Microscale heterogeneity of Fe isotopes in >3.71 Ga banded iron formation from the Isua Greenstone Belt, southwest Greenland

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ABSTRACT

We present Fe isotope compositions for magnetite crystals from >3.7 Ga banded iron formation (BIF) from the Isua Greenstone Belt and younger, spatially related pyrite obtained in situ by secondary ion mass spectrometry (SIMS). Across a distance of several millimeters, individual magnetite crystals of BIF show δ^{56}Fe values up to 2‰, and within single magnetite-rich layers, there is a >2‰ range in δ^{56}Fe. The highest positive δ^{56}Fe values are consistent with those predicted by the equilibrium fractionation factor for oxidation of ferrous to ferric Fe in aqueous solution at a likely Early Archean ocean temperature of ~70 °C, and further suggest that subsequent precipitation of ferric oxides was sufficiently slow that kinetic fractionation effects were minimal. These high values also imply that the supply of oxidant was limited. Heterogeneity in δ^{56}Fe values is attributed to diagenetic reactions occurring in limited-volume pore waters, isolated from the bulk ocean (δ^{56}Fe = 0‰), with development of isotope reservoir effects. Secondary pyrite in BIF and a conglomerate also show a distinct enrichment in heavy Fe isotopes, interpreted as redistribution and/or fractionation during postformational events.

Keywords: Isua Greenstone Belt, BIF, Fe isotopes, secondary ion mass spectrometry, Archean, paleo-oceanography.

INTRODUCTION

Banded iron formation (BIF), a chemical sedimentary rock, occurs intermittently during the Precambrian at a time when Earth experienced profound changes in the composition of the ocean and atmosphere, and major evolutionary steps in the biosphere. The primary mode of formation of BIF, oxidation of soluble ferrous Fe (Fe^{2+}_{aq}) from hydrothermal vents to insoluble ferric Fe precipitates (Fe^{3+}_{ppt}, principally oxides) initially appears simple, but details of this process remain enigmatic despite decades of study (Klein, 2005). At the center of the problem is the relative contribution of various oxidation reactions taking place during primary precipitation, as well as likely postformational reduction reactions. While bacteria are theoretically capable of producing the volume of BIF observed (Konhauser et al., 2005), inorganic mechanisms such as photo-oxidation (Braterman et al., 1983) may also be significant.

Recent rapid developments in the study of Fe isotopes (summarized by Johnson and Beard, 2006) hold out considerable promise for understanding BIF precipitation mechanisms. To date, Fe isotope studies of BIF reveal significant and wide-ranging fractionation that contrasts markedly with minimal, or absent, fractionation observed in the overwhelming majority of igneous, metamorphic, and terrigenous clastic rocks. Bulk-rock δ^{56}Fe values in Late Archean BIF range from –2‰ to +1‰ (e.g., Johnson and Beard, 2006), with oxide layers ranging up to +1.5‰ (Rouxel et al., 2005). A more restricted, and entirely positive, range of δ^{56}Fe values from 0‰ to +1‰ has been recorded in Early Archean amphibolite-facies BIF from the Isua Greenstone Belt and some, possibly related, banded Fe-rich rocks from Akilia Association enclaves in granulite-facies gneisses in the Godthåbsfjord (Dauphas et al., 2004), although there is ongoing debate over the protolith of some of the Akilia rocks (e.g., Fedo et al., 2006).

Despite the large fractionation range observed in these bulk-rock studies, no δ^{56}Fe values have yet been observed in natural samples that approach the predicted equilibrium maximum for the oxidation of Fe^{2+}_{aq} to Fe^{3+}_{aq} of ~+3‰ (Welch et al., 2003), in part because a competing and variable kinetic fractionation of –1‰ to –2‰ may occur during precipitation of Fe^{3+} as oxide or hydroxide (Beard and Johnson, 2004). In order to investigate the possibility that more extreme δ^{56}Fe values might be preserved at a scale of a few tens of micrometers, we report here the Fe isotope compositions of magnetite (Fe_3O_4) from BIF determined by high-spatial-resolution, in situ secondary ion mass spectrometry (SIMS). With a depositional age >3.71 Ga, the variants of BIF from Isua (Dymek and Klein, 1988) discussed in this paper represent the oldest well-preserved chemical sediments on Earth, formed at a time characterized by an anoxic atmosphere (Pavlov and Kasting, 2002), warm oceans (Robert and Chaussidon, 2006), and a nascent, if present at all, biosphere (Rosing, 1999). Therefore, they provide a critical reference point in understanding the behavior and evolution of Fe isotopes and their application to BIF genesis.

GEOLOGICAL SETTING AND SAMPLING

The ca. 3.7–3.8 Ga Isua Greenstone Belt in southwest Greenland is the oldest known succession of volcanic and sedimentary rocks on Earth. The stratigraphy of the belt has been substantially revised in recent years on the basis of new mapping, recognition of widespread metasomatic alteration, and re-evaluation of protolith composition and primary depositional features (Rosing et al., 1996; Appel et al., 1998; Fedo et al., 2001). A kilometer-thick succession of BIF crops out in the northeastern sector of the arcuate belt and forms the main occurrence of BIF at Isua. Meter-scale, more isolated BIF occurrences are found throughout the belt.

To assess the extent and significance of any microscale internal heterogeneity and grain-to-grain variation in Fe isotopes in the Isua BIF, our high-spatial-resolution SIMS study targeted three samples that represent distinct lithologic variants of BIF and two samples containing secondary pyrite (FeS_2). Samples were collected from what is generally considered to be a "low-strain zone" (Appel et al., 1998) relative to adjacent tectonic panels, but even this area has

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been ductilely deformed and metamorphosed at amphibolite facies (Rollinson, 2002) in the Early Archean (Frei et al., 1999). Additionally, we have studied a magnetite-bearing, banded quartz-amphibole-pyroxene rock hosted in 3.81 Ga gneisses (Nutman et al., 1999) ~10 km south of the belt. More detailed sample descriptions are given in the GSA Data Repository.[1]

RESULTS AND DISCUSSION

Fe isotope ratio measurements were carried out in situ on rock chips and on separated pyrites using a CAMECA IMS1270 ion microprobe. Full analytical details and tabulated data are given in the GSA Data Repository. All data are reported relative to the Institute for Reference Materials and Measurement distributed reference material IRMM-014 using the conventional nomenclature, $\delta^{56}Fe$ ($\delta^{56}Fe = [(^{56}Fe/^{54}Fe)_{sample}/(^{56}Fe/^{54}Fe)_{standard} - 1] \times 1000$). External reproducibility on $\delta^{56}Fe$ for standards in each analytical session was typically ±0.2‰ (1σ).

Figure 1A plots Fe isotope data from Isua BIFs and sample 409041. Within each of the three BIF samples, individual magnetite grains record a wide range in $\delta^{56}Fe$. The most isotopically homogeneous sample, IS-02-05, has a total range in $\delta^{56}Fe$ from 1.1‰ to 2.3‰. IS-02-06 and IS-02-08 are considerably more heterogeneous, ranging in $\delta^{56}Fe$ from 0.2‰ to 2.1‰ and –0.8‰ to 1.8‰, respectively. Magnetite grains in sample 409041, a banded quartz-pyroxene rock with amphibole and magnetite, also show a wide range in $\delta^{56}Fe$ from –0.5‰ to 1.8‰. Two analyses on a single grain (analyses 1 and 1b, Table DR2 in the GSA Data Repository) yield a range of almost 1‰, indicating significant subgrain-scale heterogeneity.

Implications of Heterogeneous Fe Isotopes in Magnetite for the Origin of BIF

The range in $\delta^{56}Fe$ of individual magnetite grains within each sample, determined here at the microscale by SIMS, greatly exceeds what can be expected on the basis of analytical uncertainty alone and points to considerable, previously unknown, small-scale heterogeneity. Furthermore, this range is substantially larger than $\delta^{56}Fe$ measurements of bulk magnetite layers in BIF from the Transvaal craton (Johnson et al., 2003), and magnetite-rich shales from the Kaapvaal and Pilbara cratons (Yamaguchi et al., 2005). A significant number of analyzed magnetite grains in our samples have $\delta^{56}Fe$ >1‰, and most are significantly higher than the single whole-rock analysis of Isua BIF published to date ($\delta^{56}Fe$ = 0.64‰ for sample IF-G; Dauphas et al., 2004). In all but one sample (IS-02-05), these high values are complemented by low values and likely bracket bulk-rock values that would be compatible with this previous, positive $\delta^{56}Fe$, measurement. Significantly, the values that we document come from very small areas within single bands, indicating a range of fractionation from within a single depositional "event."

In order to assess the significance of these variations, it is first necessary to consider potential effects of the ca. 3.7 Ga amphibolite-facies metamorphism at temperatures of ~550 °C (Rollinson, 2002). The extent to which isotopic re-equilibration can occur will be controlled by the diffusion rate of Fe in magnetite relative to the proximity of the analyzed spot to a grain boundary. Preservation of considerable heterogeneity in $\delta^{56}Fe$ values, despite analysis in some cases within 20 µm of a grain boundary (Fig. DR7), suggests that wholesale metamorphic re-equilibration has not occurred.

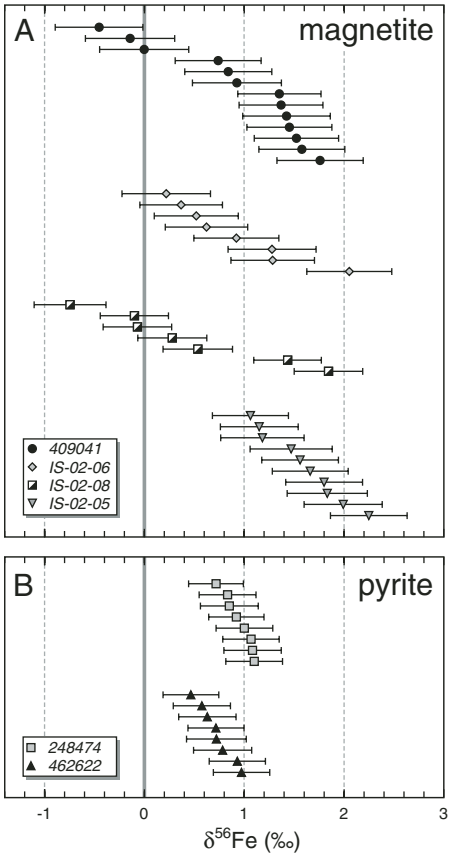

Figure 1. Plot of $\delta^{56}Fe$ (in ‰) obtained from magnetite (A) and pyrite (B) in Isua Greenstone Belt samples. Data are presented in order of increasing $\delta^{56}Fe$ within each sample. Error bars (±2σ) include the propagated external uncertainty from standard measurements in each session.

Formation of magnetite in BIF from dissolved ferrous Fe is a complex, multistage process involving a variety of intermediate primary and diagenetic species including $Fe(OH)_2$, $Fe(OH)_3$, and possibly hydromagnetite ($Fe_3O_4 \cdot nH_2O$) (Klein, 2005). Understanding the significance of both the high $\delta^{56}Fe$ values and their microscale heterogeneity requires consideration of the fractionation factors involved at each stage. Furthermore, given a possibly warmer Early Archean ocean (e.g., ~70 °C; Robert and Chaussidon, 2006), temperature dependence of fractionation factors must also be taken into account. The role of these fractionation factors is investigated in relation to our Isua data set in Figure 2.

Regardless of whether the mechanism is biogenic or abiogenic, initial oxidation of Fe^{2+}_{aq} to Fe^{3+}_{aq} is accompanied by an equilibrium fractionation that increases $\delta^{56}Fe$ of the precipitated ferric species (Fe^{3+}_{ppt}) by +2.9‰ at 22 °C (Beard and Johnson, 2004). Figure 2 shows the temperature dependence of this equilibrium fractionation, calculated from experimental observations and assuming an oceanic Fe^{2+}_{aq} reservoir with $\delta^{56}Fe$ = 0‰ (Yamaguchi et al., 2005). At 70 °C a $\delta^{56}Fe$ value of ~2‰ is obtained. Formation of magnetite from Fe^{3+}_{ppt} further requires addition of Fe^{2+}. If this Fe^{2+} comes directly from the oceanic reservoir with $\delta^{56}Fe$ = 0‰, expected magnetite $\delta^{56}Fe$ values should then lie on the model equilibrium magnetite curve in Figure 2, which predicts a value of ~1.4‰ at 70 °C. Oxi-

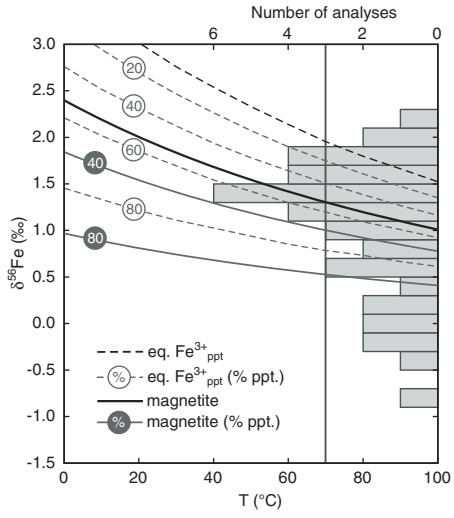

Figure 2. Temperature dependence of $\delta^{56}Fe$ for Fe^{3+}_{ppt} derived from equilibrium fractionation for Fe^{2+}_{aq} oxidation to Fe^{3+}_{aq} (dashed black line) and magnetite (solid black line) modeled by stoichiometric addition of oceanic ($\delta^{56}Fe$ = 0‰) Fe^{2+}_{aq}; negligible precipitation is assumed. Light gray lines show these products for different percentage precipitation of oxide. Magnetite $\delta^{56}Fe$ values determined in this study are shown as a histogram (with *n* values on the upper *x* axis). ppt.—precipitate.

[1]GSA Data Repository item 2007184, Tables DR1–DR3 and Figures DR1–DR6 (sample descriptions, analytical methods, standard characterization, and Fe isotope results), is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

dation of Fe^{2+}_{aq} to Fe^{3+}_{aq} is, however, only part of the process. In order to explain experimental data (Bullen et al., 2001) that did not show the maximum fractionation expected from equilibrium processes, Beard and Johnson (2004) proposed that formation of Fe^{3+} precipitates from Fe^{3+}_{aq} may involve a kinetic fractionation of up to ~2‰ towards lighter $\delta^{56}Fe$ values at room temperature. This effect depends largely on the rate of precipitation and will be minimal for exceedingly low rates, although its magnitude in natural systems is largely unknown. Recent experimental studies have demonstrated $\delta^{56}Fe$ for Fe^{3+}_{ppt} approaching values expected from equilibrium fractionation alone (Balci et al., 2006), but these experiments were conducted in acidic solutions that may be inappropriate analogues for a possibly near-neutral (Morse and Mackenzie, 1998) Early Archean ocean. Nonetheless, our data, the highest $\delta^{56}Fe$ values of which approximate predicted equilibrium values at 70 °C, may well indicate very slow precipitation of ferric oxides and hence negligible kinetic effects.

It is also important to note that the equilibrium fractionation curve in Figure 2 a priori assumes minimal formation of Fe^{3+}_{ppt} that would result from a limited supply of oxidant. The effects of oxidant supply are illustrated in Figure 2 by modeling of Fe^{3+}_{ppt} and derived magnetite (again assuming addition of Fe^{2+} with $\delta^{56}Fe = 0$‰) for different percentages of oxide formation. From this modeling, it is clear that at increased levels of precipitation, it becomes more difficult to explain the high $\delta^{56}Fe$ values in our data set. A low level of oxidant available during precipitation of the Isua BIF suggests that the ocean at this time was undersaturated in dissolved oxygen, consistent with inferences of very low atmospheric oxygen from observed mass-independent fractionation of sulfur isotopes (e.g., Whitehouse et al., 2005).

Direct precipitation is generally not considered to be a viable mechanism for producing magnetite in BIF, although hydromagnetite or a "very magnetite-like material" is considered by Klein (2005) as a potential precursor to magnetite now seen in BIFs. Estimation of the Fe^{2+}_{aq}-magnetite fractionation factors at 70 °C using the Fe^{2+}_{aq} β factor of Anbar et al. (2005) combined with the re-evaluated magnetite β factor of Polyakov et al. (2007) yields –0.3‰, a value that will have only a modest effect on making heavier magnetite, while a similarly recalculated Fe^{3+}_{aq}-magnetite fractionation factor of +1.7‰ at 70 °C actually predicts isotopically lighter magnetite (cf. Anbar et al., 2005). The larger, biologically mediated Fe^{2+}_{aq}-magnetite fractionation factor of –1.3‰ determined experimentally at 22 °C (Johnson et al., 2005) could explain some of the positive values, but it is unclear how and to what extent, if at all, biological fractionation pathways operated at Isua (Rosing, 1999; Rosing and Frei, 2004; cf. Fedo et al., 2006).

In addition to the highly fractionated $\delta^{56}Fe$ values, the small-scale heterogeneity represents an intriguing aspect of our data. Accepting that this is original and unlikely to have resulted from later metamorphic disturbance as discussed earlier, we propose that diagenetic reactions in pore water isolated from the bulk $\delta^{56}Fe = 0$‰ oceanic reservoir may be an effective way to produce the heterogeneous values observed in the Isua BIF magnetite via isotopic reservoir effects. The fluid-magnetite fractionation factors recalculated above (Fe^{2+}_{aq} or Fe^{3+}_{aq}) may also be of importance here.

Fractionated Fe Isotopes in Secondary Mineralization

The pyrite samples selected permit comparison of Fe isotope fractionation in pyrites hosted in very different lithologies, namely a BIF and a volcaniclastic sediment. Our analyses of the Fe isotope composition of pyrite in BIF sample 248474 are shown in Figure 1B and indicate both homogeneity and a clear positive Fe isotope fractionation (weighted mean $\delta^{56}Fe = 0.95 \pm 0.1$‰, MSWD = 0.44, n = 8), in excellent agreement with a conventional determination (Table DR1). Because the pyrite is clearly crosscutting, and consequently of secondary origin, this fractionated signature cannot be related to any primary depositional signal from crystallization of the BIF from seawater. In accord with the sulfur isotope evidence for remobilization (Whitehouse et al., 2005), we interpret the Fe isotopes of the pyrite to represent largely recycled Fe from the adjacent BIF, which carries a positively fractionated Fe isotopic composition (reported above; Dauphas et al., 2004). An alternative interpretation is that the Fe was sourced from a relatively unfractionated reservoir outside the BIF and obtained its present isotopic composition during mineralization and/or hydrothermal alteration. It is worth noting, however, that the homogeneity of the pyrite contrasts with the range in compositions recorded in both skarn mineralization (Graham et al., 2004) and hydrothermal alteration (Horn et al., 2006).

Analysis of euhedral and subhedral metamorphic pyrite crystals removed from conglomerate sample 462622 reveal a homogeneous and significantly positive Fe isotope composition (Fig. 1B; weighted mean $\delta^{56}Fe = 0.72 \pm 0.15$‰, 95% confidence, MSWD = 1.5, n = 8). Possible iron source reservoirs include the host conglomerate, abundant mafic volcanic rocks nearby, and adjacent BIF. The former two reservoirs are expected to be unfractionated (Johnson and Beard, 2006) and therefore not suitable, whereas adjacent BIF is positively fractionated and much more likely as a source. If BIF is the source, it indicates transport of isotopically fractionated Fe in solution across lithologic boundaries spanning distances from meters to potentially hundreds of meters. The microscale homogeneity of the pyrite Fe isotope compositions stands in marked contrast to the heterogeneity of BIF magnetite and likely reflects isotopic homogenization during fluid transport. We cautiously reject the notion of wholesale isotopic resetting during metamorphism because of our observation of preserved heterogeneity of Fe isotopes in magnetite.

In both cases, the distinctly positive values for these secondary pyrites stand in marked contrast with other Fe isotope studies of both Precambrian (Rouxel et al., 2005) and modern sedimentary pyrite (Severmann et al., 2006), which show negative $\delta^{56}Fe$ values, the likely result of biologically mediated processes. In contrast to these studies, our pyrite data lend some support to experimentally predicted Fe isotope compositions that should be positive (e.g., Polyakov et al., 2007), and might also indicate an absence of biological activity in the form of bacterial sulfate and/or Fe^{3+} reducers. Given the nearby extensive reservoir of positive $\delta^{56}Fe$ in the BIF, however, we favor the remobilization model presented above.

CONCLUSIONS

Our in situ SIMS study reveals Fe isotope compositions of magnetite crystals in >3.7 Ga BIF from the Isua Greenstone Belt that are considerably heavier than previously recorded by bulk analysis. At the same time, these data record previously undocumented heterogeneity on a submillimeter scale within individual magnetite layers that have been preserved despite metamorphism. When the effects of higher Early Archean ocean temperature are considered, the highest measured $\delta^{56}Fe$ values of ~2‰ approach values predicted by equilibrium fractionation factors alone, suggesting very slow precipitation of ferric oxides with minimal kinetic fractionation, and limited availability of oxidant. Microscale heterogeneity probably results from diagenetic equilibration of magnetite with restricted-volume pore waters that acquired variable $\delta^{56}Fe$ by isotopic reservoir effects. Recalculation of fractionation factors suggests that magnetite-fluid (both Fe^{2+}_{aq} and Fe^{3+}_{aq}) interactions may be relevant, but their role in natural systems requires further investigation.

Similar to the BIF, secondary pyrite crystals in BIF and conglomerate both show a positive fractionation of Fe isotopes. Their unambiguous secondary origin indicates that their Fe isotope composition cannot reflect primary crystallization from either seawater or magma, but instead is likely the result of the mobility and redistribution of previously fractionated iron from a BIF reservoir and/or fractionation during hydrothermal processes.

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Notes