Iron isotopes constrain the pathways and formation mechanisms of terrestrial oxide concretions: A tool for tracing iron cycling on Mars?

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ABSTRACT

New iron isotope data document open-system formation of terrestrial iron oxide concretions and the potentially important role of iron-reducing bacteria in mobilizing iron. These terrestrial insights can provide valuable models for understanding extraterrestrial hematite spherules and their diagenetic history at Meridiani Planum, Mars. Whole-rock samples of Jurassic Navajo Sandstone host rock have δ56Fe values near 0 per mil (‰), whereas concretions typically have negative δ56Fe values. Negative δ56Fe values can be explained by complete oxidation and precipitation from aqueous fluids that had δ56Fe values of −0.5‰e to −1.5‰e. The low δ56Fe values for the majority of concretions overlap those of Fe(II)aq, and reactive ferric oxides in modern marine sediments where iron-reducing bacteria are actively cycling Fe, suggesting that Fe mobilization in the Navajo Sandstone occurred through bacterial reduction of Fe oxides. Variations in δ56Fe values support an open-system model of concretion formation where Fe is recycled via different chemical reactions involving reduction, mobilization, and precipitation. If the Mars concretions formed in a similarly open system during Fe mobilization and precipitation, their δ56Fe values should also deviate from δ56Fe = 0, dependent upon the pathway, but positive δ56Fe values would be expected for oxides in the absence of a role for microbial redox cycling.

Keywords: iron isotopes, concretion, hematite, diagenesis, Mars.

INTRODUCTION

Concretions are concentrated masses of mineral cements that are typically spherical, and they are very common and widespread in sedimentary rocks throughout the geologic record (e.g., Seilacher, 2001). Remarkably, the National Aeronautics and Space Administration (NASA) Opportunity rover discovered small hematite spherules in Meridiani Planum on Mars (dubbed “blueberries”) that have been interpreted as concretions (Squyres et al., 2004; Herkenhoff et al., 2004; Christensen et al., 2004). Iron oxide concretions on both Mars and Earth are valuable records of diagenetic, postdepositional changes in sedimentary units because they preserve evidence of ancient groundwater flow (Chan et al., 2004, 2005; Ormö et al., 2004; McLennan et al., 2005), fluid-rock interactions, element cycling, and the presence of redox boundaries. The concretions typically have spherical morphologies.

The Jurassic Navajo Sandstone exposed in southern Utah contains abundant, diverse, and well-documented examples of Fe oxide (e.g., hematite and goethite) concretions (e.g., Utah “marbles”) that have morphological similarities to the Mars “blueberries” in the deposits of Meridiani Planum (Chan et al., 2004, 2005). Although no single terrestrial analog is likely to be a perfect match for all the chemical and physical traits of sulfate mineralogy and Fe oxide concretions on Mars, the sediment-hosted Navajo concretions offer a natural, terrestrial laboratory that provides insights into the Meridiani Planum deposits. In this contribution, we present new Fe isotope data that allow us to constrain the Fe sources and pathways involved in concretion formation. These data document the open-system conditions that were required for concretion formation, the important role of hydrocarbons or Fe-reducing bacteria in mobilizing Fe, and the isotopic signatures of oxidation and precipitation at redox boundaries. These results provide insight into Fe mobility and redox transformations in terrestrial environments, and potentially constrain the range in Fe isotope signatures that may be found in oxide concretions on Mars in future in situ measurements or those obtained by sample-return missions.

IRON ISOTOPE GEOCHEMISTRY

Iron isotope geochemistry is a rapidly growing field, where it is now known that measurable isotopic fractionations occur in both high- and low-temperature environments (e.g., Welch et al., 2003; Beard and Johnson, 2004; Johnson et al., 2004; Dauphas and Rouxel, 2006). Some of the largest Fe isotope fractionations occur in low-temperature systems (<100 °C) during redox transformations, but only under conditions where separation of isotopically distinct Fe pools may occur (Johnson and Beard, 2006). For example, partial oxidation of aqueous Fe(II) generally leads to ferric Fe oxide or hydroxide precipitates that have higher δ56Fe/δ54Fe ratios than the initial aqueous Fe(II). Complete oxidation, however, such as might occur when Fe(II)aq
encounters atmospheric O₂, or during weathering of Fe(II)-bearing igneous or metamorphic rocks, will produce ferric oxides or hydroxides that have essentially the same Fe isotope composition as the initial Fe(II) because oxidation ran to completion. This effect is well illustrated for surface weathering products, including suspended river loads, aerosols, and ferric Fe-rich clastic rocks that have low organic carbon or carbonate contents, all of which have Fe isotope compositions that are closely similar to those of the average crust (Beard et al., 2003b).

We report Fe isotope compositions using standard δ notation as the deviation in 56Fe/54Fe ratio of a sample relative to a reference reservoir, in units of parts per thousand, or per mil (‰):

\[
\delta^{56}\text{Fe} = \left(\frac{[56^{\text{Fe}}/54^{\text{Fe}}_{\text{sample}}]}{[56^{\text{Fe}}/54^{\text{Fe}}_{\text{reference}}]} - 1\right) \times 10^3,
\]

where 56Fe/54Fe reference is taken as the average of igneous rocks (Beard et al., 2003a). On the igneous rock scale, the IRRM-014 standard produces a δ56Fe value of −0.09‰. The total spread in δ56Fe values of terrestrial samples is ±4.5‰, and typical analytical precisions are ±0.05 to ±0.10‰ (2σ). Following standard convention, we describe the Fe isotope fractionation between two phases A and B as:

\[
\Delta^{56}\text{Fe}_{A-B} = \delta^{56}\text{Fe}_A - \delta^{56}\text{Fe}_B.
\]

This may be related to the Fe isotope fractionation factor α A-B through the approximation:

\[
10^3 \times \ln \alpha_{A-B} = \Delta^{56}\text{Fe}_{A-B}.
\]

Details on chemical separation and mass analysis methods are in Beard et al. (2003a) and Albarède and Beard (2004).

**CONCRETION GENESIS**

The porous and permeable characteristics of the Navajo Sandstone provide favorable conditions for the formation of Fe oxide concretions (Chan et al., 2004, 2005). The well-sorted, eolian quartz arenite (Beitler et al., 2005) has effective porosity that averages ~17% (Cordova, 1978) and permeability up to 1 Darcy (Lindquist, 1988). Iron oxide mineralization can be summarized as a three-step process of diagenesis, which critically includes groundwater flow (Chan et al., 2000, 2004, 2005; Chan and Parry, 2002; Beitler et al., 2003, 2005). Diagenetic temperatures <100 °C are inferred based on an estimated burial depth of 2 km (Beitler et al., 2005) and mineralogical evidence (summarized in Chan et al., 2000), as well as supporting studies on the thermal burial history and uplift of the Colorado Plateau (Dumitrut et al., 1994; Nuccio and Condon, 1996).

**Iron Sources**

Red Navajo sandstones (Fig. 1A) contain an average of 0.53 ± 0.34 wt% Fe₂O₃ (1 SD) distributed as thin Fe oxide films that coat individual sand grains (Beitler et al., 2005). This iron is likely to have been derived from detrital Fe-bearing silicate minerals within the sandstone during early weathering and diagenesis. Dissimilatory precipitation of this early diagenetic Fe oxide occurred shortly after deposition or during early burial via interaction with meteoric waters. In terms of expected Fe isotope compositions for these early Fe oxides, they probably had δ56Fe values near zero, similar to the igneous rock baseline that characterizes bulk continental crust, including low organic carbon (Corg) or carbonate (C carbonate) contents, classic sedimentary rocks, and sandstones that are rich in disseminated ferrous Fe oxide cements (Beitler et al., 2003b; Beard and Johnson, 2004; Yamaguchi et al., 2005; Johnson and Beard, 2005, 2006).

**Iron Mobilization**

After burial, reduced fluids containing hydrocarbons derived from underlying units are thought to have flowed up preferential pathways such as faults and through the porous sandstone (Chan et al., 2000). Mobilization of the early oxides is envisioned to have occurred through reductive dissolution and transport as Fe(II)aq leaving bleached, white sandstone (Fig. 1B). These bleached zones can be quite extensive, on the order of hundreds of square kilometers (Beitler et al., 2003). Bleached sandstones contain an average of 0.36 ± 0.26 wt% Fe₂O₃ (1 SD) as Fe oxide (Beitler et al., 2005). Based on total Fe contents of red and bleached sandstones, up to 30% of the Fe was removed. Reactions between hydrocarbons and ferric oxide may be expressed through reduction of Fe coupled with oxidation of organic matter as:

\[
\text{CH}_2\text{O} + 2\text{Fe}_2\text{O}_3 + 8\text{H}^+ \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 4\text{Fe}^{2+}
\]

(e.g., Chan et al., 2000). The same reaction is applicable to reduction of ferric oxides or hydroxides by disimilatory iron-reducing bacteria (DIRB) (e.g., Nealon and Saiffarini, 1994). At temperatures below 120 °C, Fe(III) reduction by organic matter does not occur in the absence of DIRB (Lovley et al., 1991).

Iron isotopes are fractionated during reduction of Fe(III) oxides or hydroxides by DIRB, where Fe(II) has δ56Fe values that are 1–3‰ lower than the initial ferric oxide or hydroxide (Beard et al., 1999, 2003a; Iopini et al., 2004; Johnson et al., 2002, 2005; Crosby et al., 2005). Low δ56Fe Fe(II) is balanced by a reactive Fe(III) layer on the oxide or hydroxide mineral surface that has high δ56Fe values, indicating that these minerals are dissolved incongruently by DIRB (Crosby et al., 2005). The low δ56Fe fingerprint of Fe(II) that is produced by DIRB has been found in Fe(III)-rich pore waters in modern marine sediments (Severmann et al., 2006; Berquist and Boyle, 2006), and low δ56Fe ferric Fe oxides in modern marine environments have been ascribed to precipitation of DIRB-produced low δ56Fe Fe(II) (Severmann et al., 2006; Staubwasser et al., 2006). The Fe isotope effects of abiotic reduction of ferric oxides or hydroxides by hydrocarbons are not known, and they likely depend on the dissolution mechanism; congruent dissolution is unlikely to produce any Fe isotope fractionation (Johnson et al., 2004), but formation of a new phase or reactive surface layer during incongruent dissolution may potentially produce an Fe isotope fractionation.

Although the form and occurrence of the Navajo Sandstone concretions are strikingly similar to the small, spherical “blueberry” hematite concretions (Figs. 1F–1H) in Meridiani Planum, the mechanisms by which Fe was mobilized may have been distinct. For example, Fe in the Mars system was probably mobilized through dissolution of primary silicates in basaltic rocks by acidic solutions (e.g., Morris et al., 2005). If this Fe mobilization occurred under reducing conditions, where aqueous Fe was largely Fe(II), no Fe isotope fractionation would be expected because no redox change would occur. Partial dissolution of silicates by organic ligands underoxic conditions can produce aqueous Fe(III) that has relatively low δ56Fe values (Brantley et al., 2001, 2004), although significant fractionations have only been observed at very low extents of dissolution (≤1%).

**Concretion Precipitation**

Precipitation of terrestrial concretions is thought to occur when Fe(II)-bearing (reduced) fluids intersected oxidizing groundwaters, where oxidation of Fe at near-neutral pH would produce immediate precipitation of Fe oxide at the mixing interface (von Gunten and Schneider, 1991). Precipitation of Fe oxide would be concentrated within a spatially limited reaction front corresponding to this mixing interface. Concretions that precipitate within such a reaction front are commonly spheroidal in shape (Figs. 1C–1E). The average Fe concentration in the Fe oxide cemented concretions is 15.12 ± 9.99 wt% Fe₂O₃ (1 SD) (Beitler et al., 2005).
where other constituents are largely SiO₂ (avg. of 77.3 wt%) and Al₂O₃ (avg. of 2.2 wt%). Age determinations of related mineralization (Chan et al., 2001) suggest that some precipitation occurred ca. 25 Ma, but mineralization appears to have been episodic and may have included older or younger events.

The Fe isotope compositions produced during oxidation and precipitation will depend upon the extent of coupled oxidation-precipitation and the degree to which precipitation occurs under equilibrium conditions (Beard and Johnson, 2004; Johnson and Beard, 2006). Partial oxidation of Fe(II)ₐq to Fe(III)ₐq, followed by complete precipitation of Fe(III)ₐq to ferric oxides or hydroxides should produce δ⁵⁶Fe values for the ferric Fe precipitates that are ~1–3‰ higher than those of the initial Fe(II)ₐq, which would allow the oxide concretions to be used as proxies for the Fe isotope compositions of the precursor aqueous Fe(II).

Fe(II)ₐq oxidation and precipitation of the Martian hematite concretions are thought to have occurred upon oxidation in a highly reactive chemical environment that included formation of evaporite and sulfate minerals (McLennan et al., 2005; Tosca et al., 2005). In both the Mars and terrestrial systems, however, the Fe isotope fractionations produced during oxidation would be expected to be similar, given the fact that generally similar fractionations are observed in a wide variety of oxidative pathways, including biological and abiological systems (Bullen et al., 2001; Croal et al., 2004; Balci et al., 2006). We therefore expect that the key component in determination of the Fe isotope compositions of concretions on Mars or Earth is the mechanism by which Fe was initially mobilized.

RESULTS

We analyzed representative samples from 16 localities of Jurassic Navajo Sandstone and 2 localities of Jurassic Entrada Sandstone across an ~400 km traverse in southern Utah (Fig. 2). These included whole-rock samples of original red host sandstone (Fig. 1A) and bleached sandstone (Fig. 1B). Whole-rock samples where color, textural, and field characteristics indicated that no late secondary Fe mobilization occurred have δ⁵⁶Fe values that lie within 0.2‰ of zero (avg. δ⁵⁶Fe = +0.04‰), the same range observed in low-C and low-S clastic sedimentary rocks that have not undergone significant anoxic diagenesis (Table DR1; Fig. 3) (Beard and Johnson, 2004; Johnson and Beard, 2006). Bleached
Iron isotopes in concretions

Figure 2. Localities of Jurassic sampling for Fe isotope analyses: 1—Snow Canyon, 2—Sand Hollow, 3—Zion National Park, 4—Cedar City, 5–10—Grand Staircase Escalante National Monument, 11–13—Lake Powell area, and 14–18—Moab area. All samples are from the Lower Jurassic Navajo Sandstone (Ss) except for localities 12 and 17, which are from the Middle Jurassic Entrada Sandstone. Generalized stratigraphic column is at left (modified after Chan et al., 2005).
rocks that have lost Fe have a similar range in δ56Fe values, although their average is slightly higher than zero. One sample that is enriched in secondary oxides has a distinctly lower δ56Fe value of −0.6‰.

Iron oxide concretions have a large range of δ56Fe values from +0.9‰ to −2.0‰. The most remarkable characteristic of the concretion data is that most samples have negative δ56Fe values, which is generally unexpected for oxide minerals, which would be enriched in 56Fe/54Fe based on Fe isotope fractionation factors (Beard and Johnson, 2004). Comparison of δ56Fe values for individual concretions with whole-rock samples from the same locality generally show large isotopic contrasts, up to 1.5‰, which provides strong support for a model in which Fe was mobilized, oxidized, and precipitated in an open, fluid-rich system. There is no systematic correlation between δ56Fe values and oxide mineralogy (hematite or goethite). There are, however, sometimes significant variations in δ56Fe values (up to 0.8‰) within individual concretions. In several cases, the interiors of concretions have higher δ56Fe values than the rims (Fig. 3; Table DR1, Fig. DR1 [see footnote 1]), but reverse zoning is also present.

**DISCUSSION**

The negative δ56Fe values for most of the oxide concretions coupled with the wide range in these values demonstrate that they did not form by simple, closed-system remobilization of Fe from earlier diagenetic oxides, but instead formed in an open system. Congruent dissolution of early diagenetic oxide minerals, followed by complete oxidation and precipitation in a closed system, would produce little change in δ56Fe values from their initial near-zero values. In principle, Fe oxides that have moderately negative δ56Fe values of −0.5‰ to −1.5‰ may be produced through oxidation and precipitation from an Fe(II)-bearing fluid that has a δ56Fe value of zero, but only under very special conditions. Assuming a Rayleigh process, the negative δ56Fe values for the majority of oxide concretions can only be produced by first oxidizing ~70% to ~90% of the Fe(II) initially present (that had an initial δ56Fe value of zero), and then selectively incorporating the last few percent of the incrementally produced Fe into the concretions (Fig. 4). This scenario seems unlikely for several reasons. The geological and geochemical evidence for the terrestrial model supports precipitation of Fe oxide at a reaction front produced by a mixing interface between reduced and O2-rich groundwater masses. If the Fe oxide was precipitating by a Rayleigh process at this interface, the great majority of the mass of the iron oxide present would have δ56Fe values significantly above 0‰ (Fig. 4). The opposite is observed; most concretions have negative δ56Fe values (Table DR1, see footnote 1). Further, the terrestrial model appears to have operated at near-neutral pH conditions based on several geochemical characteristics: adsorbed species Zn, Co, Ni, As, V, and U that imply pH 6–8 for precipitation of Fe oxides (Beitler et al., 2005); co-existence of kaolinite and illite (Chan et al., 2000); and reasonable values of K+ in solution (0.001 M) that imply pH ~ 6. At pH conditions of 6–8, oxidation will tend to run to completion at the reaction front where reduced fluids encounter O2-rich fluids. In such a scenario, selective incorporation of a narrow range of late-stage oxide products (e.g., Rayleigh process) into the concretions is not realistic.

Busigny and Dauphas (2006) analyzed several goethite-cemented concretions from the Navajo Sandstone in a few limited locality areas of southern Utah and suggested that negative δ56Fe values measured in the concretions could be explained by evolution of the fluid composition through successive precipitation (e.g., Rayleigh process) and/or adsorption of Fe. We regard the Rayleigh process as an unlikely mechanism for the reasons presented in the preceding paragraph. Moreover, our δ56Fe data on a broad range of concretion mineralogy types (many with complex layering and different δ56Fe core-to-rim trends) from different reaction fronts spanning a much larger regional area lead us to favor other models that involve open diagenetic systems and the potential role of Fe(III)-reducing bacteria.

As it seems more likely that the oxide concretions were produced by complete or near-complete oxidation of Fe(II) as reduced fluids encountered O2-rich zones, it is more appropriate to consider the integrated Fe oxide isotopic

![Figure 3. Summary of measured δ56Fe values from different Jurassic sandstone samples relative to sample locality (Fig. 2). Whole-rock samples are shown in blue squares. Concretion samples are shown in red circles. I—inner portion of concretion sample, R—rim of concretion sample. Also shown is the range in δ56Fe values for low-C and low-S clastic sedimentary rocks (light-green band) that reflects Fe(III)-rich weathering products (Beard et al., 2003b; Yamaguchi et al., 2005), which should represent the range in δ56Fe values of the early diagenetic Fe(III) oxides in the Jurassic sandstones. Vertical dashed line is the average of igneous rocks (Beard et al., 2003a).](https://pubs.geoscienceworld.org/gsa/geosphere/article-pdf/2/7/324/3335546/i1553-040X-2-7-324.pdf)
compositions (Fig. 4). In this case, however, the integrated Fe oxide can have δ56Fe values no lower than that of the initial fluid (Fig. 4). Hence, the negative δ56Fe values of ~0.5‰ to ~1.5‰ for the majority of oxide concretions is best explained by oxidation, followed by precipitation, of Fe(II) that had initial δ56Fe values that were negative. An end-member case would be one where the δ56Fe values of the oxide concretions are a direct proxy for the δ56Fe values of Fe(II)aq, which would require complete oxidation and precipitation. Alternatively, partial oxidation, but complete precipitation, may explain the data. For example, assuming an initial δ56Fe value of ~2.0‰ for Fe(II)aq, ~50%–70% oxidation may produce the range in Fe isotope compositions for the oxide concretions that have negative δ56Fe values (Fig. 4). Alternatively, the oxide concretions that have moderately negative δ56Fe values of ~0.5‰ could be explained by ~100% oxidation and precipitation of Fe(II)aq that had an initial δ56Fe value of ~0.5‰. The few concretions that have positive δ56Fe values may be explained by ~50% to ~80% oxidation of Fe(II)aq. It has been proposed that sorption of Fe(II)aq to Fe oxide minerals is at a maximum (e.g., Jeon et al., 1996) when DIRB are likely to play a major role in modern sediments (Fig. 4). Sevemann et al. (2006) demonstrated increases in porosity in reductive Fe(III) oxides coupled with oxidation of organic matter was not observed in experiments run as high as 120 °C at circumneutral pH (Lovley et al., 1991). Therefore, our preferred interpretation is that the role of hydrocarbons in Fe mobilization in the Navajo Sandstone was primarily to serve as an organic carbon source for bacterial Fe(III) reduction rather than as an abiological reductant.

Finally, we consider the possibility that the oxide concretions may reflect in situ oxidation of pyrite concretions. Because many sedimentary pyrites in modern (Sevemann et al., 2006) and ancient (Rouxel et al., 2005; Yamaguchi et al., 2005; Archer and Vance, 2006) environments have negative δ56Fe values, in situ oxidation of pyrite might explain the low δ56Fe oxide concretions. Such an explanation, however, is unlikely for several reasons. First, pyrite is rarely found in unbleached Navajo Sandstone, and only in trace abundances within bleached sandstones. There is no evidence of any remnant pyrite minerals in the numerous samples of Navajo concretions that have been examined, and if pyrite was important in the diagenetic history, some remnants would be expected. Furthermore, the Navajo Sandstone does not contain any evidence for sulfate minerals, nor is it rich in organic carbon, as is common in pyrite-bearing sedimentary rocks. Second, the widespread distribution, variety, abundance, and geometries of the Navajo concretions are very different from the features observed in pyrite-bearing sedimentary rocks, where pyrite is commonly localized within bedding and/or mineralization along fault zones. More importantly, the distribution of the Fe oxide concretions in the Navajo Sandstone is along geographically extensive redox fronts that are characterized by bleached zone boundaries that cut across primary structures. These features are not consistent with in situ oxidation of pyrite.

**Evidence for Fe(III)-Reducing Bacteria**

The range in δ56Fe values estimated for Fe(II)aq, that was the source of Fe for the Navajo oxide concretions overlapped that measured for active diagenetic systems, including modern marine sediments (Fig. 4). Sevemann et al. (2006) noted that porewater Fe(II) in suboxic sections of modern marine sediments (California margin) where DIRB are likely to play a major role in Fe cycling have low δ56Fe values, generally between ~1.0‰ and ~3.0‰ (Fig. 4). In addition, ferric hydroxides in the same sediments also have relatively low δ56Fe values, averaging ~1.0‰ (Fig. 4). Sevemann et al. (2006) interpreted the negative δ56Fe values for reactive Fe(III) oxides to reflect complete or near-complete oxidation of low δ56Fe Fe(II)aq upon interaction with O2-bearing seawater, whereas the low δ56Fe values for porewater Fe(II) were generated by DIRB deeper in the sediment column. A similar interpretation has been made by Staubwasser et al. (2006) to explain moderately negative δ56Fe values for reactive Fe(III) oxides in modern sediments from the Arabian Sea. Based on the similarly negative δ56Fe values for the Navajo oxide concretions, and the inferred low δ56Fe values for Fe(II)aq, we infer that bacterial Fe(III) reduction, coupled with hydrocarbon oxidation, was the major mechanism for mobilizing Fe in the Navajo Sandstone.

**Other Mechanisms for Producing Low δ56Fe Values**

It is unknown if low δ56Fe values for Fe(II)aq may be produced through abiotic reduction of early diagenetic Fe(III) oxides by hydrocarbons. Experimental studies by Shebl and Surdam (1996) demonstrated increases in porosity in oxide-bearing sandstone during heating (200–360 °C) in the presence of hydrocarbons, but these increases largely occurred through dissolution of carbonate cement, and there were no clear increases in Fe(II) contents during reaction. At the lower temperatures (<100 °C) estimated to have characterized Fe mobilization in the Navajo Sandstone, we would expect less reaction between hydrocarbons and sandstone cements. In addition, abiological reduction of Fe(III) oxides coupled with oxidation of organic matter was not observed in experiments run as high as 120 °C at circumneutral pH (Lovley et al., 1991). Therefore, our preferred interpretation is that the role of hydrocarbons in Fe mobilization in the Navajo Sandstone was primarily to serve as an organic carbon source for bacterial Fe(III) reduction rather than as an abiological reductant.

**A Conceptual Model**

We illustrate a conceptual model of redox cycling of Fe and formation of Fe oxide concretions in Figure 5. The δ56Fe values for the initial, early diagenetic Fe oxides should have been
Figure 4. Comparison of $\delta^{56}$Fe values produced for oxides during oxidation of Fe(II)$_{aq}$ (A) and histograms for $\delta^{56}$Fe values measured for oxide concretions (B), whole-rock sandstones (C), and reactive Fe(III) oxides and Fe(II)-bearing pore waters from modern marine sediments (D). In A, $\delta^{56}$Fe values were calculated using a Rayleigh model as a function of percent oxidation of Fe(II)$_{aq}$ for the reaction Fe(II)$_{aq}$ $\rightarrow$ Fe(III)$_{aq}$ $\rightarrow$ Fe(III) oxide; once oxidized, 100% of the Fe(III)$_{aq}$ is assumed to precipitate as oxides, which is appropriate for the circumneutral pH conditions in which the concretions formed. Upper curves (warm colors) illustrate Fe isotope compositions produced for Fe(II)$_{aq}$ that had initial $\delta^{56}$Fe = 0.0‰; lower curves (cool colors) were calculated for an initial $\delta^{56}$Fe value for Fe(II)$_{aq}$ of $-2.0$‰. Data for B and C are from Table DR1 (see text footnote 1). Data for D are from modern marine sediments from the California margin (Severmann et al., 2006); $\delta^{56}$Fe values for reactive Fe(III) oxides were estimated from acid extractions that produced Fe(III)/Fe$_{total}$ > 0.3. Porewater compositions are shown for suboxic, low-S samples where dissimilatory Fe(III)-reducing bacteria (DIRB) play a major role in Fe cycling. Thick gray line at $\delta^{56}$Fe = 0 notes average of igneous rocks and low-C, low-S clastic sedimentary rocks and weathering products. Thin gray lines were added for scale reference across the figures.

Figure 5. Conceptual grain-scale model of isotopic analyses for stages of redox reactions for Fe cycling in terrestrial examples of Navajo Sandstone concretion formation. (A) Early hematite (Fe$^{3+}$) grain coatings in original red sandstone, where initial $\delta^{56}$Fe = 0.0‰. (B) Influx of reducing fluids that “bleach” the buried sandstone during reduction of Fe$^{3+}$ to Fe$^{2+}$, where the Fe(II)-rich fluids have $\delta^{56}$Fe values between $-0.5$‰ and $-1.5$‰, probably reflecting bacterial Fe reduction. (C) Bleached sandstone pores are saturated with waters containing reduced iron (Fe$^{2+}$). (D) Influx of oxidizing groundwater creates redox front where concretions precipitate. (E) Concretions form along a reaction front with organized distribution and spherical shape, producing a range of $\delta^{56}$Fe values that are generally negative, reflecting complete oxidation and precipitation of low $\delta^{56}$Fe Fe(II)$_{aq}$.
Iron isotopes in concretions

close to zero (Fig. 5A), as shown by our measurements of Fe oxide in unbleached Navajo sandstone and an extensive database for modern and ancient Fe(III)-rich weathering products. Ion mobilization through incongruent dissolution of the early diagenetic Fe oxides produced Fe(II)$_{ox}$ that has low $^{56}$Fe values of $≈-0.5\%$ to $≈-1.5\%$ (Table 5B). On average, $≈30\%$ Fe reduction occurred based on the contrast in Fe contents between red and bleached whole-rock samples. However, the proportion of mobilized Fe that was eventually sequestered as oxide concretions is difficult to constrain. Field measurements of this proportion are complicated by the highly nonuniform distribution of the oxide concretions, which likely resulted from the superposition of multiple reaction zones of variable scales (from centimeter to kilometer scales and greater) that migrated spatially and/or operated repeatedly over time.

Reductive dissolution most likely occurred by DIRB, where oxide reduction was coupled to hydrocarbon oxidation under anoxic conditions. Reduced, Fe(II)-bearing fluids were transported away from the site of initial oxide reduction (Fig. 5C), where anoxic conditions were likely maintained by dissolved organic carbon. Fe(II)-rich fluids encountered O$_2$-bearing fluids either through ascent of reduced fluids or downward penetration of oxidizing fluids or both (Fig. 5D), which resulted in rapid and complete oxidation and precipitation of Fe(II)$_{ox}$ to ferric oxides and hydroxides at the mixing interface between these fluids. The distribution and size of oxide concretions indicate a major control by nucleation, suggesting that precipitation was rapid. Such a process should produce $^{56}$Fe values for oxide concretions that are generally reflective of the $^{56}$Fe values for the precursor Fe(II)$_{ox}$ (Fig. 5E), although isotopic zoning would be expected due to local (centimeter-scale) changes in $^{56}$Fe values imposed on the remaining Fe(II)$_{ox}$ that existed between nuclei during the oxidation process and final precipitation of the remaining Fe.

Removal of low $^{56}$Fe Fe(II)$_{ox}$ should have produced high $^{56}$Fe values for bleached rocks, but this is not uniformly observed. The $^{56}$Fe values for whole-rock samples of bleached rocks range from $-0.16\%$ to $+0.24\%$ (Table DR1, see footnote 1). It is important to note, however, that it is difficult to estimate the $^{56}$Fe value of the Fe inventory that was removed, given the fact that the oxide concretions represent only a small fraction of the Fe that was removed from the bleached zones. Moreover, the lowest $^{56}$Fe values for Fe(II)$_{ox}$ generated by reductive dissolution of Fe oxides by DIRB would be produced only at low extents of reduction (a few percent) (Johnson et al., 2005; Crosby et al., 2005), which would produce negligible changes in the $^{56}$Fe values of the remaining Fe oxide. It is therefore difficult to calculate a rigorous isotopic mass balance with the current data set, although this may be possible through much more extensive studies of the bleached zones.

CONCLUSIONS

Iron isotope compositions of oxide concretions in the Navajo Sandstone document reductive dissolution of early diagenetic oxides, aqueous transport, and final precipitation in an open groundwater terrestrial system. Although the mineralogy and inferred fluid chemistry of the Navajo concretions have some important differences from Mars concretions, Fe isotope should be similarly valuable in constraining Fe pathways and open- or closed-system behavior. In the Navajo system, the generally low $^{56}$Fe values of the oxide concretions point to initial Fe mobilization through incongruent reductive dissolution of early sandstone oxides, probably by dissimilatory Fe(III)-reducing bacteria producing Fe(II)$_{ox}$ with $^{56}$Fe $< 0$. In the Meridiani Planum system, Fe mobilization is thought to have occurred by acid sulfate weathering of primary silicate minerals in basaltic rock, and in this case, if the fluid reservoir was limited and large extents of dissolution occurred, the $^{56}$Fe values of the fluid would probably lie closer to those of the original basalt, which would be within $0.1\%$ of the $^{56}$Fe value of terrestrial basalts (Poirtrasson et al., 2004).

Precipitation of aqueous Fe in the Navajo Sandstone probably occurred when reduced groundwaters intersected O$_2$-bearing fluids, and the extent of isotopic fractionation was dependent upon the extent of precipitation that occurred in an open system. Two of the 15 concretions analyzed have $^{56}$Fe $> 0$, and partial precipitation must have occurred in an open fluid-flow system. However, 13 of the 15 concretions have $^{56}$Fe $< 0$, which indicates that complete or near-complete precipitation occurred, largely preserving the low $^{56}$Fe values of the fluid. Isotopic zonation within individual concretions would be expected in both terrestrial and Martian systems if local changes (centimeter scale) occurred in fluid composition between nuclei during oxidation and precipitation. In the Meridiani Planum system, where the inferred low pH is expected to have produced significant pools of coexisting aqueous Fe(III) and Fe(II) (Tosca et al., 2005), we might expect only partial precipitation to occur, which would tend to produce oxide concretions that had higher $^{56}$Fe values, similar to the few high $^{56}$Fe concretions found in the Navajo Sandstone.

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