Fe isotopes: An emerging technique for understanding modern and ancient biogeochemical cycles

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ABSTRACT

Fractionation of the stable isotopes of Fe occurs through a combination of differences in bonding environments and separation of mobile Fe components. These fractionations are particularly large in low-temperature systems. The very low Fe contents of modern seawater make Fe isotopes exceptionally sensitive indicators of Fe sources and pathways in the oceans. Iron cycling at redox boundaries is a major means by which Fe isotope variations are produced. Bacteria, which commonly exploit redox gradients for energy, may strongly influence the associated isotopic fractionations, and this is particularly true for Fe^{3+}-reducing bacteria. Moreover, the Fe isotope fractionations associated with Fe sulfide, which may be produced by bacterial sulfate reduction, appear to be distinct from those produced by bacterial Fe reduction. The isotopic fingerprint for bacterial Fe reduction may be found in the rock record as far back as 2.9 Ga, and evidence for coupled bacterial sulfate reduction and Fe reduction is found in rocks that are 2.7 Ga. The ancient Fe isotope record requires the existence of an oxidant on Earth's surface since at least 3.8 Ga, but the nature of this oxidant (atmospheric O_2, anaerobic photosynthesis, UV-photo oxidation) remains unclear. Continued development of Fe isotope geochemistry depends critically on expanding the database for Fe isotope fractionation factors and increasing our understanding of the kinetic effects during redox transformations and mineral precipitation.

INTRODUCTION

The first-row transition metals (Sc to Zn) share a special combination of relatively high elemental abundance and a propensity for multiple oxidation states. Seven of these elements have multiple isotopes, ranging from two (V and Cu) to five (Ti, Ni, and Zn), and yet, up until several years ago, their isotopic variations in nature had been relatively little explored. Although the relative mass differences among the isotopes of the transition metals are small compared to the light stable isotopes (e.g., 5.9%/mass for O versus 1.5%/mass for Zn), the range in isotopic compositions measured in nature is 100 times analytical error using modern techniques. Of the over 100 papers that have been published on the isotopic variations of the first transition metals, approximately three-fourths have been on Fe isotopes, placing Fe prominently among the emerging "non-traditional" stable isotope systems (Johnson et al., 2004a).

Iron is the most abundant of the transition metals at 6.7 wt% in the continental crust (Rudnick and Gao, 2004). Fe^{3+} is generally insoluble at neutral pH, although it is soluble under acidic conditions. Fe^{2+} is soluble under near-neutral pH conditions only under low-Eh, anoxic conditions, such as might be found in reducing groundwaters, restricted marine basins, or when atmospheric O_2 contents were much lower than they are today. In the highest temperature portions of Earth (deep crust and mantle), Fe largely exists as Fe^{2+}, creating a large redox potential when mantle and deep crustal rocks are exposed to surface oxidizing conditions. In terms of biological processes, Fe^{3+} is an important terminal electron acceptor for iron-reducing bacteria as part of the electron transport chains they develop for adenosine triphosphate synthesis (e.g., Nealson and Saffarini, 1994). Fe^{2+} may provide a source of electrons for processes such as anaerobic photosynthetic Fe oxidation, which has been hypothesized to have been an important metabolic pathway in early Earth (e.g., Widdel et al., 1993). It is within this broad landscape of biogeochemical pathways and bonding environments, in part created through redox state and in part by ligand chemistry, that substantial isotopic fractionations may occur among the different isotopes of Fe. Here we focus on redox changes in low-temperature environments, modern and ancient, where the isotopic fractionations are relatively large. Recent in-depth reviews on Fe isotope geochemistry may be found in Anbar (2004), Beard and Johnson (2004), Johnson et al. (2004b), and Dauphas and Rouxel (2006).

NUTS AND BOLTS: DATA PRESENTATION AND FRACTIONATION FACTORS

There are four naturally occurring stable iron isotopes: ^{54}Fe (5.84%), ^{56}Fe (91.76%), ^{57}Fe (2.12%), and ^{58}Fe (0.28%), and isotopic data are typically reported using a standard δ notation in units of per mil (‰) (deviations in parts per 1000 relative to a reference ratio), using either $^{56}Fe/^{54}Fe$ or $^{57}Fe/^{54}Fe$ ratios. All of the data discussed here are reported in $\delta^{56}Fe$ values relative to the average for igneous rocks (Beard et al., 2003a):

$$\delta^{56}Fe = (^{56}Fe/^{54}Fe_{Sample}/^{56}Fe/^{54}Fe_{Ig\ Rxs} - 1) \times 10^3.$$

A common interlaboratory standard that allows comparison across labs is the Fe metal isotope standard IRMM-014, which is also used as a reference ratio in defining $\delta^{56}Fe$ and $\delta^{57}Fe$ values in a number of laboratories. The two reference frames for δ values may be related by

$$\delta^{56}Fe_{Ig\ Rxs} = \delta^{56}Fe_{IRMM\text{-}014} - 0.09‰$$

(Beard et al., 2003a). The reader should be aware that Fe isotope data are reported in the literature in a variety of ways, and a detailed discussion may be found in Beard and Johnson (2004). Details on the various analytical methods used for Fe isotope analysis may be found in Albarède and Beard (2004).

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Isotopic fractionation factors are key to understanding natural isotope variations. The Fe isotope fractionation between two species, *A* and *B*, may be defined as:

$$\Delta^{56}Fe_{[A]-[B]} = \delta^{56}Fe_{[A]} - \delta^{56}Fe_{[B]}$$

following standard convention. $\Delta^{56}Fe_{[A]-[B]}$ may reflect equilibrium or kinetic fractionations, and a process may reflect a combination of equilibrium and kinetic effects. Some of the largest Fe isotope fractionations occur between Fe^{3+} and Fe^{2+} species (e.g., Schauble, 2004). For example, the net Fe isotope fractionation that occurs during oxidation of Fe^{2+}_{aq} to Fe^{3+}_{aq}, followed by precipitation of Fe^{3+}_{aq} to ferric oxide, under equilibrium conditions, is $\Delta^{56}Fe_{[Fe\ Oxide]-[Fe^{2+}_{aq}]} = +3.0‰$ at room temperature, reflecting a Fe^{3+}_{aq}-Fe^{2+}_{aq} fractionation of +2.9‰ and a ferric oxide–Fe^{3+}_{aq} fractionation of +0.1‰ (Beard and Johnson, 2004); the equilibrium fractionation between ferric oxide and Fe^{3+}_{aq} is small because Fe does not change oxidation state or coordination. In most experimental and natural systems, however, the observed ferric oxide–Fe^{2+}_{aq} fractionation is much less, generally between +0.9 and +1.6‰, reflecting the combined effects of an equilibrium Fe^{3+}_{aq}-Fe^{2+}_{aq} fractionation (+2.9‰) and a kinetic ferric oxide–Fe^{3+}_{aq} fractionation (−1.3 to −2.0‰) upon precipitation (Beard and Johnson, 2004). Large gaps remain in our understanding of Fe isotope fractionations for the carbonate and sulfide mineral groups, which are critical for interpreting the geologic record; experimental studies of these groups are a high priority for future work.

THE Fe ISOTOPE CYCLE OF MODERN EARTH

We summarize Fe isotope variations in modern Earth in Figure 1. In surface environments, the existence of an O_2-bearing atmosphere provides an oxidant for Fe^{2+} but also produces a very low solubility for Fe^{3+}_{aq} at neutral pH, which generally restricts Fe isotope variations to environments where redox boundaries exist. Fe-S interactions are also important (although incompletely understood), and such interactions are also closely tied to redox boundaries. Significant Fe isotope variations may also occur in aqueous systems that are oxic, such as the oceans, where the aqueous Fe contents are so low that they are highly sensitive to changes in input fluxes over short time scales or geographic distance.

The major igneous fluxes that create oceanic and continental crust appear to have $\delta^{56}Fe$ values of zero (Beard et al., 2003a). Exceptions exist for some silicic granitic rocks and mantle xenoliths, but they are minor in terms of the overall Fe budget of the crust and mantle. In terms of Fe in the sedimentary cycle, an important observation is that the near-zero $\delta^{56}Fe$ values of the bulk continental crust are largely retained in bulk clastic sediments during weathering processes, despite a large increase in Fe^{3+}/Fe^{2+} ratios (Beard et al., 2003b). Although there are large equilibrium isotope fractionations between Fe^{3+} and Fe^{2+} aqueous species and minerals, conversion of Fe^{2+}-rich igneous or metamorphic rocks to insoluble Fe^{3+} weathering products under oxic conditions occurs without significant loss of Fe, producing little net change in Fe isotope compositions during formation of clastic sedimentary rocks. These observations indicate that in terms of Fe cycling, virtually all of the Fe in igneous, metamorphic, and clastic sedimentary rocks is isotopically homogeneous and has a $\delta^{56}Fe$ value of zero (Fig. 1). This provides an important reference frame for recognizing and understanding the processes and environments that produce Fe isotope variations.

Iron isotope variations in modern marine sediments are produced by diagenetic processes that reflect the interplay between Fe^{2+}_{aq} and ferric oxide during bacterial iron reduction (BIR), Fe^{2+}_{aq} and S^{2-}_{aq} during bacterial sulfate reduction (BSR), and ferric oxide–sulfide interactions. Both BIR and BSR may occur in the same sediment section, reflecting extensive cycling of Fe and S before they are ultimately sequestered in the rock record as pyrite (e.g., Canfield et al., 1993). Recent studies of shelf sediments from the California margin and the Arabian Sea demonstrate that reactive Fe pools may have highly variable Fe isotope compositions (Severmann et al., 2006; Staubwasser et al., 2006), but the bulk sediment has $\delta^{56}Fe$ values close to the average of clastic sedimentary rocks, indicating that Fe cycling largely occurs as a closed system within the sediment column or at most on the small basin scale (Staubwasser et al., 2006). Although porewater Fe^{2+} lost during marine diagenesis may be a significant flux to the oceans (Severmann et al., 2006), from the sediment perspec-

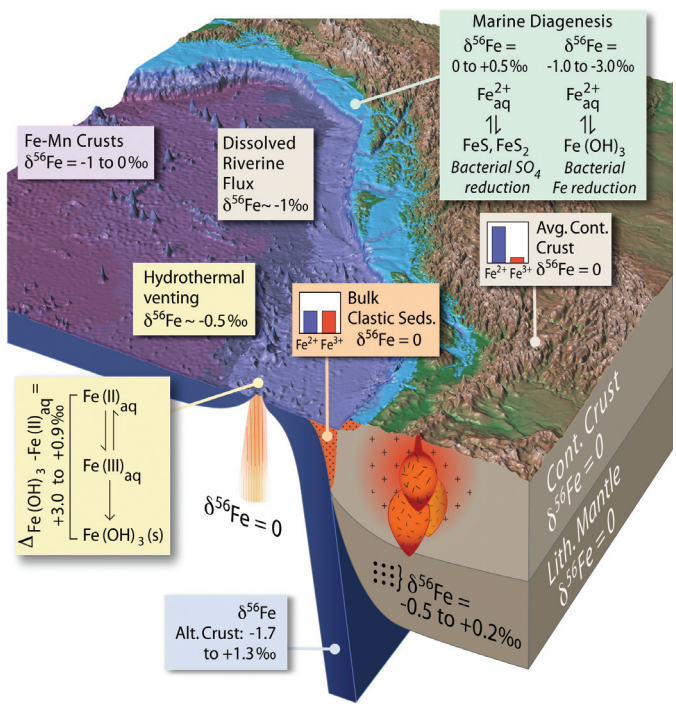

Figure 1. Illustration of the modern biogeochemical cycle for Fe isotopes (three-dimensional rendering of Pacific Northwest and British Columbia region). The oceanic and continental igneous flux has $\delta^{56}Fe = 0‰$, indicating that the bulk of the mantle, with the exception of isolated domains that reside largely in the lithosphere (dot pattern), is isotopically homogeneous, as are bulk clastic rocks that have low-C and -S contents, despite an increase in Fe^{3+}/Fe^{2+} ratios. Marine diagenesis is in part driven by bacterial sulfate and iron reduction, and these two metabolisms appear to have distinct Fe isotope compositions. The dissolved riverine and marine hydrothermal fluxes have negative $\delta^{56}Fe$ values, and the hydrothermal flux may become increasingly negative through near-vent ferric oxide or hydroxide precipitation; isotopically heterogeneous seawater is expected due to the low residence time of Fe in modern seawater, and this is confirmed in Fe-Mn crusts that are used as a proxy for seawater Fe isotope compositions.

tive, the amount that is lost is small relative to the size of the Fe reservoir in the sediment column. Severmann et al. (2006) found that in suboxic sediment sections, where BIR was active, the reactive Fe pool was dominated by Fe^{2+}_{aq} and ferric oxides or hydroxides, which had negative δ^{56}Fe values of ~−1.0 to −3.0‰. In contrast, the reactive Fe pool in anoxic, sulfide-dominated sections consisted of Fe^{2+}_{aq} and FeS that had higher δ^{56}Fe values of 0 to +0.5‰. These observations highlight the distinct Fe isotope signatures that may be associated with BIR and BSR. Although the ultimate end product of Fe-S cycling in marine sediments is generally considered to be pyrite (e.g., Schoonen, 2004, and references therein), Severmann et al. (2006) noted that pyrite does not appear to be in Fe isotope equilibrium with Fe^{2+}_{aq} in the California margin sediments, and FeS and pyrite have dramatically different Fe isotope compositions. We are therefore far from understanding the factors that determine the Fe isotope compositions of sedimentary pyrite, in large part because experimental studies of Fe isotope fractionations in Fe-S systems have only just begun (Butler et al., 2005).

The quantity of *dissolved* Fe that exists under the oxic conditions of modern Earth is extremely small (ppb to ppt). The dissolved riverine Fe flux has low δ^{56}Fe values, perhaps ~−1‰ (Fantle and DePaolo, 2004). The major source of Fe to the upper oceans that are far from continental margins is atmospheric dust (e.g., Jickells and Spokes, 2001), which has a δ^{56}Fe value of zero (Beard et al., 2003b). Ligand-complexed Fe^{3+}_{aq} derived from partial dissolution of dust, however, may have negative δ^{56}Fe values, perhaps <−1‰, based on partial dissolution studies using organic ligands (Brantley et al., 2004). Direct emanations of Fe^{2+}_{aq} from marine hydrothermal vents have δ^{56}Fe ~−0.5‰ (Sharma et al., 2001; Beard et al., 2003b), and these may become more negative through near-vent oxidation and precipitation (Severmann et al., 2004). Altered oceanic crust may have a large range of δ^{56}Fe values (Fig. 1), but probably has an average δ^{56}Fe value near zero (Rouxel et al., 2003), consistent with only minor Fe loss via hydrothermal fluids. Finally, pore fluids emanating from marine sediments during bacterial reduction of iron oxides can have δ^{56}Fe values as low as −3‰ (Severmann et al., 2006). It is important to note that the dissolved Fe fluxes to the oceans under an O_2-bearing atmosphere are miniscule relative to the inventory of Fe in rocks, and therefore the isotopic compositions of the bulk "lithologic" inventory of Fe is largely unaffected under such conditions.

The Fe residence time in the oceans is estimated to be 70–140 yr (e.g., Bruland et al., 1994), which predicts that the Fe isotope composition of the modern oceans should be heterogeneous on short temporal and geographic scales (Beard et al., 2003b). The expected isotopic provinciality of modern seawater has been confirmed by Fe isotope studies of Fe-Mn crusts (Zhu et al., 2000; Levasseur et al., 2004; Chu et al., 2006), indicating that Fe isotopes may constrain Fe sources and pathways in the oceans. Temporal variations in Fe isotope compositions of Fe-Mn crusts, coupled with transition-metal abundances, may distinguish hydrothermal Fe sources from other sources of low-δ^{56}Fe components (Chu et al., 2006). In addition, time-series analysis of an Fe-Mn crust in the central Pacific suggests that Fe sources to the deep oceans far from continental margins may be decoupled from the dust-dominated sources in the surface ocean (Chu et al., 2006); such conclusions bear on Fe pathways in models for nutrient upwelling on continental margins (e.g., Mackey et al., 2002) or the effects of Fe fertilization on the surface ocean (e.g., Boyd et al., 2000). Iron cycling in the oceans is of great interest because phytoplankton productivity is linked to Fe availability, which in turn affects atmospheric CO_2 drawdown and global climate (e.g., Martin, 1990). It seems likely that future isotope research in modern marine systems will contribute greatly to tracing metal sources and pathways, although direct Fe isotope analysis of seawater is very difficult due to extremely low Fe contents.

IRON OXIDES AS RECORDS OF BIOLOGIC AND ABIOLOGIC Fe REDOX CYCLING

Using Fe isotopes to trace biological redox cycling has been debated since the initial papers appeared in the literature (e.g., Beard et al., 1999; Bullen et al., 2001). The isotopic compositions of Fe oxides are central to this discussion, and we first focus on oxidative processes. Abiologic oxidation of Fe^{2+}_{aq} by O_2 occurs in terrestrial and marine hydrothermal systems at circum-neutral pH, but in acidic systems (pH < 3), acidophilic Fe^{2+}-oxidizing bacteria are much more efficient at oxidation than abiotic reactions involving O_2 (e.g., Singer and Stumm, 1970). Under low-O_2 conditions, abiotic oxidative processes include UV-photo oxidation (Braterman et al., 1983), but anaerobic photosynthetic Fe^{2+} oxidation has been identified as a biologic pathway for oxidation in the absence of O_2 (Widdel et al., 1993); in both of these cases, oxidation is restricted to environments that have relatively high light intensities, such as the photic zone in marine settings. All of these processes involve two steps: oxidation of Fe^{2+}_{aq} to Fe^{3+}_{aq}, followed by precipitation of Fe^{3+}_{aq} to ferric oxide or hydroxide. The evidence at hand suggests that the Fe isotope fractionations between initial Fe^{2+}_{aq} and ferric oxide or hydroxide precipitate for all of these pathways are similar (Bullen et al., 2001; Croal et al., 2004; Balci et al., 2006; Staton et al., 2006), ranging from ~+1 to +3‰ (Fig. 2A), where the smaller fractionations are dominated by kinetic effects. Iron isotopes do not, therefore, appear to provide a clear distinction between abiologic and biologic pathways that involve *oxidation*. This does not mean, however, that Fe isotopes have limited value in tracing oxidation processes. As noted above, complete oxidation in situ, such as weathering under an oxic atmosphere, will produce no net isotopic change, and therefore ferric oxides or hydroxides that have positive δ^{56}Fe values must have formed through incomplete oxidation of Fe^{2+}_{aq}, suggesting close proximity to an aqueous anoxic-oxic boundary.

An unexpected finding in studies of ferric oxides or hydroxides has been the increasingly common occurrence of negative δ^{56}Fe values from terrestrial (Fig. 2B) and marine (Fig. 2C) environments. These isotopic compositions cannot be explained by partial oxidation of Fe^{2+}_{aq}, which would produce relatively high δ^{56}Fe values, but must reflect complete or near-complete oxidation of Fe that had low δ^{56}Fe values. Low δ^{56}Fe values in bulk analyses and acid extractions of soils have been interpreted to reflect a combination of organically bound Fe and Fe that has been cycled through multiple oxidation and reduction steps (e.g., Fantle and DePaolo, 2004; Emmanuel et al., 2005). Emmanuel et al. (2005) demonstrated, through mixing rela-

tions, that ferric oxides in semiarid and forest soils may have significantly negative δ^{56}Fe values, down to −1 or −2‰ (Fig. 2B). These compositions cannot be produced by a single oxidation step but instead appear to reflect isotopic fractionation during reductive dissolution of detrital oxide and silicate minerals and creation of a labile low-δ^{56}Fe Fe^{2+} pool, followed by complete oxidation. In addition, a labile low-δ^{56}Fe pool may be produced by complexation of Fe^{3+} by organic ligands.

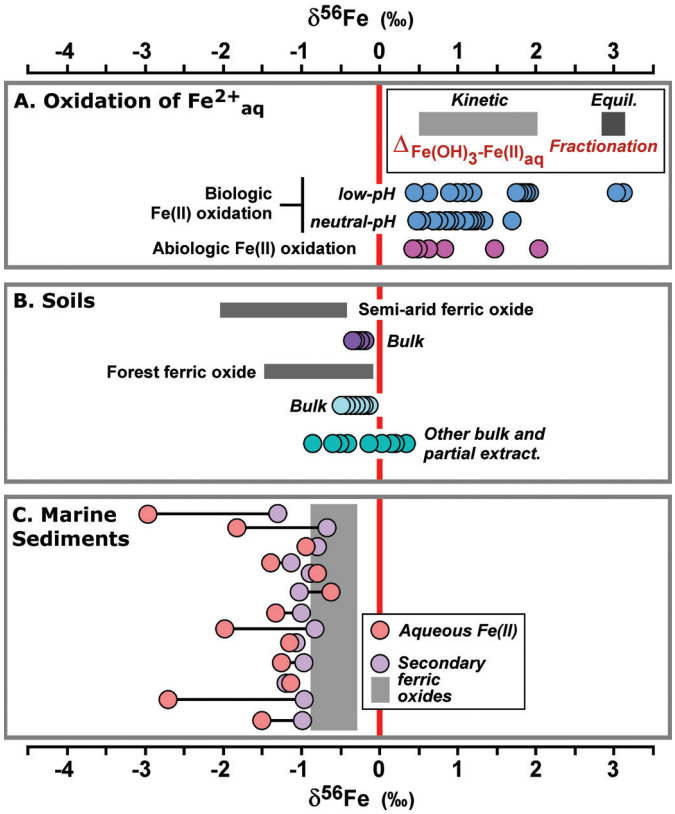

Figure 2. Fe isotope compositions for ferric oxides or hydroxide minerals from various environments that reflect oxidation or redox cycling. Vertical red lines indicate average isotopic composition of igneous and low-C and -S clastic sedimentary rocks, which serve as an isotopic mass-balance reference. (A) Experimental studies of biologic (blue symbols) and abiologic (pink symbols) oxidation of Fe^{2+}_{aq}. The maximum fractionation for the initial precipitate for the two-step reaction $Fe^{2+}_{aq} \rightarrow Fe^{3+}_{aq} \rightarrow Fe(OH)_3$, which is $\Delta_{[Fe(OH)_3] - [Fe^{2+}_{aq}]}$ = +3.0‰, occurs under equilibrium conditions, whereas kinetic fractionation upon precipitation decreases this to ~+0.9 to +1.6‰ for the initial precipitate under many conditions; this range can be increased depending upon the extent of reaction, as observed in experiments. Data from Bullen et al. (2001), Croal et al. (2004), and Balci et al. (2006). (B) Soils. Data from bulk or partial acid extractions, including inferred compositions for ferric oxides (gray bars) and associated bulk soils (purple and light blue symbols), as well as data from other soil samples (blue-green symbols). Data from Brantley et al. (2001); Fantle and DePaolo (2004); Emmanuel et al. (2005). (C) Marine environments. Data from the California coastal margin are shown in circles for Fe^{2+}_{aq} (light pink) and secondary ferric oxides or hydroxides (light purple) for samples where Fe^{3+}/Fe_{total} ratios exceed 0.3, reflecting an important influence by Fe^{3+}-reducing bacteria (Severmann et al., 2006). Grey box indicates range in secondary ferric oxides or hydroxides from modern marine sediments from the Arabian Sea (Staubwasser et al., 2006).

The low-δ^{56}Fe values for ferric oxides or hydroxides in modern marine sediments (Fig. 2C) have been interpreted to reflect oxidation of low-δ^{56}Fe Fe^{2+}_{aq} that was produced by BIR (Severmann et al., 2006; Staubwasser et al., 2006). Porewater Fe^{2+}_{aq} in sediments from the California margin that are dominated by BIR have δ^{56}Fe values equal to or lower than those of coexisting ferric oxides or hydroxides (Fig. 2C). We interpret the negative δ^{56}Fe values for ferric oxide or hydroxide minerals in marine sediments to ultimately be related to BIR followed by oxidation when anoxic porewaters encounter O_2-rich zones. Detailed experimental studies have shown that BIR produces low δ^{56}Fe values of −1 to −3‰ for Fe^{2+}_{aq} (Johnson et al., 2005a, and references therein), which occurs through reduction of ferric oxides and hydroxides via coupled electron and atom exchange between a secondary high-δ^{56}Fe Fe^{3+} surface layer in the oxide substrate and Fe^{2+}_{aq} (Crosby et al., 2005). We conclude that negative δ^{56}Fe values for Fe^{2+}_{aq}, either measured directly or inferred from ferric oxide or hydroxide minerals, appear to be signatures for biological iron *reduction*. Alternative explanations, such as sorption of Fe^{2+} to oxides, are unlikely (Crosby et al., 2005).

LOOKING INTO THE PAST

If the atmosphere of ancient Earth had significantly lower O_2 contents (e.g., Rye and Holland, 1998), the global Fe cycle illustrated in Figure 1 would have been significantly different than it is today. In particular, lower levels of oxidants for Fe would have kept Fe in solution in seawater for much longer periods; the estimated residence time for Fe in the Archean oceans is ~10^6 yr (Johnson et al., 2003). In the absence of an oxidant, the range in Fe isotope compositions of the fluxes to the Archean oceans would have been more restrictive than they are today, where, for example, both riverine and marine hydrothermal fluxes would have had a δ^{56}Fe of ~0‰ (Yamaguchi et al., 2005). In contrast, a wide range of mostly negative δ^{56}Fe values has been found in Proterozoic and Archean sedimentary rocks, spanning lithologies from oxide and carbonate layers in banded iron formations (BIFs), pyrite nodules and disseminated pyrite in shales, to black shales and graywackes with Fe budgets dominated by magnetite or Fe-rich carbonates (Fig. 3).

The contradictory prediction of small Fe isotope variations in an anoxic world and the observed variations in the rock record can be reconciled if Fe cycling in the Archean involved interaction between anoxic reservoirs and those that contained an oxidant. It is generally agreed that an oxidant is required to explain the occurrence of positive δ^{56}Fe values in Archean sedimentary rocks and minerals through oxidation of seawater Fe^{2+}_{aq} (Johnson et al., 2003; Dauphas et al., 2004; Rouxel et al., 2005; Yamaguchi et al., 2005). The nature of the Archean oxidant, however, is debated, and possibilities include atmospheric O_2 (e.g., Ohmoto, 1997), as well as UV-photo oxidation and anaerobic photosynthetic bacteria. The oxidant reservoir most likely existed in the upper ocean, because all oxidation mechanisms require proximity to either an O_2-bearing atmosphere or solar radiation, and such stratification is commonly invoked to explain sequences such as BIFs (e.g., Beukes et al., 1990).

Superimposed upon the isotopic compositions produced during oxidation are those produced during diagenesis under

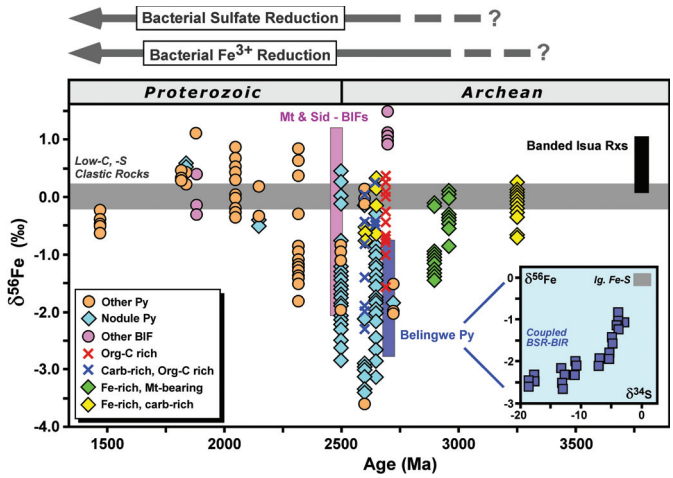

Figure 3. Iron isotope variations in Early Proterozoic to Archean sedimentary rocks and minerals. Range of low-C and -S clastic sedimentary rocks of Archean to modern age shown in horizontal gray band (Beard et al., 2003b; Yamaguchi et al., 2005), encompassing the range of igneous rocks and providing an isotopic mass-balance reference for the total crust. Isotopic data for high-grade metamorphosed banded rocks from Isua Supracrustal belt and adjacent regions shown in dark gray vertical box at right ("Banded Isua Rxs") (Dauphas et al., 2004). Bulk shale samples rich in Fe, C, and/or S are shown in blue and red "X" and green and yellow diamond symbols (Yamaguchi et al., 2005). Data for nodule and other pyrite (py) shown in tan circles and light blue diamonds (Rouxel et al., 2005). Compositions for magnetite and siderite (mt, sid) from the 2.5 Ga Kuruman and Brockman banded iron formations (BIFs) shown in vertical pink bar (n = 166, Johnson et al., 2003, 2005b; Rouxel et al., 2005). Additional data for oxide layers in BIFs (pink circles) from Rouxel et al. (2005). Coupled Fe and S isotope variations for pyrite from the Belingwe basin shown in inset; Fe isotope data shown in dark blue bar on main diagram (Archer and Vance, 2006). Shown along top of figure are the inferred times for the origin of bacterial sulfate reduction (Canfield, 2001) and bacterial Fe^{3+} reduction (Yamaguchi et al., 2005). BIR—bacterial iron reduction; BSR—bacterial sulfate reduction.

reducing conditions. Because the long residence time of Fe in the Archean oceans prevents rapid changes in Fe isotope compositions, the range in Fe isotope compositions in Figure 3 cannot directly reflect that of the Archean oceans. Low δ^{56}Fe values for magnetite in BIFs and shales have been interpreted to reflect equilibration with diagenetically produced Fe^{2+}_{aq} that had low-δ^{56}Fe values generated by BIR (Johnson et al., 2005a; Yamaguchi et al., 2005), providing a time marker for development of this important metabolism on Earth at 2.9 Ga or earlier. Archer and Vance (2006) discovered a remarkable correlation between Fe and S isotope compositions for pyrite from a 10-cm shale section from the 2.7 Ga Belingwe sedimentary basin (Fig. 3, inset). They interpret the covariation in Fe and S isotopes to reflect BIR and BSR during marine diagenesis, where the low-δ^{56}Fe and -δ^{34}S values were produced in shallower sections of the sediment column where BIR was supported by ferric oxide or hydroxide minerals and BSR was less likely to have been SO_4-limited, providing the maximum S isotope fractionation. The high-δ^{56}Fe and -δ^{34}S values are interpreted to have been produced at deeper levels in the sediment column where BIR was minor and SO_4 became limiting.

The abundance of low-δ^{56}Fe values that have been measured for Late Archean to Early Proterozoic sedimentary rocks and minerals is striking (Fig. 3), and we interpret these to dominantly reflect anoxic diagenetic processes, because such rocks are either rich in organic C, carbonate, and/or sulfide or reflect chemical precipitates such as magnetite- and siderite-rich layers in BIFs. Although low-δ^{56}Fe sedimentary pyrite is not restricted to the Archean (Severmann et al., 2006), as originally suggested (Rouxel et al., 2005), the low-δ^{56}Fe inventory in the Late Archean–Early Proterozoic record is clearly significant. It is important to note that low-C and -S clastic rocks have δ^{56}Fe = 0‰ through this time interval (Yamaguchi et al., 2005), indicating that the low-δ^{56}Fe values cannot reflect simple weathering and sediment transport processes. A logical question is, given the important mass-balance constraints provided by the δ^{56}Fe = 0‰ reservoirs of igneous, metamorphic, and low-C and -S clastic rocks, where are the positive δ^{56}Fe components? In a broad survey of sedimentary sulfides from Late Archean to Phanerozoic rocks, Rouxel et al. (2005) hypothesized that the high-δ^{56}Fe component may lie in oxide layers in BIFs or ferric oxides or hydroxides dispersed on continental shelves. Although it is true that oxide minerals (hematite and magnetite) from Late Archean to Early Proterozoic rocks may have high δ^{56}Fe values, this is not uniformly so. If we look at BIFs that have not been subjected to significant metamorphism, the δ^{56}Fe values for magnetite range from −1 to +1‰ but have an average value of +0.04‰ (n = 73; Johnson et al., 2003, 2005b; Rouxel et al., 2005). It is possible that the high-δ^{56}Fe component may not be preserved in the rock record. Important reservoirs that remain unknown are ancient altered oceanic crust and Late Archean–Early Proterozoic seawater.

Generally positive δ^{56}Fe values were measured for the 3.8 Ga banded Isua and Akilia rocks of SW Greenland (Fig. 3; Dauphas et al., 2004), some of which may have been BIFs. Because these rocks have been subjected to amphibolite- to granulite-facies metamorphism, there is some uncertainty regarding the effects of high-grade metamorphism. Dauphas et al. (2004) interpreted the high-δ^{56}Fe values to reflect partial oxidation of hydrothermally sourced Fe^{2+}_{aq}, which may have been caused by atmospheric O_2, anaerobic photosynthetic Fe oxidation, or UV-photo oxidation. Although Fe isotopes cannot, by themselves, distinguish among these possibilities, the isotopic data highlight the importance of an oxidant in the earliest period of Earth's history, and the positive δ^{56}Fe values require oxidation that did not run to completion, implying that the oxidant was limited. An important focus for future research will be investigation of a possible transition from the high-δ^{56}Fe values at 3.8 Ga to the low-δ^{56}Fe values at 2.7–2.5 Ga in the sedimentary rock record (Fig. 3), which could constrain the timing of development of iron-reducing metabolisms and the abundance of an oxidant on Earth's surface. Anaerobic photosynthesis preceded oxygenic photosynthesis (Xiong et al., 2000; Brocks et al., 2003), and although bacterial Fe reduction is also thought to be an ancient metabolism (Vargas et al., 1998), it must have formed after a significant oxidant developed on Earth (Nealson and Saffarini, 1994).

CONCLUSIONS

In the relatively short period since the field of Fe isotope geochemistry began, the expectation that measurable isotopic fractionations would be produced through differences in

bonding environments that accompany redox and mineral-fluid reactions has been realized in a wide variety of natural systems. The Fe isotope literature, reflecting nearly 80 publications through mid-2006 from roughly two dozen research groups, now contains several thousand isotopic analyses, attesting to the remarkable speed with which this new field has developed. Most of the Fe that is part of the modern Fe cycle has δ^{56}Fe values within one or two tenths per mil of zero, including the majority of the mantle, most igneous and metamorphic rocks, and low-C and -S clastic sedimentary rocks. The environments in which Fe isotope fractionations are produced on Earth today are therefore quite specific.

In modern aqueous environments, such as the oceans, dissolved Fe contents are so low that their isotopic compositions are sensitive indicators of Fe sources and pathways. Iron isotopes are exceptional indicators of Fe redox cycling, particularly in low-temperature environments where isotopic fractionations are relatively large and where significant pools of Fe^{2+} and Fe^{3+} may coexist. In modern Earth, such environments comprise a relatively small portion of the global Fe biogeochemical cycle, and in many cases these environments are populated by Fe^{2+}-oxidizing and/or Fe^{3+}-reducing bacteria that exploit redox gradients for energy. The evidence is clear that in many cases the observed Fe isotope fractionations reflect bacterially mediated redox cycling, and this is particularly true for bacterial Fe^{3+} reduction, where Fe isotopes appear to be most robust as a "biosignature." In addition, coupled Fe-S cycling induced by sulfide produced by bacterial sulfate reduction appears to produce Fe isotope compositions in Fe^{2+}_{aq} and FeS that are distinct from those of Fe^{2+}_{aq} and ferric oxides or hydroxides that are associated with bacterial iron reduction, providing a potential marker for the two metabolisms. Abiologic processes clearly fractionate Fe isotopes, but we contend that biologic and abiologic processes may be distinguished in many cases when the likely processes involved and mass balance issues are carefully considered.

We are only just beginning to study the Fe isotope cycle in early Earth. If a low-O_2 atmosphere and Fe^{2+}-rich ocean characterized the Archean, the global Fe isotope balance must have been significantly different than it is today. For example, Fe isotope compositions provide powerful evidence that bacterial iron reduction was established ca. 2.9 Ga, which in turn requires a mechanism to produce ferric oxide or hydroxide minerals. Major challenges involve understanding the connection between what is preserved in the rock record, which may be strongly affected by diagenesis and later alteration or metamorphism, and the ambient surface conditions in the past. Full understanding of the Fe isotope mass balance of ancient Earth, which is powerfully constrained by the near-zero δ^{56}Fe values of igneous and low-C and -S clastic sedimentary rocks, requires estimating the isotopic compositions and elemental inventories of important Archean reservoirs such as the "oxidized zone" or those that we cannot measure directly, such as ancient oceanic crust and seawater. Critical to the success of all of these studies will be careful theoretical and experimental determination of Fe isotope fractionation factors under kinetic and equilibrium conditions, as well as quantifying the rates of isotopic exchange in systems that are analogous to nature.

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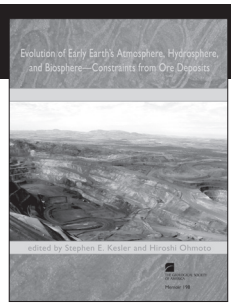

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