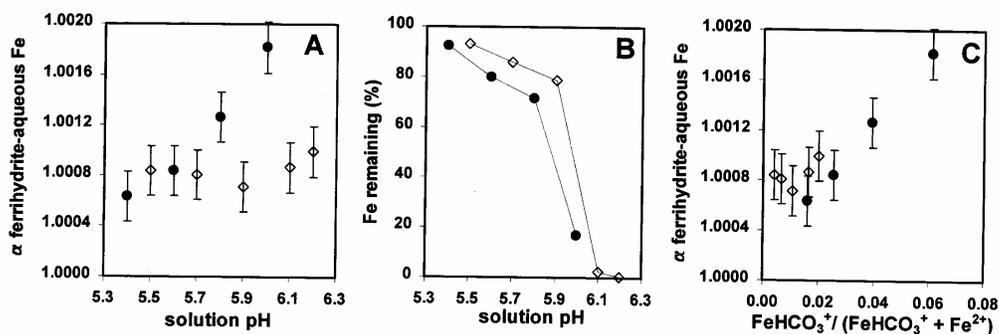


Figure 3. A: Values for  $\alpha_{\text{ferrihydrate-aqueous Fe}}$  determined for steady-state experiments plotted as function of solution pH. B: Percentage of aqueous Fe remaining in steady-state solutions plotted as function of pH. C:  $\alpha_{\text{ferrihydrate-aqueous Fe}}$  determined for steady-state experiments plotted as function of relative proportion of predominant aqueous species  $\text{Fe}^{2+}$  and  $\text{FeHCO}_3^+$ . Error bars represent maximum uncertainty based on agreement of all replicates within 0.2%. Solid symbols—5% CO<sub>2</sub>, open symbols—1% CO<sub>2</sub>.

experiment, allowing steady-state Fe(II) aqueous concentrations to provide a direct comparative measure of the Fe(II) oxidation rate (Fig. 3).

Solid-liquid fractionation factors ( $\alpha$ ) defined by the ratio of the Fe isotope composition of ferrihydrite to that of coexisting aqueous Fe are plotted in Figure 3A as a function of solution pH and composition of the gas mixture used to establish the pH buffer. The value for  $\alpha$  is consistently greater than 1.0, indicating that  $\delta^{56}\text{Fe}$  of the ferrihydrite is greater than that of aqueous Fe. There is a positive trend of  $\alpha$  with solution pH for the experiments that utilized 5% CO<sub>2</sub>, but no trend for those in which 1% CO<sub>2</sub> was used. Because Fe(II)-oxidation rates in these experiments are largely determined by solution pH, it is clear from Figure 3A that the amount of Fe isotope fractionation is not determined by Fe(II)-oxidation rate alone.

#### DISCUSSION

Fe(II) oxidation involves hydrolysis and electron transfer steps that convert  $\text{Fe(II)}_{\text{(aq)}}$  species to a series of  $\text{Fe(II)}_{\text{(aq)}}$  transition complexes and  $\text{Fe(III)}_{\text{(aq)}}$  intermediates prior to precipitation as ferrihydrite (Millero, 1985). At pH > 5 the electron transfer step is essentially irreversible, and all  $\text{Fe(III)}_{\text{(aq)}}$  produced is immediately precipitated as ferrihydrite with little to no tendency for back reaction. For a given  $\text{Fe(II)}_{\text{(aq)}}$  species, kinetic reaction theory predicts that molecules containing the lighter Fe isotopes will be most reactive, owing to their inherently weaker bonds (Urey, 1947) and thus that  $\delta^{56}\text{Fe}$  of the  $\text{Fe(III)}$  products should be less than that of the  $\text{Fe(II)}$  reactant. Therefore, the fact that  $\delta^{56}\text{Fe}$  of the ferrihydrite is consistently greater than that of the coexisting aqueous Fe under both field and experimental conditions is unexpected and requires an additional mechanism such as equilibrium fractionation of Fe isotopes among coexisting  $\text{Fe(II)}_{\text{(aq)}}$  species prior to oxidation.

Although the dominant  $\text{Fe(II)}_{\text{(aq)}}$  species are (in order of decreasing concentration)  $\text{Fe}^{2+}_{\text{(aq)}}$  and  $\text{FeHCO}_3^+_{\text{(aq)}}$  in the experimental waters and  $\text{Fe}^{2+}_{\text{(aq)}}$ ,  $\text{FeHCO}_3^+_{\text{(aq)}}$ , and  $\text{FeSO}_4_{\text{(aq)}}$  in the natural waters,  $\text{Fe(III)}_{\text{(aq)}}$  is derived primarily by oxidation of the minor  $\text{Fe(II)(OH)}_{\text{(aq)}}$  species due to their high oxidation-rate constants. For example, even though the ratio of calculated concentrations  $\text{Fe(II)(OH)}_{\text{(aq)}}^+ / \text{Fe}^{2+}_{\text{(aq)}}$  in spring water from the Tongariro field site is  $10^{-4}$ , the ratio of oxidation rate constants is  $10^7$  (Millero, 1985). Thus, the isotopic impact of  $\text{Fe(II)(OH)}_{\text{(aq)}}^+$  on the ferrihydrite is  $10^3$  greater than that of  $\text{Fe}^{2+}_{\text{(aq)}}$ . The isotopic impact of even less abundant but more oxidizable  $\text{Fe(II)(OH)}_{\text{(aq)}}^2$  may be of similar magnitude. Thus, we propose that a plausible mechanism to explain the difference in Fe isotope composi-

tion between ferrihydrite and aqueous Fe is the preferential distribution of relatively heavy Fe into the  $\text{Fe(II)(OH)}_{\text{(aq)}}^+$  species, or possibly into a transition complex that maintains isotopic equilibrium with  $\text{Fe(II)(OH)}_{\text{(aq)}}^+$ .

At given pH, the rate of Fe(II) oxidation in the experiments using 5% CO<sub>2</sub> was approximately twice that in the experiments using 1% CO<sub>2</sub> (Fig. 3B). The only difference in Fe speciation between the two sets of experiments at given pH is the relative proportion of  $\text{FeHCO}_3^+_{\text{(aq)}}$ . This suggests that Fe in  $\text{FeHCO}_3^+_{\text{(aq)}}$  is highly reactive and may hydrolyze and/or oxidize rapidly. Lacking independent experimental evidence that Fe in  $\text{FeHCO}_3^+_{\text{(aq)}}$  is itself efficiently oxidized, we propose that  $\text{FeHCO}_3^+_{\text{(aq)}}$  mainly provides an especially efficient hydrolysis pathway for replenishment of Fe to the  $\text{Fe(II)(OH)}_{\text{(aq)}}^+$  species as oxidation proceeds.

The discrepancy between the two flow-through reactor data sets (Fig. 3A) is reduced if  $\alpha$  is plotted as a function of the relative proportion of  $\text{FeHCO}_3^+_{\text{(aq)}}$  (Fig. 3C). One explanation for the resulting trend of increasing  $\alpha$  with increasing proportion of  $\text{FeHCO}_3^+_{\text{(aq)}}$  is that Fe in  $\text{FeHCO}_3^+_{\text{(aq)}}$  is isotopically heavy compared to bulk  $\text{Fe(II)}_{\text{(aq)}}$ . Isotope mass balance considerations support this explanation. For example, at pH ~6 the increase in the proportion of  $\text{FeHCO}_3^+_{\text{(aq)}}$  from ~1% in the experiments using 1% CO<sub>2</sub> to ~6% in the experiment using 5% CO<sub>2</sub> (Fig. 3C) corresponds to an increase in  $\alpha$  of ~1‰ (Fig. 3A). If  $\delta^{56}\text{Fe}$  of  $\text{FeHCO}_3^+_{\text{(aq)}}$  was less than that of bulk Fe, then  $\delta^{56}\text{Fe}$  of  $\text{Fe}^{2+}_{\text{(aq)}}$  in the experiment using 5% CO<sub>2</sub> would have to be greater by ~1‰ compared to that of  $\text{Fe}^{2+}_{\text{(aq)}}$  in the experiment using 1% CO<sub>2</sub> to account for the increased value of  $\alpha$ . Isotope mass balance would then require that  $\delta^{56}\text{Fe}$  of  $\text{FeHCO}_3^+_{\text{(aq)}}$  be ~20‰ less than that of bulk Fe. This amount of Fe isotope fractionation between coexisting  $\text{Fe(II)}_{\text{(aq)}}$  species is unlikely, owing to the relatively heavy atomic weight of Fe. Thus, we infer that  $\delta^{56}\text{Fe}$  of  $\text{FeHCO}_3^+_{\text{(aq)}}$  is greater than that of bulk  $\text{Fe(II)}$ , and by mass balance,  $\delta^{56}\text{Fe}$  of  $\text{Fe}^{2+}_{\text{(aq)}}$  is less than that of bulk  $\text{Fe(II)}$ .

Anbar et al. (2000) called upon equilibrium distribution of Fe isotopes among coexisting  $\text{Fe(III)Cl}_{\text{(aq)}}$  species to explain the isotope fractionation trends observed in their anion resin column experiments. In that study, the heavier Fe isotopes were found to be associated with the more strongly bound configurations, as predicted by the general principles of atomic bonding theory (Bigeleisen and Mayer, 1947). In our field and experimental study systems, the strength of the metal-ligand bonds in the  $\text{Fe(II)(OH)}_{\text{(aq)}}^+$  species should be greater than those between  $\text{Fe}^{2+}_{\text{(aq)}}$  and the six hydration molecules that surround it, and

thus our prediction that  $\delta^{56}\text{Fe}$  of  $\text{Fe(II)(OH)}_{\text{M(aq)}}$  is greater than that of  $\text{Fe}_{\text{(aq)}}^{2+}$  is consistent with theory. Although the strength of Fe bonding in  $\text{FeHCO}_{3\text{(aq)}}^{-}$  is more difficult to predict, the mass-balance considerations noted above suggest that Fe in  $\text{FeHCO}_{3\text{(aq)}}^{-}$  is likewise more strongly bound compared to  $\text{Fe}_{\text{(aq)}}^{2+}$ . We stress that the amount of Fe isotope fractionation between coexisting  $\text{Fe(II)}_{\text{(aq)}}$  species is probably no more than a few per mil.

Equilibrium isotope contrasts between Fe aqueous species will persist and evolve along reaction pathways, as we have demonstrated for both natural and experimental abiotic systems. Moreover, the tendency of Fe oxidation products to rapidly become physically and chemically separated from the reactive system through aggregation and sedimentation processes suggests that Fe isotope variations developed through abiotic mechanisms can be preserved in nature and are not merely transitory phenomena. Thus, the fact that the magnitude of the abiotic Fe isotope fractionation reported here is similar to that recently reported for microbially mediated Fe reduction suggests that Fe isotopes considered alone cannot provide an effective biosignature. Furthermore, at this early stage of Fe isotope research, it is unclear whether fractionation associated with microbial activity is due to a characteristic vital effect or merely the expression of an aqueous speciation effect. Clearly, more study of microbially mediated Fe isotope fractionation under conditions of varying solution chemistry is warranted.

We anticipate that Fe isotopes will eventually become a widely applied biogeochemical tracer. However, as with all isotope and chemical systems, use of a single parameter often provides ambiguous results. We suggest that a multi-tracer approach, such as considering both the oxygen and iron isotope compositions of iron oxyhydroxide minerals in a system, may provide a more robust biosignature than that assumed from consideration of Fe isotopes alone.

#### CONCLUSIONS

We have presented the first evidence of abiotic Fe isotope fractionation in a natural system, have reproduced the observed fractionation in a series of laboratory experiments, and have proposed a plausible abiotic Fe isotope fractionation mechanism. The evidence suggests that Fe isotope fractionation observed in the abiotic ferrihydrite + water system results from isotope distribution among coexisting  $\text{Fe(II)}_{\text{(aq)}}$  species due to the different bonding environments of those species. We infer that  $\delta^{56}\text{Fe}$  of  $\text{Fe(II)(OH)}_{\text{M(aq)}}$  and  $\text{FeHCO}_{3\text{(aq)}}^{-}$  is greater than that of  $\text{Fe}_{\text{(aq)}}^{2+}$ . The apparent fractionation factor  $\alpha_{\text{ferrihydrite-water}}$  depends largely on the relative proportions of the coexisting aqueous Fe species and is greatest under  $\text{CO}_2$ -enhanced conditions. However, the amount of Fe isotope fractionation observed in the abiotic system is similar to that recently reported for microbially mediated Fe reduction, and thus Fe isotopes considered alone cannot be used to distinguish the products of abiotic and biotic Fe processing in the geologic record.

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