Fe, C, and O isotope compositions of banded iron formation carbonates demonstrate a major role for dissimilatory iron reduction in ~2.5 Ga marine environments

Adriana Heimann a,b,c,⁎, Clark M. Johnson a,b, Brian L. Beard a,b, John W. Valley a,b, Eric E. Roden a,b, Michael J. Spicuzza a,b, Nicolas J. Beukes d

A R T I C L E  I N F O

Article history:
Received 11 August 2009
Received in revised form 8 February 2010
Accepted 9 February 2010
Available online 1 April 2010

Editor: R.D. van der Hilst

Keywords:
Fe isotopes
BIF
Kuruman carbonates
Archean/Paleoproterozoic

A B S T R A C T

Combined Fe, C, and O isotope measurements of ~2.5 Ga banded iron formation (BIF) carbonates from the Kuruman Iron Formation and underlying BIF and platform Ca–Mg carbonates of the Gamboaan Formation, South Africa, constrain the biologic and abiologic formation pathways in these extensive BIF deposits. Vertical intervals of up to 100 m were sampled in three cores that cover a lateral extent of ~250 km. BIF Fe carbonates have significant Fe isotope variability (δ56Fe = +1 to −1‰) and relatively low δ13C (down to −12‰) and δ18O values (δ18O = +21‰). In contrast, Gamboaan and stratigraphically-equivalent Campbellrand Ca–Mg carbonates have near-zero δ13C values and higher δ18O values. These findings argue against siderite precipitation from seawater as the origin of BIF Fe-rich carbonates. Instead, the C, O, and Fe isotope compositions of BIF Fe carbonates reflect authigenic pathways of formation in the sedimentary pile prior to lithification, where microbial dissimilatory iron reduction (DIR) was the major process that controlled the C, O, and Fe isotope compositions of siderite. Isotope mass-balance reactions indicate that the low-δ13C and low-δ18O values of BIF siderite, relative to those expected for precipitation from seawater, reflect inheritance of C and O isotope compositions of precursor organic carbon and ferric hydroxide that were generated in the photic zone and deposited on the seafloor. Carbon–Fe isotope relations suggest that BIF Fe carbonates formed through two end-member pathways: low-δ13C, low-δ18O Fe carbonates formed from remineralized, low-δ56Fe aqueous Fe3+ produced by partial DIR of iron oxide, whereas low-δ13C, high-δ56Fe Fe carbonates formed by near-complete DIR of high-δ56Fe iron oxides that were residual from prior partial DIR. An important observation is the common occurrence of iron oxide inclusions in the high-δ56Fe siderite, supporting a model where such compositions reflect DIR “in place” in the soft sediment. In contrast, the isotopic composition of low-Fe carbonates in limestone/dolomite may constitute a record of seawater environments, although our petrographic studies indicate that the presence of pyrite in most low-Fe carbonates may influence the Fe isotope compositions. The combined Fe, C, and O isotope data from Kuruman BIF carbonates indicate that BIF siderites that have negative, near-zero, or positive δ56Fe values may all record biological Fe cycling, where the range in δ56Fe values records differential Fe mobilization via DIR in the sediment prior to lithification. Our results demonstrate that the inventory of low-δ56Fe marine sedimentary rocks of Neoarchean to Paleoproterozoic age, although impressive in volume, may represent only a minimum of the total inventory of Fe that was cycled by bacteria.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Interpretations of the isotopic compositions of ancient marine sedimentary rocks often divide into two groups; one, where these compositions are taken to reflect direct proxies for ancient seawater, and a second, where early authigenic mineral formation and soft-sediment diagenesis are thought to control the measured isotopic compositions. An example of these contrasting interpretations can be found in the Fe isotope record of Archean and Proterozoic marine sedimentary rocks. Rouxel et al. (2005) and Anbar and Rouxel (2007) interpret the Fe isotope compositions to directly reflect those of ancient seawater and call upon abiologic processes involving extensive precipitation of iron oxides to produce the negative δ56Fe excursion in rocks of Neoarchean to Paleoproterozoic age, whereas Yamaguchi et al. (2005) and Johnson et al. (2008a,b) do not generally interpret the Fe isotope compositions to be a direct proxy for seawater and instead favor microbial iron cycling in the soft sediment prior to lithification as an

⁎ Corresponding author. East Carolina University, Department of Geological Sciences, 101 Graham Building, Greenville, NC 27858, USA. Tel.: +1 252 328 5206; fax: +1 252 328 4391.
E-mail address: heimanna@ecu.edu (A. Heimann).

0012-821X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2010.02.015
explanation for the Fe isotope variability. This debate echo’s one that has existed for several decades in the literature on C isotopes, where the highly negative δ13C values for iron formation carbonates have been interpreted by some studies to record microbial oxidation of organic matter (Becker and Clayton, 1972; Baur et al., 1985; Beukes and Gutzmer, 2008; Fischer et al., 2009), whereas other studies called upon an ocean that was stratified in C isotopic compositions to explain the data (Beukes et al., 1990; Winter and Knauth, 1992; Klein, 2005).

Studies of iron formations, including banded iron formations (BIFs), provide an important test of the different interpretations for the major Fe isotope excursion towards negative Fe isotope compositions (Fig. 1) in ~2.7 to 2.4 Ga marine sedimentary rocks, because Fe-rich rocks place important mass-balance constraints on processes that may fractionate Fe isotopes. Periods of BIF deposition represent times when marine Fe fluxes were very high, including very high rates of Fe-rich sediment deposition, dramatically different than those of the modern marine iron cycle (Trendall, 2002; Trendall et al., 2004; Klein, 2005). Possible Fe pathways for producing the large inventories of Fe3+ in BIFs include oxidation of hydrothermal or riverine Fe2+ through reaction with O2 produced by oxygenic photosynthesis (e.g., Cloud, 1968), or Fe3+ oxidation that was metabolically coupled to reduction of CO2 (Konhauser et al., 2005, Rouxel et al., 2005, Archer and Vance, 2006, and Johnson et al., 2008a). The Kuruman BIF was subjected to a very low degree of deformation and metamorphism (T = 110–170 °C, P < 2 kbar; Miyano and Beukes, 1984). Beukes et al. (1990) and Klein and Beukes (1989) defined siderite-, magnetite-, and Fe silicate-rich BIF facies, all of which contain variable amounts of chert. The samples analyzed in this study came exclusively from the siderite-rich facies layers of the Kuruman BIF; from three stratigraphically-equivalent drill cores, DI-1, AD-5, and WB-98 (Fig. 2; Klein and Beukes, 1989). The sequence of rocks records a transition from limestone/dolomite platform carbonates of the lower Gamohaan Formation through the BIFs of the upper Gamohaan Formation (Tsingem Member or “Bruno’s BIF”; Beukes and Gutzmer, 2008), to the Fe carbonate-rich BIF of the Kuruman Iron Formation (Klein and Beukes, 1989). The BIF package was deposited over a period of 1.08 to 3.25 million years, based on calculated sedimentation rates for the Kuruman BIF (e.g., Allmenn and Nelson, 1998). The cores studied here represent BIF deposition in the shallower parts of the Transvaal basin (Beukes et al., 1990; Beukes and Gutzmer, 2008).

One hundred samples of carbonate laminations were obtained from the Kuruman BIF and underlying Gamohaan BIF, limestone, and dolomite, following detailed petrographic study of a larger sample set. We emphasize that milligram-size samples were analyzed because it was important to maintain a small sample size in these finely laminated sediments. Major-element chemistry and modal mineralogy were determined by electron microprobe and scanning electron microscope (SEM) analysis. Iron, carbon, and oxygen isotope compositions were determined using standard methods, and reported as δ56Fe, δ13C, and δ18O values, respectively. See the Appendix for details.

3. Petrography and mineral chemistry

Zones of Fe-rich carbonate commonly coexist with chert, or are interlaminated with carbonate-bearing chert. Most BIF carbonate laminations contain siderite (FeCO3) and ankerite ([Ca,Fe]MgCO3) in different proportions (Tables S1, S3). Siderite is, in most cases, very fine-grained (~5 μm), but also occurs as fine-grained individual subhedral rhombohedral crystals (~10 μm in size). Ankerite is coarser grained (~30 μm) than siderite and contains abundant siderite inclusions, indicating that it formed after siderite (Fig. 3A, B). We found trace amounts of minute (~1 μm) Fe-oxide inclusions in ankerite and siderite, identified as hematite (Fe2O3) based on petrographic analysis (red color of larger crystals under plane-polarized light, anisotropic under crossed-polarized light) and energy dispersive spectrometry (EDS) spectra (Fig. 3A, B; Fig. S1); the common occurrence of hematite inclusions in siderite forms an important clue to Fe pathways, as will be discussed below. In addition, preliminary electron back-scattered diffraction (EBSD) and transmission electron microscope (TEM) analysis shows that some of the iron oxide inclusions are nano-size magnetite. Only trace amounts of pyrite, stilpnolomane, and greenalite are present in a small number of the samples selected for study (Fig. 3C; Table S1). Limestone and dolomite from the Gamohaan Formation commonly contain coexisting calcite and ferroan dolomite (Fig. 3D). Although areas that contained Fe-bearing phases other than carbonate were avoided, pyrite is a common inclusion in a number of samples (Fig. 3D). The
compositions of coexisting ankerite and siderite in BIFs, and calcite and ferroan dolomite in limestone and dolomite, are shown in Fig. 4 (Table S3). Based on image analysis and mineral compositions, the Fe budget in siderite–ankerite samples and in most calcite/dolomite samples is dominated by the carbonate (Fig. S3).

4. Isotopic compositions

Oxygen ($\delta^{18}$O) and carbon ($\delta^{13}$C) isotopic compositions for BIF carbonate vary from +19 to +21‰, SMOW and −2.6 to −12‰, PDB, respectively, and overlap the range measured for siderite-facies BIF in the Gamohaan Formation and Kuruman Stratigraphy (Beukes et al., 1990; Beukes and Klein, 1990; Kaufman, 1996), and Fischer et al. (2009). Oxygen isotopic compositions for iron carbonates in oxide- and Fe silicate-facies BIFs of the Gamohaan and Kuruman formations determined by Beukes et al. (1990), Beukes and Klein (1990), and Kaufman (1996), however, extend to significantly lower $\delta^{18}$O values, as low as +16‰, and these facies also tend to have the lowest $\delta^{13}$C values (Fig. 5A). In contrast, $\delta^{18}$O values for Ca–Mg carbonates in the Gamohaan Formation (Beukes et al., 1990; Beukes and Klein, 1990; Kaufman, 1996) and stratigraphically-equivalent Campbellrand platform rocks (Fischer et al., 2009) have significantly higher $\delta^{18}$O values, generally between +21 and +24‰, and $\delta^{13}$C values cluster around −1.0‰ (Fig. 5A; Table S1 and Figs. S4–S8).

Iron isotope compositions ($\delta^{56}$Fe) in all the analyzed carbonates range from +1.0 to −1.7‰ (Fig. 5B), and overlap those determined by Johnson et al. (2003). The range in Fe isotope compositions measured here also overlaps that determined for Campbellrand Ca–Mg carbonates by von Blanckenburg et al. (2008). In contrast to the positive correlation between $\delta^{13}$C and $\delta^{18}$O for the BIF and Ca–Mg carbonates (Fig. 5B), there are, however, important relations between $\delta^{56}$Fe values and carbonate composition and the nature of mineral inclusions (see Fig. 5B caption). Siderite–ankerite samples that contain magnetite and/or hematite inclusions are restricted to samples that have $\delta^{56}$Fe $<0$‰, and ~2/3 of the siderites that have positive $\delta^{56}$Fe
values contain magnetite and/or hematite inclusions (Fig. 5B). It is important to note that despite the common occurrence of Fe-oxide inclusions in the $\delta^{56}$Fe$_{\text{N}}^{0}$‰ siderite, in no case do the inclusions exert a significant effect on the measured Fe isotope composition of these Fe-rich carbonates (Fig. S3B). A group of siderite–ankerite samples that have $\delta^{56}$Fe values $\sim -0.8$‰ contain minor pyrite inclusions (Fig. 5A), although the proportion of Fe contained in pyrite, relative to that in siderite, is very low, only as high as 0.05% (Fig. S3A). About half of the calcite/dolomite samples analyzed contain pyrite inclusions, and, given the low Fe contents of these carbonates, pyrite may comprise up to 50% of the Fe budget of the material sampled (Fig. S3A), and therefore may have influenced the measured $\delta^{56}$Fe values.

5. Discussion

We first discuss the C, O, and Fe isotope compositions measured in Fe-rich BIF and Ca–Mg carbonates in terms of isotopic equilibrium or disequilibrium with ancient seawater, as evaluated in light of theoretical and experimental isotopic fractionation factors. Based on this evaluation, we next discuss the possible reaction pathways associated with DIR, which predict specific C, O, and Fe isotope compositions distinct from those that would be produced by precipitation from seawater. Finally, we discuss the internal re-distribution of Fe that may occur in the soft sediment during authigenic mineral formation by DIR that can explain the range in measured Fe isotope compositions.
carbonates analyzed in these rocks (calcite/dolomite, ankerite, and siderite) cannot be explained by equilibrium O isotope fractionation factors if they precipitated from a common fluid. The contrast in the Δ18Ocalcite-water (Kim and O’Neil, 1997) and Δ18Osiderite-siderite (Carother et al., 1998) fractionation factors at room temperature indicates that siderite should be ~4‰ higher in δ18O than calcite if these minerals precipitated from a common fluid. In contrast, the δ18O values for siderite in siderite-facies BIF are, on average, ~2 to 3‰ lower than temporally equivalent Ca–Mg carbonates of the Campbellrand–Kuru-
man sequence, and the contrast is even larger, up to 9‰, when considering siderite in oxide-facies BIF (Fig. 5A); assuming a common fluid, such contrasts would require precipitation temperatures ~100 °C higher for siderite. The contrast in δ18O values cannot be explained through metamorphic re-equilibration, as indicated by independent evidence that metamorphism in the rocks studied did not exceed 170 °C (Miyano and Beukes, 1984), and the relatively low δ18O values for siderite are unlikely to reflect recrystallization through interaction with meteoric water, given the petrographic evidence for early primary textures in siderite and the fact that interbedded cherts have high δ18O values (Kaufman, 1996). The majority of BIF siderites analyzed in this study do not have δ56Fe values that are expected to reflect those in equilibrium with Neoarchean or Paleoproterozoic seawater (Fig. 5B), a conclusion reached by Johnson et al. (2008a) in their study of siderite from the broadly correlative Dales Gorge Member of the Brockman Iron Formation, Australia. Moreover, the small-scale Fe isotope variability measured millimeters to centimeters apart also suggests that the BIF Fe carbonates could not have precipitated in isotopic equilibrium with seawater, given the long residence time expected for an Fe2+-rich ocean (Johnson et al., 2008a). Neoarchean or Paleoproterozoic seawater that had high concentrations of Fe2+ probably had δ56Fe values between ~0.2 and 0.0‰ (Yamaguchi et al., 2005; Johnson et al., 2008b). As noted by Johnson et al. (2008a), Fe-poor regions of the oceans, such as the photic zone, could have had significantly negative δ56Fe values, but siderite would be an unlikely precipitate from such seawater. Based on these estimates for Fe-rich seawater, and the Fe2+-siderite 56Fe/54Fe fractionation factor of 0.5% of Wiesli et al. (2004), siderite that precipitated in equilibrium with Neoarchean or Paleoproterozoic seawater would be expected to have a δ56Fe value between ~0.5 and ~0.7‰. The conclusion that BIF siderites that have δ56Fe values > ~0.5‰ cannot reflect precipitation from seawater holds if alternative Fe2+–siderite δ56Fe/54Fe fractionation factors are used instead of that of Wiesli et al. (2004); combining the calculated δ56Fe factors available for Fe2+–siderite fractionations that are 1.1 to 2.2‰ higher than the experimentally determined fractionation of Wiesli et al. (2004). These calculations make it even more difficult to explain the δ56Fe values for BIF siderite that are > ~0.5‰ through equilibrium with seawater.

5.1. Isotopic disequilibrium with seawater

Virtually none of the siderites analyzed in this study have C, O, and Fe isotope compositions that match those expected for equilibrium precipitation from a common Neoarchean or Paleoproterozoic seawater (Fig. 5A, B). Only the calcite and dolomite samples have the near-zero δ13C values that are common for Ca–Mg carbonates of this age (Shields and Veizer, 2002), which are interpreted to reflect direct precipitation from seawater. Because the fractionation factor for carbon isotopes between siderite and calcite (Δ13C siderite–calcite) is ~−0.5‰ at room temperature (Jimenez-Lopez et al., 2001; Jimenez-Lopez and Romanek, 2004), siderite and calcite should have similar δ13C values if they precipitated in equilibrium with DIC from a common seawater. The differences in δ18O values among the different
1990), could be interpreted to reflect a shift to negative δ13C values for dissolved inorganic carbon (DIC) during deepening of the basin. A closer inspection of the stratigraphic and isotopic profiles, however, shows this apparent trend to be mineral-dependent, where siderite, which has the most negative δ13C values of the various carbonates, increases in abundance up section. As noted above, the mineralogic effect on 13C/12C fractions is small for carbonates, and therefore these observations are inconsistent with a water column that was stratified in δ13C values. Recent work by Fischer et al. (2009) documented no systematic difference in δ13C values for shallow- and deep-water carbonates in similar-age samples from the Campbellrand–Kuruman platform, where δ13C values of Neoarchean or Paleoproterozoic seawater were estimated to lie between −2 and 0‰. Based on C-flux modeling, Fischer et al. (2009) noted that large vertical δ13C gradients in ancient seawater would suggest very high levels of productivity, which seems unlikely at ~2.5 Ga. We conclude, therefore, in agreement with current models for BIF formation (e.g., Beukes and Gutzmer, 2008), that the negative δ13C values for Fe-rich BIF carbonates require other C sources in addition to DIC from seawater, and therefore cannot reflect seawater stratification in C isotope compositions. A stratified ocean cannot explain the up to 9‰ range in δ18O values for BIF carbonates (Fig. 5A). The maximum δ18O gradient in modern restricted basins such as the Black Sea is ~4‰, where the lowest δ18O values are found in surface waters, reflecting local meteoric input (e.g., Swart, 1991). Assuming an analogous relation to a Kuruman–Campbellrand restricted basin, the shallow water Ca–Mg carbonates would be expected to have δ18O values lower than the deeper water, Fe-rich carbonates, opposite to the observed trends (Fig. 5). We stress that although there remains uncertainty in the paleotemperatures and O isotope compositions of Precambrian seawater (e.g., Knauth, 2005; Kasting et al., 2006), the relative trends in δ18O values discussed here do not depend upon knowledge of the absolute δ18O values or temperature of ancient seawater; we conclude, therefore, that the O, and C, isotope compositions of ankerite and siderite from the Kuruman BIF do not reflect direct formation from seawater, although the Ca–Mg carbonates appear likely to have formed by precipitation from seawater.

5.2. Biologic pathways for BIF siderite formation

If the C, O, and Fe isotope compositions for the BIF siderites studied here cannot be explained by direct precipitation from seawater, even from a stratified water column or restricted basin, we turn to authigenic and early diagenetic processes in the soft sediment prior to lithification as an explanation of the data. Most models for BIF formation call upon Fe3+ oxidation and formation of ferric iron precipitates in the shallow oceans (e.g., Beukes et al., 1990; Klein, 2005). Oxidation of Fe2+ may occur indirectly by O2 generated by photosynthesis:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2
\]  
(1)

and

\[
4\text{Fe}^{3+} + \text{O}_2 + 8\text{OH}^- + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3.
\]  
(2)

Eqs. (1) and (2) provide a flux of 1 mol of organic carbon (CH2O) for every 4 mol of iron oxide (Fe(OH)3) to the seafloor. Oxidation of hydrothermal Fe2+ may also occur by anaerobic phototrophy (e.g., Kappler et al., 2005):

\[
4\text{Fe}^{3+} + \text{CO}_2 + 11\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + 8\text{H}.
\]  
(3)

which also provides a 1:4 flux of CH2O and Fe(OH)3 to the seafloor. A third oxidation pathway has been discussed in the literature, UV photo-oxidation (e.g., Cairns-Smith, 1978), although this has been recently shown to be unlikely in natural seawater compositions (Konhauser et al., 2007).

A flux of reactive iron oxide and organic carbon to the seafloor in Neoarchean oceans that had generally low levels of dissimilatory sulfate reduction (DSR) would have provided conditions highly favorable to DSR (Johnson et al., 2008b). Under conditions of complete iron oxide reduction, two sources of C are required for siderite formation:

\[
4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + 3\text{HCO}_3^- \rightarrow 4\text{FeCO}_3 + 3\text{OH}^- + 7\text{H}_2\text{O}.
\]  
(4)

The most abundant source of HCO3– would come from seawater infiltration into the soft sediment, below the seawater/sediment interface. If HCO3– is not present in excess, complete reduction will produce Fe3+ in addition to siderite:

\[
4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + 2\text{HCO}_3^- \rightarrow 3\text{FeCO}_3 + 2\text{Fe}_3^{2+} + 5\text{OH}^- + 6\text{H}_2\text{O}.
\]  
(5)

If no external source of HCO3– is available, complete reduction may be written as:

\[
4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + \text{HCO}_3^- \rightarrow 2\text{FeCO}_3 + 2\text{Fe}_3^{2+} + 6\text{OH}^- + 4\text{H}_2\text{O}.
\]  
(6)

If excess Fe(OH)3 is available relative to CH2O, the excess Fe3+ produced in Eq. (7) may result in magnetite formation:

\[
3\text{Fe}_3^{2+} + 6\text{OH}^- + 6\text{Fe(OH)}_3 \rightarrow 3\text{Fe}_3\text{O}_4 + 12\text{H}_2\text{O}.
\]  
(8)

Similar reactions may be written for magnetite formation accompanying Eqs. (5) and (6).

The stoichiometries of Eqs. (4)–(7) predict specific C, O, and Fe isotope variations for siderite that are distinct from those produced by precipitation from seawater (Table 1). We assume organic carbon (CH2O) input to the seafloor had a δ13C value of −30‰, based on the average δ13C value for organic carbon in the 2.5 Ga Campbellrand–Kuruman carbonates (Beukes et al., 1990; Kaufman, 1996; Fischer et al., 2009). The isotopic composition of DIC (HCO3–) in seawater is assumed to have a δ13C value of 0‰, where no vertical gradient existed in the water column, based on the results of Fischer et al. (2009). For complete Fe(OH)3 reduction and complete utilization of organic carbon with no production of excess Fe3+ (Eq. (4)), the lowest possible δ13C value is −7.5‰ for siderite whose Fe has been entirely processed by DIR. The majority of δ13C values for siderite in siderite-facies BIF scatter about the δ13C value predicted by Eq. (4), consistent with the large proportion of Fe carbonate produced by Eq. (4) relative to other Fe products. The O isotope compositions of siderite produced by DIR are expected to deviate strongly from those produced by precipitation from seawater, where decreasing δ18O values will accompany decreasing δ13C values, using the constraints imposed by Eqs. (4) through (7) (Table 1). We illustrate two relations between δ18O and δ13C for siderite produced by DIR based on two assumed δ18O values for Neoarchean and Paleoproterozoic seawater. One set of calculations assumes a seawater δ18O of −1‰, essentially a modern, ice-free ocean value (Muehlenbachs, 1998), and a second set assumes a δ13C value of −4‰, a conservative alternative value that lies midway between that of modern seawater and that predicted by Kasting et al. (2006) for seawater at ~2.5 Ga. The decreasing δ18O values for siderite produced by Eqs. (4) through (7) reflect an increasing contribution of O from the precursor Fe(OH)3 produced in the photic zone (Table 1), using the δ18O of hydroxide–water fractionation factors of ~1% of Bao and Koch (1999) and Bao et al. (2000). The δ13C–δ18O relations predicted by Eqs. (4) through (7), when a modest range in possible δ18O values for seawater is considered, encompass most of the data for BIF siderite in the current and previous studies (Fig. 5A), and predict that the lowest δ13C and δ18O values for siderite should occur in oxide- and Fe silicate-facies BIF, where excess
The very low organic carbon contents of BIFs, particularly in oxide-facies BIFs (e.g., Klein, 2005), or to support metamorphic formation of siderite or magnetite through reaction of organic carbon and iron oxides (e.g., Perry et al., 1973). Alternatively, the low organic carbon contents are consistent with a major role for DIR (together with later Fe mineral transformations of marine sediments that record microbial C and Fe cycling, and DIR predicts that organic carbon contents should be correlated with δ13C values for sidersite in BIFs (Fig. S9), a relation that cannot be explained by abiogenic reactions of organic carbon and iron oxide. Indeed, the fact that the lowest organic carbon contents (and lowest δ13C values) are found in oxide-facies BIFs is exactly that predicted by DIR.

The range in Fe isotope compositions permitted by the model in Table 1 is very restricted because complete reduction of Fe(OH)3 is assumed. The photic zone produced Fe(OH)3 is assumed to have a δ56Fe value of 0‰ and δ18Ovalue of 0‰, which would reflect complete or near-complete oxidation of hydrothermal Fe2+ via the pathways described by Eqs. (1) through (3), assuming a near-zero δ56Fe value for hydrothermal Fe2+ (Johnson et al., 2008b). Near-zero δ56Fe values for Fe(OH)3 would also be expected for detrital iron oxide/hydroxides (Beard et al., 2003b; Yamaguchi et al., 2005). Partial oxidation of hydrothermal Fe2+ by any of the pathways described by Eqs. (1) through (3) would produce positive δ56Fe values for Fe(OH)3, most likely between ~0 and ~+1‰ (Bullen et al., 2001; Beard and Johnson, 2004; Croal et al., 2004), and this scenario would produce higher δ56Fe values for siderite than those listed in Table 1. The slightly negative δ56Fe values for siderite predicted by Eqs. (5) through (7) reflect isotopic equilibration between FeCO3 and Fe2+, using the δFe/δFe fractionation factor from Wiesli et al. (2004) and the mass-balance constraints imposed by the stoichiometry of the equations. The negative δ56Fe values measured for siderite in the current study cannot be explained by complete reduction by DIR, nor can siderite that has positive δ56Fe values be explained by complete reduction by DIR unless the precursor Fe(OH)3 had positive δ56Fe values, as noted above.

#### Table 1

| Fe–O isotope mass-balance reaction pathways for siderite formation via DIR. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Eq. (4)         | 4Fe(OH)3 + CH2O + 3HCO3 → 4FeCO3 + 3OH– + 7H2O | δ13C (‰) | 0.00          | δ18O (‰) | 0.00          |
| δ56Fe (‰)      | 0.00            | δ18O (‰) | 0.00          | δ56Fe (‰) | 0.00          |
| δ13C (‰)       | −30.0           | δ18O (‰) | −7.5          | δ13C (‰) | −7.5          |
| δ56Fe (‰)      | −4.0            | δ18O (‰) | 22.6          | δ13C (‰) | 22.6          |
| Eq. (5)         | 4Fe(OH)3 + CH2O + 2HCO3 → 3FeCO3 + 4OH– + 6H2O + Fe2+ | δ13C (‰) | −0.13         | δ18O (‰) | 0.38          |
| δ56Fe (‰)      | 0.00            | δ18O (‰) | −10.0         | δ13C (‰) | −10.0         |
| δ56Fe (‰)      | −2.0            | δ13C (‰) | −4.5          | δ56Fe (‰) | −4.5          |
| δ18O (‰)       | −5.0            | δ13C (‰) | −7.5          | δ18O (‰) | −7.5          |
| Eq. (6)         | 4Fe(OH)3 + CH2O + HCO3 → 2FeCO3 + 5OH– + 5H2O + 2Fe2+ | δ13C (‰) | −0.25         | δ18O (‰) | 0.25          |
| δ56Fe (‰)      | 0.00            | δ13C (‰) | −5.9          | δ18O (‰) | −5.9          |
| δ13C (‰)       | −30.0           | δ13C (‰) | −8.9          | δ18O (‰) | −8.9          |
| δ56Fe (‰)      | −2.0            | δ13C (‰) | −4.0          | δ18O (‰) | −4.0          |
| δ18O (‰)       | −5.0            | δ13C (‰) | 26.0          | δ18O (‰) | 18.5          |
| Eq. (7)         | 4Fe(OH)3 + CH2O → FeCO3 + 6OH– + 4H2O + 3Fe2+ | δ13C (‰) | −0.38         | δ18O (‰) | 0.13          |
| δ56Fe (‰)      | 0.00            | δ13C (‰) | −30           | δ18O (‰) | −30           |
| δ56Fe (‰)      | −2.0            | δ13C (‰) | −18.1         | δ18O (‰) | −18           |
| δ13C (‰)       | −5.0            | δ13C (‰) | −7.9          | δ18O (‰) | −7.9          |

Notes: Equation numbers correspond to those in the text and in Fig. S9. Input isotope compositions are as follows: δ18O correspond to two models calculated using different seawater isotopic compositions: δ18Osw = −1‰ (Muehlenbachs, 1998), and δ18Osw = −4‰ (Kasting et al., 2006), respectively; δ13C for organic carbon = −30‰ (Fischer et al., 2009); δ56Fe for DIC = 0‰; δ56Fe for Fe(OH)3 = 0‰. Fractionation factors used are as follows: δ18OFeCO3 = 26‰ (50 °C; Carothers et al., 1988); δ18OSiCO3 = 10‰ (20 °C; Beck et al., 2005); δ18OFeOH3 = 0‰ (Guy et al., 1993); Δ18OSid = 0‰ (20 °C; Bao and Koch, 1999; Bao et al., 2000); δ13CFe(III) = 0.5‰ (Wiesli et al., 2004). Siderite in equilibrium with seawater has δ13C = 0‰, and δ56Fe = +25‰, for δ18O = +22‰ for a and δ18O = +25‰ for b.

5.2.1. Other seawater components

Eq. (4) requires significant C contributions from HCO3− from seawater and other elements could come from seawater. Rare earth elements (REE) and Y in carbonates, for example, are widely used as a proxy for seawater (e.g., Webb and Kamber, 2000; Kamber and Webb, 2001). The high sorption capacity of ferricyanides for REE + Y (e.g., Bau, 1999; Quinn et al., 2006a, b) raises the possibility that REE + Y released by microbial reduction of ferricyanides could contribute seawater-like compositions, although it is important to note that the experimentally determined REE + Y adsorption coefficients are variable. REE contents may be very high in pore fluids from sections of marine sediments that record microbial C and Fe cycling, and in some cases the REE patterns mimic those of seawater (e.g., Elderfield and Sholkovitz, 1987; Haley et al., 2004; Caetano et al., 2009). We conclude that, through a combination of direct contributions from seawater that accompanies seawater HCO3− addition, and release through microbial reduction of ferricyanides, REE + Y contents of DIR-generated Fe-rich carbonates could closely resemble those of seawater despite the fact that 100% of the Fe(II) might have been generated by DIR. Testing this possibility will require much larger sampling than that done in the current study, where mg-size samples were taken to maximize spatial selectivity, relative to the 100 mg-size carbonate samples commonly used for REE + Y analyses.

In addition to trace element proxies for seawater, a logical question, given the expected high seawater Ca2+ and Mg2+ contents, is can DIR produce low-δ13C Ca–Mg carbonates? Carbonate formation during DIR has been shown to mostly (but not entirely) exclude dissolved Ca2+ and Mg2+, favoring siderite formation despite the presence of abundant dissolved alkaline earth ions (Mortimer et al., 1997; Roden et al., 2002). For siderite formation by DIR via Eqs. (5) through (7), decreasing quantities of seawater-derived HCO3− predict decreasing δ13C values for siderite, and increasing quantities of Fe2+ under conditions of complete Fe(OH)3 reduction (Table 1). If excess Fe(OH)3 is present, free Fe2+ would react to form magnetite (Eq. (8)), or, in the presence of silica, Fe silicates. The observation that the lowest δ13C values for BIF siderite are found in oxide- and Fe silicate-facies BIFs (Fig. S9) is exactly that expected for DIR.
5.3. Fe isotope evidence for multi-stage DIR

The average and median $\delta^{56}$Fe values for BIF siderite analyzed in the current study are $-0.03$ and $-0.07\%$, respectively, suggesting that the overall Fe flux that generated the siderite layers had a near-zero $\delta^{56}$Fe value. We interpret this to reflect the average Fe isotope composition of the flux of Fe(OH)$_2$ from the photic zone to the seafloor. This model follows that of Johnson et al. (2008a), who noted that magnetite and siderite from the $-2.5$ Ga Dales Gorge Member of the Brockman Iron Formation, Australia, have an average $\delta^{56}$Fe value near zero. If the Fe(OH)$_2$ flux to the seafloor had a $\delta^{56}$Fe value near zero, and siderite did not generally form in Fe isotope equilibrium with seawater, then the range in $\delta^{56}$Fe values measured for BIF siderite must reflect processes in the sediment, beneath the sediment/seawater interface, prior to lithification.

Partial microbial reduction of iron oxide produces Fe$_{aq}^{2+}$ that has negative $\delta^{56}$Fe values, reflecting isotopic fractionation between Fe$_{aq}^{2+}$ and a reactive surface layer on the oxide substrate of $-3$ to $-13\%$ (Johnson et al., 2005; Crosby et al., 2005, 2007; Wu et al., 2009; Tangalos et al., in press). Assuming an average Fe$_{aq}^{2+}$-reactive iron oxide fractionation of $-2\%$, appropriate for a mixture of ferrhydrite and goethite (Tangalos et al., in press), reduction of 50% of the oxide substrate would, broadly speaking, produce Fe$_{aq}^{2+}$ with a $\delta^{56}$Fe value of $-13\%$. The remaining oxide would have a $\delta^{56}$Fe value of $+1\%$, assuming simple mass balance and equilibrium conditions. Siderite that formed from DIR-generated Fe$_{aq}^{2+}$ that was mobile in the sediment would be expected to be relatively free of inclusions of iron oxide substrate. In contrast, siderite that formed "in place" by reduction of the ferric oxide substrate could contain inclusions of residual iron oxide minerals if reduction did not quite go to completion. Siderites formed in this manner would be expected to have zero or positive $\delta^{56}$Fe values, depending upon the extent of reduction that involved prior loss of low-$\delta^{56}$Fe Fe$_{aq}^{2+}$. Our observation that siderites that contain iron oxide inclusions have $\delta^{56}$Fe values $\geq 0\%$ provides strong support for such a multi-step process of DIR in the soft sediment prior to lithification. Although they are a minor component in the Fe mass balance of the system (Figs. 5B and S3), these iron oxides are expected to have positive $\delta^{56}$Fe values. Dehydration and phase transformation of residual ferric hydroxides is the best explanation for the presence of hematite and magnetite inclusions in these carbonates (e.g., Schwertmann and Cornell, 1991).

We illustrate the effects of variable extent of DIR in different locations in the soft-sediment section, along with mixing of variable C sources, in Fig. 6. Mixing of percolating Neoarchean/Paleoproterozoic seawater Fe ($\delta^{56}$Fe $-0\%$, 28 ppm, Ewers, 1980) and DIC ($\delta^{13}$C $-0\%$, 20 ppm, Holland, 1984), and end-member Fe and C isotope compositions derived from the reactions discussed above (Table 1), is shown by two sets of mixing lines. One set of lines shows the mixing of C with the lowest $\delta^{13}$C value of $-7.5\%$, expected from reaction (4), in which the ratio of HCO$_3^-$ derived from oxidation of CH$_2$O (HCO$_3^-$Org) to total HCO$_3^-$ (HCO$_3^-$Total) is 1/4. In the second model, we consider a lower $\delta^{13}$C value reflecting a greater component of HCO$_3^-$Org (HCO$_3^-$org/HCO$_3^-$Total $=1/4$). Seawater Fe was mixed with Fe$_{org}^{2+}$ that had $\delta^{56}$Fe values of $-13\%$, 0%, and $+1\%$, as discussed above. Conceptually, these $\delta^{56}$Fe values reflect partial DIR, complete DIR, and reduction of residual Fe(OH)$_2$ left over from partial DIR, respectively (points A, B, and C in Fig. 6). Combined, these mixing lines (see figure legend) produce C and Fe isotope compositions that encompass the range in measured $\delta^{13}$C and $\delta^{56}$Fe values, taking into account the Fe isotope effects of different degrees of DIR, Fe$_{aq}^{2+}$ mobilization, and various ratios of HCO$_3^-$Org to HCO$_3^-$Total.

A schematic view of the pathways involved in producing the observed $\delta^{13}$C- $\delta^{56}$Fe relations is shown in Fig. 7. Partial reduction of Fe (OH)$_2$ will produce Fe$_{aq}^{2+}$ with a $\delta^{56}$Fe of $-1\%$ or less if the extent of reduction is $\leq 50\%$. As highlighted by Johnson et al. (2008b), quasi-steady-state generation of low-$\delta^{56}$Fe Fe$_{aq}^{2+}$ could be sustained in sediments by a continual downward flux of Fe(OH)$_2$ and CH$_2$O produced in the photic zone. Production of Fe$_{aq}^{2+}$ and HCO$_3^-$ with $\delta^{56}$Fe $= -1\%$ and $\delta^{13}$C $= -30\%$ via partial Fe(OH)$_2$ (OH$_2^-$) reduction is referred to as "stage 1" in Fig. 7. These mobile species may encounter HCO$_3^-$ in seawater (HCO$_3^-$SW) in "stage 2" (Fig. 7), producing siderite that has $\delta^{56}$Fe and $\delta^{13}$C values of $-1\%$ and $-7.5\%$, respectively, via a reaction such as:

$$4\text{Fe}^{2+} + 3\text{HCO}_3^- + 4\text{H}_2\text{O} \rightarrow 4\text{FeCO}_3^- + 4\text{H}_2\text{O}.$$  (9)

BIF carbonates that have these Fe-C isotope compositions are plotted as "Group I" in the inset to Fig. 7, if additional HCO$_3^-$ SW beyond the 3 mol required in Eq. (9) is provided from seawater, intermediate $\delta^{13}$C values for carbonate may be produced via the mixing relations in Fig. 6.

The residual Fe(OH)$_2$ from partial reduction by DIR in "stage 1" should have positive $\delta^{56}$Fe values, perhaps $+1\%$, based on isotopic mass balance, which is consistent with inferences from natural samples (Staubwasser et al., 2006). Further reduction of this residual Fe(OH)$_2$ would produce Fe-C isotope compositions that fall in the "Group II" data field in Fig. 7. Conversion of high-$\delta^{56}$Fe Fe(OH)$_2$ to siderite by DIR requires additional HCO$_3^-$ from seawater, which would result in siderite with $\delta^{56}$Fe $> +1\%$ and $\delta^{13}$C $= -7.5\%$. We label this pathway as "near-complete" reduction because of the common presence of micron-size ferric oxide (hematite, magnetite) inclusions in high-$\delta^{56}$Fe siderites, a key petrographic indicator of DIR, as discussed above. We note that Peccotis et al. (2009) observed hematite inclusions in siderite from the Dales Gorge Member of the Brockman Iron Formation, Australia, and proposed that this relation reflected an oxide residue during siderite production through early sediment diagenesis by DIR.

6. Conclusions

The high abundance of siderite in Archean marine sedimentary rocks, including BIFs that were deposited below wave base, has provided...
some of the most widely cited evidence for a stratified ocean that was anoxic and Fe2+-rich in its deeper portions (e.g., Ohmoto et al., 2004; Rice and Lowe, 2004). The C, O, and Fe isotope data presented in this study, however, argue that virtually none of the siderites analyzed here might explain this observation. The isotope mass-balance reactions presented here provide a solution to the long-standing problem that may now be successfully explained by production of Fe(OH)3 from Feaq produced by near-complete reduction of high-δ56Fe residual Fe(OH)3 from stage 1, which will produce siderite with δ13C~+1‰ and δ18O~−7.5‰. In this case, DIR and siderite formation are envisioned to occur “in place,” and a small amount of un-reacted Fe(OH)3 is later converted (by dehydration and recrystallization) to ferric oxide, forming hematite inclusions. This process is represented by carbonates that contain ferric oxide inclusions and fall in Group II of isotope compositions.

The wide range in δ56Fe values for siderite from the Kuruman Iron Formation indicates that few siderites were in Fe isotope equilibrium with seawater, but instead records authigenic and early diagenetic mineral formation in the soft sediment prior to lithification. Simple flux models demonstrate that the oceans may become stratified in δ56Fe values through processes such as extensive oxide precipitation in the photic zone, but this stratification can only occur if the photic zone contains very low dissolved Fe contents (Johnson et al., 2008a), and such environments cannot produce extensive deposition of Fe-rich carbonates. We therefore draw an important distinction between Ca–Mg carbonates whose Fe isotope compositions may directly reflect those of seawater (e.g., von Blanckenburg et al., 2008; Czaja et al., 2010) and the Fe-rich carbonates that are the focus of the current study.

It is understandable that the debates on the cause of the Fe isotope signals recorded in Neoarchean and Paleoproterozoic marine sedimentary rocks has focused on the samples that have negative δ56Fe values, because these deviate most strongly from the near-zero δ56Fe values that characterize the continental and oceanic crust, detrital Fe loads, and hydrothermal Fe fluxes. The results from the current study, however, indicate that the inventory of Fe that has negative δ56Fe values may be but a small fraction of that cycled by low-temperature biological processes during this time. BIFs are particularly valuable in assessing the quantities of Fe that may have been biologically cycled in ancient marine environments because the combination of their very high Fe contents and non-zero δ56Fe values are very difficult to explain through abiological redox processes such as extensive oxide precipitation (Johnson et al., 2008b). The Fe isotope data presented

---

**Fig. 7.** Schematic diagram that shows a conceptual model for the diagenetic origin of BIF Fe carbonates based on mineralogical, chemical, and C, O, and Fe isotope data. Two main groups of carbonates that have low δ13C values (~−7.5‰) are defined by low δ56Fe values (~+1‰, Group I) and high δ56Fe values (~−1‰, Group II), which originate through a multi-step process (see Section 5.3). For Group I data, in “stage 1,” partial microbial reduction of Fe(OH)3 with δ56Fe~+0‰ and oxidation of CH4O with δ13C~−30‰ results in generation of Feaq with δ56Fe~−1‰ and HCO3 with δ13C~−30‰. In “stage 2,” low δ56Fe Feaq is mobilized and reacts elsewhere in the sediment column with (i) HCO3 derived from stage 1, and (ii) seawater HCO3 to form siderite with δ56Fe~−1‰ and δ13C~−7.5‰. Because Feaq and HCO3 have been mobilized prior to Fe carbonate precipitation, Fe carbonates in this group do not contain Fe-oxide inclusions. Group II data are interpreted to reflect Feaq produced by near-complete reduction of high-δ56Fe residual Fe(OH)3 from stage 1, which will produce siderite with δ56Fe~+1‰ and δ13C~−7.5‰. In this case, DIR and siderite formation are envisioned to occur “in place,” and a small amount of un-reacted Fe(OH)3 is later converted (by dehydration and recrystallization) to ferric oxide, forming hematite inclusions. This process is represented by carbonates that contain ferric oxide inclusions and fall in Group II of isotope compositions.
here, when considered in light of C and O isotope compositions determined on the same samples, indicate that authigenic and early diagenetic minerals that have negative, near-zero, or even positive δ²⁸O values may also record biological cycling, demonstrating that a complete understanding of the extent of biological versus abiological Fe cycling requires multiple lines of evidence and careful petrographic sample characterization.

Acknowledgements

We thank John Fournelle for his help with electron microprobe, SEM, and EBSD determinations and Hiromi Konishi and Huifang Xu for performing preliminary TEM analysis. We thank Max Coleman for useful discussions. Journal reviews by editor Rick Carlson, Balz Kamber, and an anonymous reviewer helped to improve the manuscript. This research was funded by the NASA Astrobiology Institute and the National Science Foundation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.epsl.2010.02.015.

References

Beveridge, K., Knoll, A.H., 2009. Isotopic constraints on the Late Archean carbonate cycle from the Transvaal Supergroup along the western margin of the Kaapvaal Craton, South Africa. Precamb. Res. 169, 15–27.
Klein, C., Beukes, N.J., 1989. Geochemistry and sedimentology of a facies transition from limestone to iron-formation deposition in the early proterozoic Transvaal Supergroup. South Africa. Econ. Geol. 84, 1731–1774.
Klein, C., 2005. Some Precambrian banded iron formations (BIFs) from around the world: their age, geologic setting, mineralogy, metamorphism, geochemistry, and origin. Am. Mineral. 90, 1473–1496.
Kleinitz, C., Beukes, N.J., 1989. Geochemistry and sedimentology of a facies transition from limestone to iron-formation deposition in the early proterozoic Transvaal Supergroup. South Africa. Econ. Geol. 84, 1731–1774.


