Pore-fluid Fe isotopes reflect the extent of benthic Fe redox recycling: Evidence from continental shelf and deep-sea sediments

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ABSTRACT

Pore-fluid Fe isotopes may be a unique tracer of sediment respiration by dissimilatory Fe-reducing bacteria, but to date, pore-fluid Fe isotope measurements have been restricted to continental shelf settings. Here, we present $\delta^{56}Fe$ values of pore fluids from two distinct sedimentary settings: (1) a riverine-dominated site on the northern California margin (Eel River shelf; 120 m water depth) and (2) biogenic opal-rich volcaniclastic deep-sea sediments from the Southern Ocean (north and south of the Crozet Plateau; 3000–4000 m water depth). The Fe isotope compositions of Crozet region pore fluids are significantly less fractionated ($\delta^{56}Fe$ = +0.12‰ to –0.01‰) than the Eel River shelf ($\delta^{56}Fe$ = –0.65‰ to –3.40‰) and previous studies of pore-fluid Fe isotopes, relative to average igneous rocks. Our data represent the first measurements of Fe isotope compositions in pore fluids from deep-sea sediments. A comparison of pore-fluid $\delta^{56}Fe$ with the relative abundance of highly labile Fe in the reactive sedimentary Fe pool demonstrates that the composition of Fe isotopes in the pore fluids reflects the different extent of sedimentary Fe redox recycling between these sites.

INTRODUCTION

Iron is an essential micronutrient for intracellular processes, and in many macronutrient-replete oceanic regions (high nutrient, low chlorophyll [HNLC]), primary production is limited by the availability of Fe (Martin, 1990). Consequently, the supply of Fe to HNLC regions has been proposed as a major contributing factor to the regulation of carbon drawdown on glacial to interglacial time scales (Martin et al., 1990). Much of the Fe input in HNLC regions has commonly been attributed to aerosol deposition and dissolution, but, increasingly, studies highlight the potential importance of sedimentary Fe sources for the coastal, and even open, ocean (Lam et al., 2006; Nishioka et al., 2007). In continental margin sedimentary settings, the benthic transport of dissolved Fe has been found to be significant (McManus et al., 1997; Berelson et al., 2003; Elrod et al., 2004), and enrichment of Fe in the pore fluids and bottom waters is driven by the reductive dissolution of Fe during organic carbon decomposition.

Iron isotopes have emerged as a new tool to evaluate iron cycling in aquatic environments (Anbar and Rouxel, 2007; Johnson et al., 2008). Incubation experiments have demonstrated that the reduction of Fe(III) in the presence of dissimilatory Fe-reducing bacteria produces aqueous Fe^{2+} with $\delta^{56}Fe$ values that are 0.5‰–2‰ lower than the initial Fe(III) substrate (Beard et al., 1999; Icopini et al., 2004; Crosby et al., 2007). Pore fluids from sediments where organic matter oxidation proceeds through significant microbial Fe reduction yield isotope compositions for dissolved Fe^{2+} that are ~1‰–3‰ lighter than average igneous rocks, suggesting that benthic Fe inputs to the ocean may carry a unique isotopic fingerprint (Severmann et al., 2006).

Dissimilatory iron reduction (DIR) is a form of chemolithotrophy that is widespread during diagenesis of marine sediments, and the rate of this process is controlled by organic carbon oxidation and the availability of Fe(III) substrates (Froelich et al., 1979). DIR was one of the earliest metabolic pathways to evolve on Earth (Vargas et al., 1998), and it has been suggested that sedimentary Fe isotopes may be used to reconstruct past Fe cycling in the Archean ocean (Rouxel et al., 2005; Yamaguchi et al., 2005; Severmann et al., 2008).

Pore-fluid Fe isotope measurements have so far been restricted to the continental shelves where DIR is extensive (Bergquist and Boyle, 2006; Severmann et al., 2006). There have been no measurements of Fe isotopes in low–organic-carbon, suboxic sediment pore fluids, in deep-water settings where sediment accumulation rates are much slower and oxygen penetration is deeper than on the continental shelves, or in sediments where abiotic processes such as adsorption or ligand complexation may significantly imprint the pore-fluid Fe isotope composition. The need for comparison of Fe isotopes in shallow- and deep-water environments has been identified (Johnson et al., 2008), and characterization of the Fe isotopic fingerprint of DIR in natural, complex aqueous systems is important for the effective interpretation of the sedimentary record, and for developing the potential utility of Fe isotopes as a tracer of benthic Fe fluxes.

We present here new $\delta^{56}Fe$ data for surface sediment pore fluids (0–25 cmbsf [centimeters below seafloor]) from two distinct sedimentary settings: (1) a riverine-dominated site on the northern California margin (Eel River shelf; 120 m water depth), where the organic carbon accumulation rate is high (~26.7 g C m^{-2} a^{-1}; Sommerfield and Nittrouer, 1999) and carbon remineralization is driven by extensive Fe redox cycling, and (2) mixed biogenic opal-rich volcaniclastic sediments from two deep-sea sites in the Southern Ocean (M6: 4222 m; and M10: 3227 m), where organic carbon accumulation rates are low (M6: ~0.011 g C m^{-2} a^{-1}; M10: ~0.113 g C m^{-2} a^{-1}) and diagenetic Fe cycling is limited by the availability of reactive organic carbon (see the GSA Data Repository[1] for additional sample site information).

RESULTS

Pore-fluid nitrate penetration depth provides a qualitative tool for comparing the sedimentary redox status of our study sites. This depth is greatest at the Southern Ocean site (M6; 20–30 cmbsf), intermediate at the Southern Ocean northern site (M10; ~10 cmbsf), and shallowest at the Eel River shelf site (~5 cmbsf) (Fig. 1A). The shallowest nitrate penetration depth occurs at the site of highest mean organic carbon content at the Eel River shelf (0.87%, 0–22 cmbsf), which also has the greatest proportion of highly labile Fe phases ($Fe_{h\text{-}lab}$) relative to reactive hydrous Fe oxide (HFO) substrates ($Fe_{h\text{-}lab}$/[$Fe_{h\text{-}lab}$ + HFO] = 0.63–0.69 for Eel River compared to 0.02–0.20 in Crozet sediments; see Table DR1 in the Data Repository). The relative proportions of $Fe_{h\text{-}lab}$ (Na acetate leachable) and HFO (hydroxylamine-HCl leachable) were estimated using the sequential sediment extrac-

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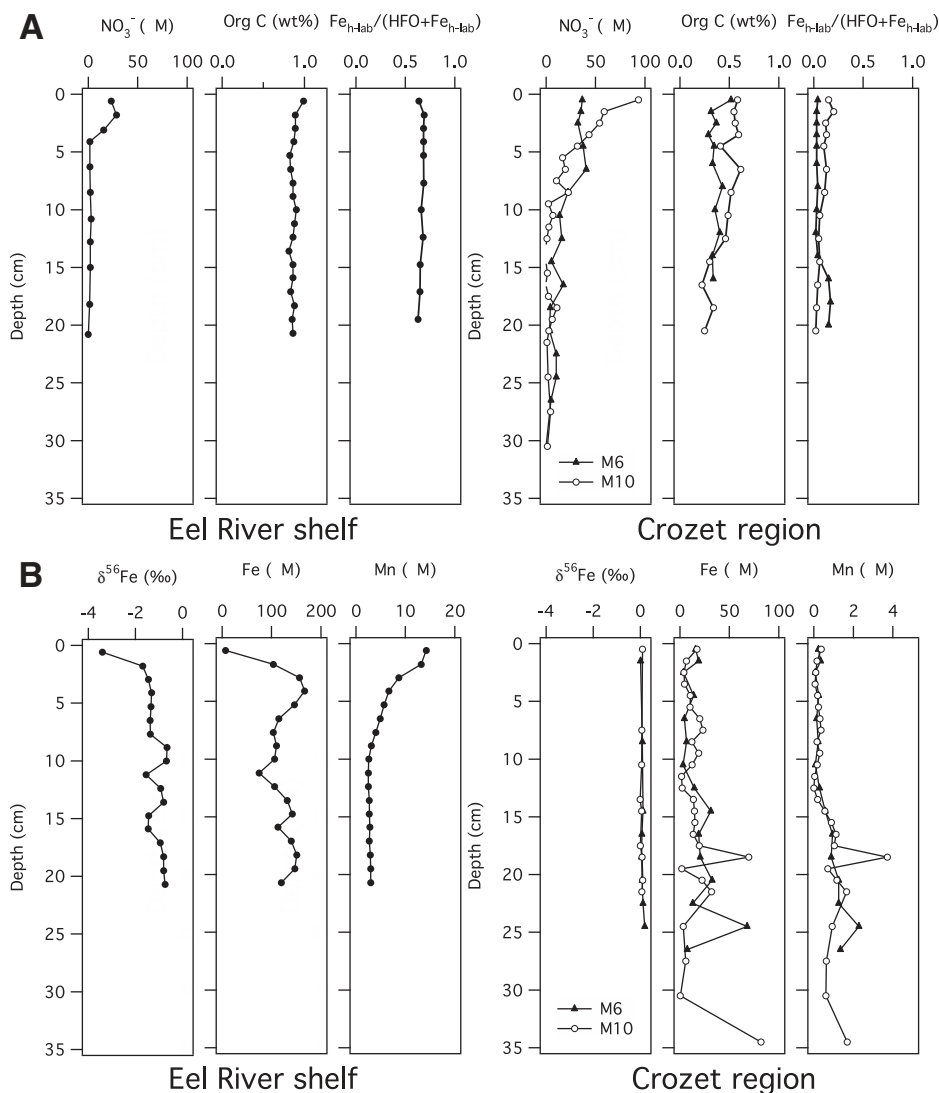
Figure 1. A: Pore-fluid nitrate, solid-phase organic carbon, and the proportion of highly labile Fe (Fe_{h-lab}) relative to hydrous Fe oxide (HFO) profiles. Nitrate penetration depth provides a qualitative tool to assess the redox conditions of the study sites. The Fe_{h-lab}/(HFO + Fe_{h-lab}) ratio records the relative proportion of highly labile Fe in a reactive Fe pool utilized during dissimilatory iron reduction (DIR). B: Concentration of Fe, Mn, and $\delta^{56}Fe$ in Crozet region and Eel River shelf pore fluids.

Figure 2. Pore-fluid Fe and Mn concentration at M10 and M6 sampled sequentially by two different filter sizes. Pore-fluid Fe and Mn are partitioned between <0.2 to >0.02 μm, and <0.02 μm size fractions at these sites, and they are inferred to make up a significant colloidal and/or nanoparticulate component of the pore fluids.

surements from deep-sea Southern Ocean sites (<0.1 μM Fe; King et al., 2000); the equatorial Pacific (<5 μM Fe; Haeckel et al., 2001); tropical northeast Atlantic (1–13 μM Fe; Froelich et al., 1979); and many coastal shelf settings (Canfield et al., 1993; McManus et al., 1997). Additionally, the biogeochemical zonation of NO_3^-, Mn, and Fe in the Crozet region pore fluids is less apparent than at the Eel River shelf site and provides little evidence for DIR-dominated diagenesis.

An analysis of two different dissolved size fractions (0.2 μm and 0.02 μm; see the Data Repository) in Crozet region pore fluids demonstrates that significant colloidal and/or nanoparticulate (herein after "colloidal") phases are present (Fig. 2). We speculate that these colloids are composed of adsorbed and/or organic ligand–bound Fe^{2+}/Fe^{3+} that may be utilized during DIR along with nanoparticulate basaltic weathering products. We suggest that the distribution of colloidal phases in the pore fluids is influenced by the episodic supply of organic carbon, which disrupts the steady-state pore-fluid composition (Gehlen et al., 1997); the vertical mixing of volcaniclastic sediments through slumping and turbidite emplacement in this region (Marsh et al., 2007); the influence of bioirrigation and bioturbation (Aller, 1990); and the uncertain role of stabilizing organic complexes in the pore-fluid environment (Luther et al., 1992).

Eel River shelf pore-fluid $\delta^{56}Fe$ compositions are consistent with previous studies of Fe-reducing continental margin sediments where DIR catalyzes the fractionation of Fe isotopes

tion procedure given in Poulton and Canfield (2005) (see the Data Repository for details of all methods and analyses). The ratio Fe_{h-lab}/(Fe_{h-lab} + HFO) provides an estimate of the extent of diagenetic redox recycling of Fe.

Crozet region pore-fluid $\delta^{56}Fe$ values range between +0.12‰ and –0.01‰ relative to average igneous rocks (Fig. 1B) and closely resemble those of average continental weathering products (0.2‰ ± 0.7‰; Beard et al., 2003). In contrast to both these sites, Eel River shelf $\delta^{56}Fe$ pore-fluid values lie between –0.65‰ and –3.40‰, and the greatest isotopic fractionation is closest to the sediment-seawater interface (Fig. 1B). Crozet pore-fluid Fe concentrations are ~1–80 μM at M10 and M6, and they are characterized by similar Mn distributions (up to 4 μM), with maxima at ~17 and 25

cmbsf at M10 and M6, respectively. At the Eel River shelf site, pore-fluid Fe concentrations reach a subsurface maximum of 167 μM at 5 cmbsf, and Mn concentrations are highest (14 μM) in the upper 0–5 cmbsf (see Data Repository Table DR2).
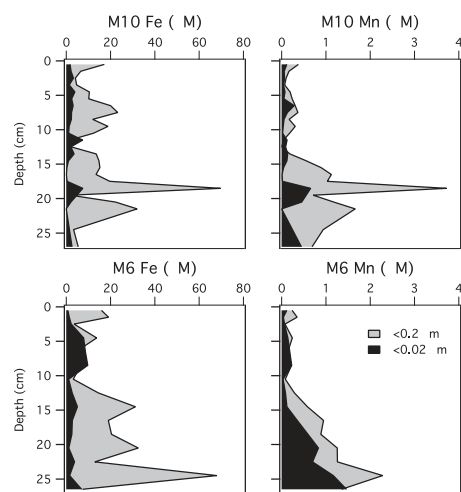
DISCUSSION

The distributions of Fe and Mn in Eel River shelf pore fluids are broadly consistent with the biogeochemical zonation of respiratory processes (Froelich et al., 1979), indicating the transition from aerobic respiration through to DIR between 0 and 5 cmbsf. However, Fe and Mn values in Crozet region pore fluids are not typical of deep-sea profiles, and values are relatively high (1–20 μM Fe; 0.1–0.3 μM Mn) in the upper 10 cm compared with previous mea-

during redox cycling (Severmann et al., 2006) (Fig. 3). Crozet region pore-fluid δ^{56}Fe values are significantly less fractionated than previous values reported for suboxic pore fluids (Fig. 3). Severmann et al. (2006) noted that near-zero δ^{56}Fe values for pore fluids might reflect equilibrium with FeS. There is no evidence for sulfide diagenesis in Crozet region Holocene sediments (Marsh et al., 2007). Therefore, the comparison of the Eel River shelf and Crozet region suggests that either a mechanism other than DIR is releasing a substantial amount of Fe (up to 80 μM; δ^{56}Fe ~0.0‰) into the Crozet pore fluids, or that DIR alone may be insufficient to generate the low δ^{56}Fe values we observe in continental margin sediments.
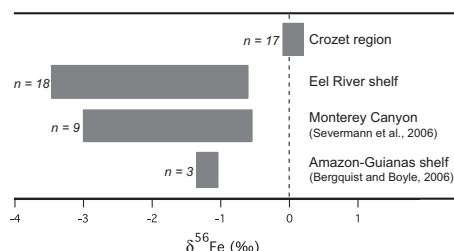
Figure 3. Comparison of Crozet region and Eel River shelf pore-fluid Fe isotope compositions with published data from dissimilatory iron reduction (DIR)–dominated reducing sediments on continental shelves.

Experiments have shown that Fe isotope fractionations of >1‰ in aqueous systems can also be produced by abiotic processes. For example, ligand-promoted dissolution of mineral substrates, such as goethite, ferrihydrite, and hornblende (Brantley et al., 2004), abiotic sorption and surface exchange (Icopini et al., 2004; Crosby et al., 2007), and isotope exchange between free and organically or inorganically complexed Fe (Dideriksen et al., 2008) could potentially contribute to variations in isotope compositions in nature that are indistinguishable from biological fractionations. Deconvolution of these processes in nature presents a major challenge; however, it has been argued that abiotic processes alone cannot generate the large inventories of isotopically fractionated Fe that have been identified in continental margin sediments (Johnson et al., 2008). We hypothesize that the observed variation in Fe isotope composition between our study sites reflects differences in the extent of biogenic benthic recycling of the reactive Fe pool.

The sedimentary reduction and oxidation of Fe during early diagenetic redox recycling has been estimated to occur 100–300 times prior to ultimate burial below the redoxcline (Canfield et al., 1993), where the extent of bioturbation and

bioirrigation may enhance the redox recycling of Fe substrates by oxidizing Fe^{2+} and suppressing the onset of sulfide diagenesis (Canfield et al., 1993). The composition of Fe isotopes in sediment pore fluids is inferred to reflect the extent of redox recycling of Fe between DIR-derived Fe^{2+}_{aq} and highly labile oxidation products, such as amorphous Fe-(oxyhdr)oxide (Severmann et al., 2008). Experimental investigations of the mechanism producing Fe isotope fractionation during DIR have shown that the generation of light dissolved Fe^{2+}_{aq} can be attributed to a coupled electron and isotope exchange between sorbed Fe^{2+} and a reactive ferric Fe component on the surface of the Fe-oxide that is open to isotope exchange (Crosby et al., 2007). These authors argue that changes in the absolute δ^{56}Fe values of Fe^{2+}_{aq} in their experiments reflect changes in the relative sizes of the reactive Fe pools. The reactivity of Fe-oxide minerals may therefore be the primary control on the pore-fluid Fe isotope composition. Although we did not quantify the reactive Fe(III) component in the ferric oxide surfaces directly, the coincidence of low pore-fluid δ^{56}Fe values with high $Fe_{h-lab}/(Fe_{h-lab} + HFO)$ in sediments from the Eel River shelf is consistent with the continuous reoxidation of Fe^{2+}_{aq} to amorphous Fe-(oxyhdr)oxides, providing an abundance of surface sites for isotope exchange, which are lacking in the Crozet sediments (Fig. 4).

We interpret the organic carbon supply to the Eel River shelf to be sufficient to sustain DIR and the redox recycling of Fe, thereby enriching highly labile Fe phases in the reactive Fe pool and accounting for the highest pore-fluid Fe isotope fractionation. In contrast, the low organic carbon input to the deep Crozet region

sediments limits DIR and redox recycling of Fe. We speculate that highly seasonal organic carbon inputs to M10 (Pollard et al., 2009) may promote the episodic contribution of DIR to sediment respiration and account for the relative enrichment of highly labile Fe in M10 surface sediments and in M6 turbidite layers. In these circumstances, processes that contribute to the generation of colloids and/or nanoparticulates in the pore fluids (van der Zee et al., 2003) are likely to have near crustal isotope compositions and dilute the isotopic signature of DIR.

CONCLUSIONS

High dissolved Fe pore-fluid contents indicate suppression of sulfide diagenesis in Eel River shelf sediments and volcaniclastic weathering in Southern Ocean sediments. We demonstrate that the pore-fluid Fe isotope compositions reflect the extent of Fe recycling during early diagenesis, which is driven by supply of reactive organic carbon and Fe. We invite future interpretations of the rock record to consider the importance of Fe isotope processing in carbon-limited environments. Additionally, the unique isotopic fingerprint of pore-fluid Fe in continental shelf settings is confirmed, drawing further attention to the potential utility of Fe isotopes as a tracer of shelf-derived Fe inputs to seawater.

Figure 4. Comparison of Eel River shelf (ER) and Crozet region (M10 and M6) sediment $Fe_{h-lab}/(HFO + Fe_{h-lab})$ composition with pore-fluid δ^{56}Fe. The sample depth of data is represented by the grayscale. The $Fe_{h-lab}/(HFO + Fe_{h-lab})$ ratio provides an estimate of the relative enrichment of highly labile Fe phases in the reactive sedimentary pool driven by the extent of redox recycling of Fe during early diagenesis. The published $Fe_{h-lab}/(HFO + Fe_{h-lab})$ composition of riverbed sediments provides an estimate of the end-member composition of the reactive Fe pool prior to early diagenesis. The contrast between the $Fe_{h-lab}/(HFO + Fe_{h-lab})$ ratio of the Eel River shelf and Crozet region is attributed to the much greater supply of reactive organic carbon to the Eel River shelf, which enhances the redox recycling of Fe. The slight increase in $Fe_{h-lab}/(HFO + Fe_{h-lab})$ ratio at M10 (0–8 cmbsf) is attributed to episodic organic carbon inputs to the surface sediments at this site (Pollard et al., 2009), and to a turbidite layer at M6 (15–20 cmbsf; Marsh et al., 2007).
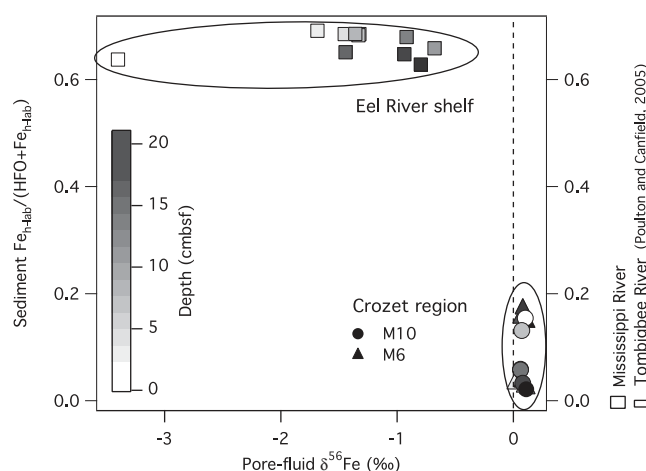
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