

# Iron isotope constraints on Fe cycling and mass balance in oxygenated Earth oceans

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## ABSTRACT

The Fe isotope composition of Proterozoic to modern clastic sedimentary rocks and aerosols defines a range in  $\delta^{56}\text{Fe}$  values that is only slightly more variable than the range of Fe isotope compositions measured in terrestrial igneous rocks, indicating that chemical weathering, sedimentary transport, and diagenesis play only a minor role in producing Fe isotope variations in environments where Fe redox conditions have been controlled by current levels of atmospheric oxygen. In contrast, the Fe isotope compositions of hot fluids ( $>300\text{ }^\circ\text{C}$ ) from mid-ocean-ridge (MOR) spreading centers define a narrow range that is shifted to lower  $\delta^{56}\text{Fe}$  values by 0.2‰–0.5‰ as compared to igneous rocks. These new data allow a conceptual model for the Fe isotope composition of the oxic oceans that predicts large ranges in Fe isotope composition under conditions of changing aerosol and MOR Fe fluxes, such as during periods of major worldwide glaciation.

**Keywords:** Fe isotopes, ferromanganese crust, aerosol, mid-ocean-ridge vent fluid, iron.

## INTRODUCTION

The Fe content of the modern oceans is very low,  $<1\text{ nM}$  in the open oceans (e.g., Johnson et al., 1997), and it is now recognized that marine productivity is Fe limited in much of the open oceans (e.g., Johnson et al., 1997). Nevertheless, hydrogenous accumulation of Fe and other metals occurs in the open oceans through deposition of Fe-Mn crusts (e.g., Abouchami et al., 1999; Reynolds et al., 1999), providing an isotopic record of past ocean compositions. Isotopic analysis of well-dated layers from an Fe-Mn crust from the Atlantic Ocean shows that the Fe isotope composition of layers that span an age from 6 to 1.7 Ma have a constant Fe isotope composition ( $\delta^{56}\text{Fe} = -0.69\text{‰}$

$\pm 0.10\text{‰}$ ), but layers that are younger than 1.7 Ma have increasing  $\delta^{56}\text{Fe}$  values with decreasing age, reaching a value of  $+0.04\text{‰}$  at 0.15 Ma (Zhu et al., 2000). If there are no significant mineralogic differences through this crust profile, and diagenetic effects are minor, the Fe isotope composition of this Fe-Mn crust provides strong evidence for relative changes in the Fe isotope composition of ocean water with time. Noting a strong correlation between Pb and Fe isotope compositions in this Fe-Mn crust, Zhu et al. (2000) suggested that the secular variation in Fe isotope composition was caused by changes in the Fe isotope composition of terrigenous material that was delivered to the Atlantic Ocean over time. Five crusts scattered throughout the northern Atlantic Ocean display similar secular changes in Pb isotope compositions, suggesting that changes in isotopic composition are not a result of local phenomena, such as diagenesis (Reynolds et al., 1999).

The low Fe concentration in the world's oceans today produces a short residence time of Fe in seawater, 70–200 yr (Johnson et al., 1997). Because of the short residence time for Fe in oceans, the Fe isotope composition of seawater can be subject to rapid changes if the isotope composition of material that is delivered to the oceans changes, or through changes in relative fluxes of Fe that have distinct Fe isotope compositions. In order to determine which of these contrasting possibilities may be responsible for producing the observed secular changes in Fe isotope compositions inferred for the oceans (Zhu et al., 2000), it is necessary to determine the Fe isotope composition of the major fluxes of Fe that are delivered to the world's oceans. Worldwide, Fe fluxes include a riverine load, an atmospheric load, Fe from hydrothermal fluids generated at the mid-ocean-ridge (MOR) spreading system, and a small flux from extraterrestrial sources (Table 1).

## RESULTS AND DISCUSSION

We have directly measured the Fe isotope composition of the particulate riverine and atmospheric loads, as well as the Fe isotope composition of fluids from high-temperature ( $>300\text{ }^\circ\text{C}$ ) MOR vents.

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TABLE 1. Fe FLUX AND ISOTOPE COMPOSITION DELIVERED TO SEAWATER

Flux	Fe content ( $\times 10^{12}\text{ g/yr}$ )	Fe isotope composition	Contribution (%)	Alternative contribution (%)
Riverine particulate load*	110	$0.02 \pm 0.10$	72.0	–
Riverine dissolved load*	1	$\leq 0$	0.65	2.3
Atmospheric particulate load†	29	$0.01 \pm 0.07$	19.0	67.4
Atmospheric dissolved load†	3	$\leq 0$	2.0	7.0
Hydrothermal load‡	10	$-0.21\text{ to }-0.54$	6.5	23.2
Extraterrestrial flux*	0.004	$+0.5\text{ to }-0.8$	0.003	–

Note: Fe isotope composition for riverine particulate flux is average of shales, modern marine sediments, suspended river sediments, and soil (57 samples). Fe isotope composition of atmospheric load is the average of aerosols and loess from this study (24 samples). The range for hydrothermal flux is based on seven analyses of mid-ocean-ridge hydrothermal fluids from the Atlantic and Pacific Oceans. For data sets, see footnote 1 in text. Fe isotope composition of dissolved Fe fluxes has not been measured; values reported are estimates (see text for discussion). Fe isotope composition of extraterrestrial flux is based on variable Fe isotope compositions measured in chondritic meteorites (Zhu et al., 2001), but we note that  $\sim 4\%$  of extraterrestrial flux (Taylor et al., 1998) is composed of iron spherules that have  $\delta^{56}\text{Fe}$  values ranging from  $+10\text{‰}$  to  $+40\text{‰}$  (Herzog et al., 1999). Alternative contribution percent is based on assumption that riverine particulate load is stored on continental shelves and will not contribute significantly to Fe contents of seawater.

\*Riverine flux rate from GESAMP (1987).

†Atmospheric flux rate from Duce and Tindale (1991).

‡Hydrothermal flux from Elderfield and Schultz (1996).

\*Extraterrestrial flux rate calculated by using meteorite flux of Taylor et al. (1998) with an assumed Fe content equal to chondritic meteorites.

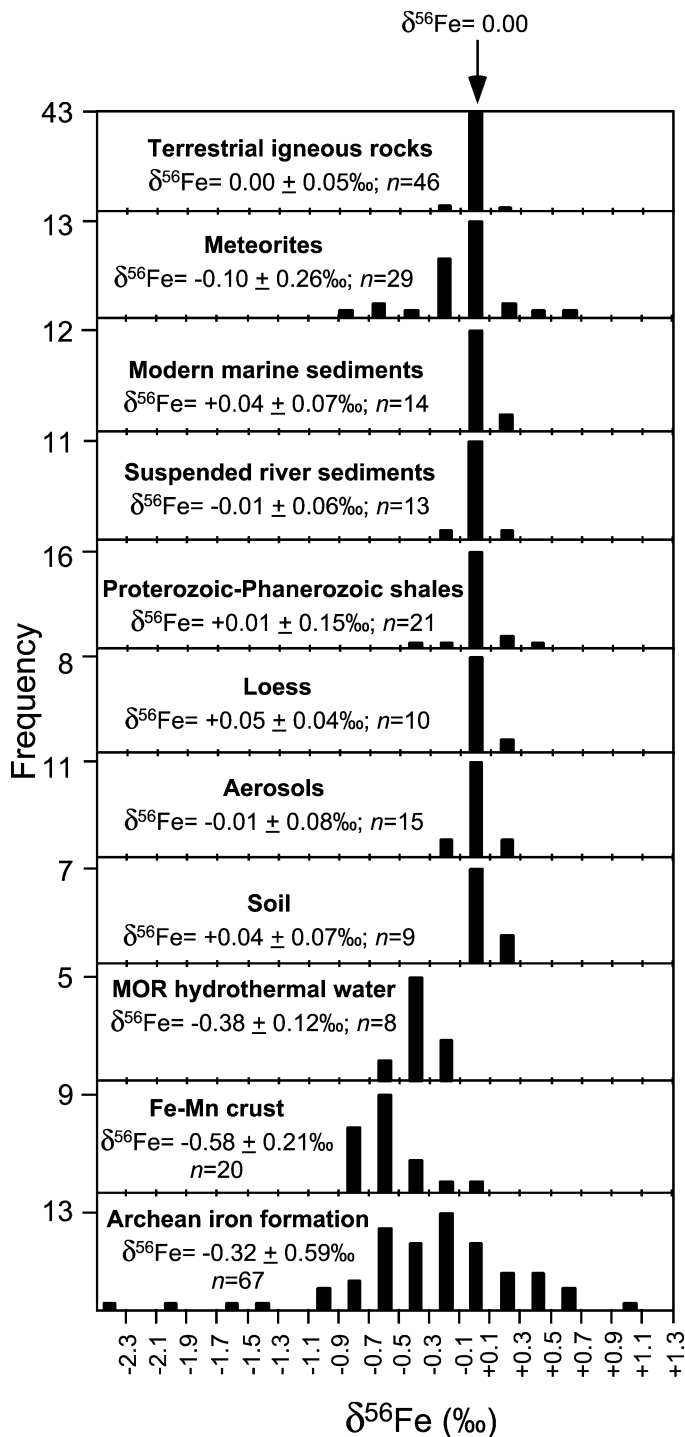


Figure 1. Histogram plot of Fe isotope compositions of igneous rocks, clastic sedimentary rocks, and chemically precipitated sedimentary rocks. Igneous rock data from Beard et al. (2003), meteorite data from Zhu et al. (2001), Fe-Mn crust from Zhu et al. (2000), and banded iron formation data from Johnson et al. (2003). Clastic sedimentary rock and mid-ocean-ridge (MOR) hydrothermal fluid data are from this study. Data not from University of Wisconsin (Zhu et al., 2000, 2001) have been corrected for interlaboratory bias by setting the  $\delta^{56}\text{Fe}$  value of IRMM-014 to  $-0.09\text{‰}$ , the measured  $\delta^{56}\text{Fe}$  for IRMM-014 relative to our bulk earth Fe baseline (Beard et al., 2003).

Eighty-two clastic sedimentary rocks and atmospheric components have been analyzed for their Fe isotope compositions (Fig. 1) using a multicollector-inductively coupled plasma-mass spectrometer that produces an external precision of  $\pm 0.05\text{‰}$  for  $\delta^{56}\text{Fe}$  values (see Appen-

dix<sup>1</sup>). Aerosols, loess, modern marine sediments, the suspended load from rivers, and soil define a limited range in  $\delta^{56}\text{Fe}$  values (average  $\delta^{56}\text{Fe} = +0.02\text{‰} \pm 0.07\text{‰}$ ), which is nearly identical to the range of Fe isotope compositions measured for 46 terrestrial igneous rocks (average  $\delta^{56}\text{Fe} = 0.00 \pm 0.05\text{‰}$ ; Fig. 1). This suite of data constrains the particulate load of Fe that reaches the modern oceans.

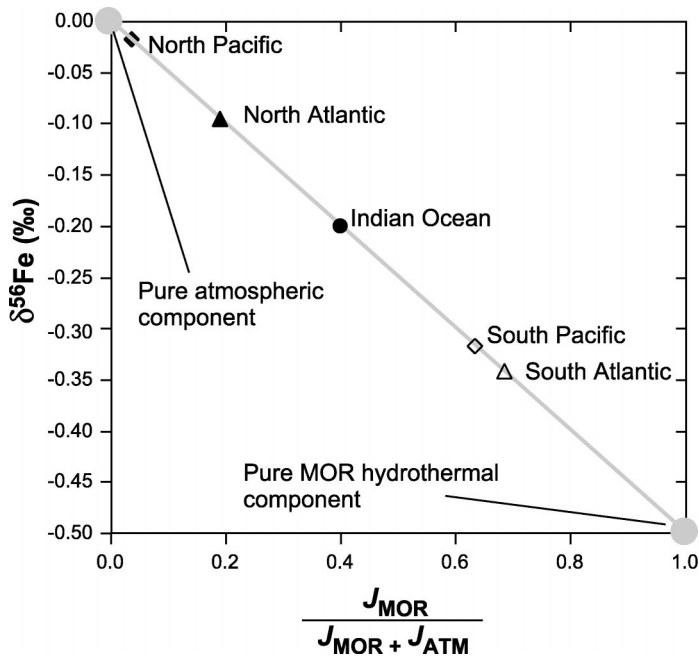
Seven MOR hydrothermal fluids have been analyzed for their Fe isotope composition, including both vapor and liquid (brine) phases from the Atlantic and Pacific Oceans (Table DR7 [see footnote 1]). These analyses are of high precision ( $\pm 0.05\text{‰}$ ) and include analyses of the dissolved phase and of the particles that precipitated within the water-sampling bottles, and therefore are total values for the Fe composition of the fluids as they exited the seafloor (Table DR8 [see footnote 1]). These analyses clearly document that hydrothermal fluids have an isotope composition significantly different from that of terrestrial igneous and clastic sedimentary rocks. A similar range of Fe isotope compositions for hydrothermal fluids and minerals from the Juan de Fuca Ridge was reported by Sharma et al. (2001), but the precision of those analyses ranged from  $\pm 0.04\text{‰}$  to  $\pm 0.68\text{‰}$ .

The Fe isotope analyses of clastic sedimentary rocks, aerosol particles, and MOR vent fluids directly determine the Fe isotope composition of the major Fe fluxes to the oceans. The isotopic composition of the dissolved Fe flux delivered by rivers and the atmosphere is unknown, but the relative contributions of the dissolved riverine and atmospheric fluxes are small ( $<3\%$ ), compared to the particulate and hydrothermal Fe fluxes (Table 1). If we assume that the particulate flux ( $\delta^{56}\text{Fe} = 0\text{‰}$ ) and hydrothermal flux ( $\delta^{56}\text{Fe} = -0.2\text{‰}$  to  $-0.5\text{‰}$ ) contribute Fe in their modern relative proportions (Table 1), then the ocean average is expected to have an Fe isotope composition of  $\delta^{56}\text{Fe} = -0.01\text{‰}$  to  $-0.03\text{‰}$ , a value weighted toward the high flux of particulate Fe delivered by rivers. However, it is likely that the riverine particulate flux is largely stored on continental shelves as sediments (e.g., Chester, 1990), and its influence in controlling the Fe isotope composition in the open oceans is probably smaller than that implied by the fluxes summarized in Table 1. If we assume that the particulate riverine load is completely unreactive and is directly transported to an unreactive sedimentary reservoir, then the relative fluxes of Fe delivered to the world's oceans is essentially controlled by the atmospheric particulate flux and the MOR hydrothermal flux, which, on average, comprise 67% and 23%, respectively.

Because the atmospheric Fe flux to different ocean basins is controlled by the location of continental masses, the relative proportions of atmospheric fluxes are variable among ocean basins. For example, the atmospheric Fe flux is high to northern oceans and low to southern oceans (e.g., Duce and Tindale, 1991). Simple mixing calculations suggest that the northern oceans should have  $\delta^{56}\text{Fe}$  values close to zero because of the high atmospheric flux (Fig. 2). In contrast, the southern oceans receive a minimal amount of Fe from atmospheric sources, and we would expect them to have relatively low  $\delta^{56}\text{Fe}$  values because of a greater proportion of hydrothermal input (Fig. 2).

As a possible test for the validity of this two-component mixing model for the Fe isotope composition of seawater, we note that the Fe isotope composition of the most recent layer from the Fe-Mn crust analyzed by Zhu et al. (2000) has a  $\delta^{56}\text{Fe}$  value of  $+0.04\text{‰}$ . If we assume that there is no isotopic fractionation between seawater Fe and the iron-manganese oxyhydroxides, then the measured isotopic composition of the surface of this crust (dredged from the Atlantic Ocean, 30°N) is quite close to the Fe isotope composition predicted for the North Atlantic Ocean ( $\delta^{56}\text{Fe} = -0.1\text{‰}$ ). However, the range of Fe isotope compositions measured in this crust ( $\delta^{56}\text{Fe}$  from  $-0.86\text{‰}$  to

<sup>1</sup>GSA Data Repository item 2003088, Appendix and Tables DR1–DR8, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at [www.geosociety.org/pubs/ft2003.htm](http://www.geosociety.org/pubs/ft2003.htm).



**Figure 2.** Calculated Fe isotope composition of seawater from different oceans based on simple two-component mixing between Fe from aerosol particles and Fe from mid-oceanic-ridge (MOR) hydrothermal solutions. Atmospheric Fe fluxes ( $J_{ATM}$ ) for different ocean basins from Duce and Tindale (1991); MOR hydrothermal Fe fluxes ( $J_{MOR}$ ) to different ocean basins were proportioned relative to ridge-axis length.

+0.04‰) exceeds the range of Fe isotope compositions in our simple two-component mixing calculations. The low values recorded in the crust analyzed by Zhu et al. (2000) may reflect lower  $\delta^{56}\text{Fe}$  values for the MOR hydrothermal fluids than those of the seven samples that we have analyzed. In addition, we have ignored the input of dissolved Fe from atmospheric and riverine sources, in our calculations. No  $\delta^{56}\text{Fe}$  values have been published for the dissolved riverine and atmospheric inputs. If this dissolved Fe is reactive, it may have a significant influence on the Fe isotope compositions of the oceans relative to its small flux.

Although the Fe isotope composition of the riverine and atmospheric dissolved Fe fluxes has not been directly measured, it is possible to place limits on their Fe isotope compositions. Dissolved Fe concentrations in rivers are strongly controlled by the nonconservative behavior of Fe as freshwater interacts with seawater in estuaries (e.g., Sholkovitz et al., 1999). If precipitation of iron hydroxide from an aqueous Fe solution produces an Fe isotope fractionation, then the dissolved Fe of rivers may have an anomalous Fe isotope composition. In particular, because dissolved Fe concentrations are low, a nonzero fluid-mineral isotopic fractionation could produce significant Fe isotope variations in the dissolved fraction because it would represent the minor component. Isotopic fractionation of  $\sim 1\%$  in  $^{56}\text{Fe}/^{54}\text{Fe}$  has been measured between ferrihydrite and aqueous Fe in a cool-spring environment (Bullen et al., 2001), but it is difficult to apply these results to rivers because the Bullen et al. (2001) study involves oxidation of aqueous Fe(II), followed by precipitation of ferrihydrite. In riverine systems, dissolved Fe is overwhelmingly ferric, and therefore the +2.8‰ isotope fractionation in  $^{56}\text{Fe}/^{54}\text{Fe}$  that occurs between aqueous Fe(III) and Fe(II) (Johnson et al., 2002) will not be applicable.

The best analogue to precipitation and flocculation of ferric hydroxides in rivers is perhaps represented by experimental studies that measure the isotopic fraction during slow precipitation of hematite from an aqueous Fe(III) (Skulan et al., 2002). Although the mineralogical differences between ferrihydrite and hematite introduce some

uncertainties, it is the only published study of mineral-fluid fractionation that does not involve oxidation changes in Fe. During slow precipitation of hematite in aqueous Fe(III), there is no significant isotopic contrast between hematite and Fe(III) (Skulan et al., 2002). The lack of Fe isotope fractionation between hematite and aqueous Fe(III) may indicate that flocculation of Fe particles in estuaries will not produce any Fe isotope fractionation.

The suspended load of rivers (Table DR5 [see footnote 1]) has  $\delta^{56}\text{Fe}$  values from +0.13‰ to -0.11‰. Partial leaching of these suspended-load sediments shows that 20%–50% of the Fe is from non-silicate sources and that 4%–35% of the Fe is in poorly crystalline iron oxide (oxalate extractable Fe; Canfield, 1997). If this poorly crystalline iron oxide formed in isotopic equilibrium during precipitation, the dissolved riverine Fe should have a  $\delta^{56}\text{Fe}$  value of  $\sim 0\%$ . Preliminary Fe isotope data from the Amazon River, however, suggest that the dissolved Fe may have a  $\delta^{56}\text{Fe}$  of  $\sim -2\%$  (Berquist and Boyle, 2002). On a global scale, the quantity of dissolved Fe from riverine sources is minor (Table 1). However, dissolved riverine Fe may be quite important in the Pacific Ocean, where significant quantities of dissolved Fe may be delivered to seawater by rivers that drain oceanic islands (Sholkovitz et al., 1999).

Dissolved atmospheric Fe is predominately (50%–80%) ferrous iron and may be a very important source of bioavailable Fe in the open ocean (e.g., Behra and Sigg, 1990; Kieber et al., 2001). The source of dissolved Fe in rainwater lies in reductive dissolution of solid ferric hydroxide particles (Behra and Sigg, 1990). The Fe isotope composition of modern aerosol particles and loess, which are the source of dissolved atmospheric Fe, ranges from  $\delta^{56}\text{Fe}$  of +0.15‰ to -0.12‰ (Tables DR1 and DR2 [see footnote 1]). If the solid ferric hydroxide particles are completely dissolved, aqueous Fe in precipitation would have the same Fe isotope composition as the solid.

It is possible that redox cycling of Fe in clouds may produce net Fe isotope variations if components are preferentially lost from the system, given the significant equilibrium Fe isotope fractionation between dissolved Fe(III) and Fe(II) (Johnson et al., 2002). If we assume attainment of isotopic equilibrium, the dissolved Fe(II) may have a lower  $\delta^{56}\text{Fe}$  value than the Fe(III) component if Fe is lost from the system. Considering that Fe in rainwater is 50%–80% Fe(II), the Fe(II) component might be expected to have a  $\delta^{56}\text{Fe}$  value between -1.4‰ and -0.5‰ and the Fe(III) component might be expected to have a  $\delta^{56}\text{Fe}$  value between +1.4‰ to +2.2‰, depending on the Fe(II) to total Fe ratio of the dissolved atmospheric Fe. Because the Fe(II) component is not immediately oxidized in the oceans, it may be an important source of Fe to the oceans that may be ultimately sequestered into Fe-Mn crusts, and it is possible that such Fe has a low  $\delta^{56}\text{Fe}$  value. The ferric component of atmospheric Fe is likely to be non-reactive and sequestered as particulate Fe that settles to the ocean depths.

Despite the uncertainties in the Fe isotope composition of the dissolved Fe fluxes for riverine and atmospheric Fe, the dissolved components should have  $\delta^{56}\text{Fe}$  values that are similar to or lower than the Fe isotope composition of the particulate flux. Overall, the relative importance of these dissolved components is minor because the dissolved Fe flux is small, relative to the particulate and hydrothermal Fe fluxes. For example, if the total atmospheric Fe flux is proportioned into 90% particulate flux ( $\delta^{56}\text{Fe}$  value = 0‰) and 10% dissolved Fe flux ( $\delta^{56}\text{Fe}$  value = -1.4‰), the predicted Fe isotope composition of the oceans must be decreased by 0.13‰ for the North Pacific Ocean, which has the relatively highest contribution of Fe delivered from atmospheric fluxes.

## CONCLUSIONS

The sensitivity of the Fe isotope compositions of the modern (oxic) open oceans to the relative proportions of atmospheric and MOR

Fe sources suggests that Fe isotope compositions will be dependent upon tectonic or climatic changes that may vary these contributions, including major glaciation events. Although Zhu et al. (2000) explained correlated Fe and Pb isotope compositions of individual layers in the Fe-Mn crust from the North Atlantic to reflect changes in the Fe and Pb isotope composition of lithologic material that reached the oceans, the homogeneous isotope composition of Fe that would be delivered to the oceans in the form of aerosol particles and the suspended load of rivers discussed here makes the proposal unlikely. We instead propose that initiation of Northern Hemisphere glaciation at 2.6 Ma could be a driving force by increasing detrital loads to the open oceans by ice rafting or by an increase in riverine and atmospheric fluxes due to increased mechanical weathering at the expense of chemical weathering. Increases in atmospheric Fe flux delivered to seawater from aerosol particles have been inferred to have occurred during the Last Glacial Maximum (e.g., Edwards et al., 1998), perhaps indicating that there is a link to glaciation and the content of Fe delivered to the open oceans (Martin, 1990). On the basis of our simple two-component mixing calculations, we think that such a phenomenon should manifest itself as an increase in  $\delta^{56}\text{Fe}$  values in ocean water as the quantity of atmospheric Fe delivered to the oceans increases. If this model is correct, we would expect significant Fe isotope excursions to have occurred in the oceans during the Paleozoic Gondwanaland glaciations (Hambrey and Harland, 1981), as well as during the large-scale Neoproterozoic glaciations; indeed in the Neoproterozoic (the snowball Earth model; Kirschvink, 1992), we would expect very large deviations in  $\delta^{56}\text{Fe}$  values for ocean water, possibly shifting entirely to MOR sources.

The most likely alternative to our model would call upon mixing of water masses, which has been invoked to explain Pb and Nd isotope variations measured in numerous Fe-Mn crusts (e.g., Abouchami et al., 1999), in light of the predicted isotope variability among modern (oxic) ocean basins (Fig. 2). For example, an increase in the ventilation of Labrador Sea water to the North Atlantic would drive the  $\delta^{56}\text{Fe}$  value measured in this Fe-Mn crust toward zero, which would represent a lessening in the contribution of Fe from southern-component water that would have an Fe isotope composition that is dominated by MOR hydrothermal Fe. Onset of Labrador Sea water ventilation is estimated to have begun at 4–3 Ma (Abouchami et al., 1999), and therefore there may be a problem in timing, because the major shift in Pb and Fe isotope compositions measured in this North Atlantic Fe-Mn crust occurred at 1.8 Ma. However, if Fe isotope shifts are largely due to mixing of water masses, but such shifts occur rapidly (faster than plate-tectonic reorganizations of continental configurations), it seems most likely that such shifts are fundamentally related to major climate changes such as worldwide glaciations.

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