Isotopic evidence for Fe cycling and repartitioning in ancient oxygen-deficient settings: Examples from black shales of the mid-to-late Devonian Appalachian basin

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Abstract

We have measured iron (Fe) isotope compositions of bulk samples and chemically extracted pyrite in two black shale units: the Oatka Creek Formation (OCF) and the younger Geneseo Formation (GF) deposited in the Appalachian basin during the mid-to-late Devonian. The depositional redox conditions for these units are well established through multiple paleoproxies, including degree of pyritization (DOP) and ratios of total Fe to Al (FeT/Al), suggesting that both deposits reflect oxygen-deficient environments, but that euxinia (anoxia with hydrogen sulfide in the bottom waters) was more frequent and persistent during deposition of the OCF. Iron isotopes show systematic variations that are consistent with the inferred water column redox conditions. Samples from the OCF yield low and variable bulk Fe isotope compositions ( −0.44‰ to 0.03‰ in δ56Fe relative to average igneous rocks) that are inversely correlated with FeT/Al, whereas bulk δ56Fe values (δ56FeT) of the GF fall in a narrower range ( −0.09‰ to 0.12‰), δ56Fe values of pyrite (δ56FePy) display good correlation with δ56Fe in the OCF, but no such correlation is observed in the GF. The Fe isotope data and other paleo-redox indicators, when viewed collectively, point to a benthic Fe source on the shelf and shelf-to-basin transfer that operated during deposition of the OCF, similar to what has been observed in the modern Black Sea. For the first time this study confirms the strength of Fe isotopes in delineating this Fe enrichment mechanism in the ancient geological record and emphasizes the utility of the Fe isotope proxy for fingerprinting and quantifying ancient biogeochemical cycling of Fe.

1. Introduction

An understanding of iron (Fe) isotopes in the geologic record may help address crucial questions about marine Fe sources and cycling over Earth history (Dauphas et al., 2004; Rouxel et al., 2005; Johnson et al., 2008b). A growing database of Fe isotope compositions for black shales and pyrite hosted in those rocks has drawn special attention, because these materials yield the largest isotopic range measured in natural samples so far (δ56Fe = −3.6‰ to 1.2‰ relative to average igneous rocks) (Matthews et al., 2004; Rouxel et al., 2005; Yamaguchi et al., 2005; Archer and Vance, 2006). One of the most intriguing observations is a notable secular shift in δ56Fe values observed for black shale pyrites spanning geological time (Rouxel et al., 2005). In the late Archean to early Proterozoic, 2.8 to 2.3 billion years (Ga) ago, the δ56Fe of sedimentary pyrite is variable but typically negative, with values between 0.5‰ and −3.5‰. From 2.3 Ga to 1.7 Ga, negative δ56Fe values disappear, replaced by positive data ranging up to 1.2‰. After 1.7 Ga, δ56Fe generally stays within the narrow range defined by igneous rocks and hydrothermal sources (Rouxel et al., 2005; Yamaguchi et al., 2005).

The exact cause of these shifts is uncertain, but Fe isotope fractionations of 2 to 3‰ are only known to occur during reactions involving multiple redox states of Fe (Schauble et al., 2001; Johnson et al., 2002; Anbar et al., 2005; Polyakov et al., 2007). It is therefore generally accepted that the large shift at ~2.3 Ga from dominantly negative values during the Archean to values near or slightly above zero during the early Proterozoic reflects a fundamental shift in the geochemical cycling of Fe in the oceans associated with the rise of O2 in the early Proterozoic atmosphere (Rouxel et al., 2005). However, the mechanisms by which changes in ocean/atmosphere oxygenation led to variation in Fe isotopes are debated (Johnson and Beard, 2005; Yamaguchi and Ohmoto, 2006).

Rouxel et al. (2005) invoked large-scale oxidation of dissolved Fe2+ and precipitation of Fe(III) oxides to account for the very low δ56Fe values expressed during late Archean and early Proterozoic — a period known for voluminous deposition of Fe(III)-rich banded iron
formations. Based on the observations of Bullen et al. (2001) and Welch et al. (2003), this process would preferentially remove heavy Fe isotopes from solution, leaving behind a dissolved Fe$^{2+}$aq pool with generally negative $\delta^{56}$Fe relative to the starting value. However, this scenario has been challenged because the large negative seawater isotopic shifts inferred from the observed $\delta^{56}$Fe values of the late Archean pyrites as low as $-3.5\%$ would require precipitation of a very large proportion of the dissolved Fe pool of the whole ocean (50% to 90%) (Yamaguchi and Ohmoto, 2006; Johnson et al., 2008a).

Alternatively, sedimentary Fe isotope variations may be decoupled from overall environmental redox conditions if variable and negative $\delta^{56}$Fe values are produced locally in reducing sedimentary environments via diagenetic pathways, such as dissolution of oxides and precipitation of magnetite or pyrite (Yamaguchi et al., 2005; Archer and Vance, 2006; Yamaguchi and Ohmoto, 2006). For example, Archer and Vance (2006) suggested that the Fe and sulfur (S) isotope variations observed in Archean sedimentary pyrites represent coupled microbial Fe and sulfate reduction during local anoxic diagenesis. Although important, localized diagenetic processes cannot explain the full isotopic range in bulk sedimentary rocks (Rouxel et al., 2006; Dauphas and Rouxel, 2006). Diagenesis can facilitate isotopic re-partitioning among diverse mineral phases within sediments (Severmann et al., 2008). However, without a mechanism to physically separate the isotopically distinct Fe pools (Severmann et al., 2008), diagenetic processes alone cannot explain the low bulk $\delta^{56}$Fe values observed for Archean shales, magnetite-dominated banded iron formations (BIFs) and carbonates (Yamaguchi et al., 2005).

Localized sedimentary processes can account for isotope variations on the scale of an individual basin if redox conditions in the water column favor re-partitioning of the distinct early diagenetic Fe pools. For example, Severmann et al. (2008) attributed the light Fe isotope compositions observed in sediments of the deep modern Black Sea to a net basinward transport of isotopically light Fe derived from the shelf. Previous studies of Fe concentrations and fluxes in the Black Sea also point to this basinward “Fe shuttle” (Canfield et al., 1996; Wijsman et al., 2001; Raissel and Anderson, 2005; Lyons and Severmann, 2006). The light isotopic signature in the deep basinal sediments is thought to originate from the suboxically or oxically deposited shelf sediments (“suboxic” refers to bottom water condition where dissolved O$_2$ is low but hydrogen sulfide is absent; Murray et al., 1995; “suboxic sediments” here refer to sediments deposited beneath a suboxic water column). During diagenetic Fe redox cycling, reductive processes, specifically dissimilatory iron reduction (DIR) and/or abiotic reduction through reaction with dissolved sulfide, generate light porewater Fe$^{2+}$aq (Severmann et al., 2008). Such porewater Fe$^{2+}$ could become even isotopically lighter when coupled with Fe$^{2+}$aq re-oxidation (Severmann et al., 2008). Mobilized porewater Fe$^{2+}$aq escapes from the sediments, particularly when rates of bacterial sulfate reduction are low and Fe precipitation as pyrite is correspondingly small — as in the source region of the Black Sea. In a redox-stratified basin like the Black Sea, this mobilized Fe may then be transferred laterally along the anoxic redoxcline — i.e., “shuttled” — to the deep basin, where it is trapped by pyrite formed in the euxinic water column (“euxinic waters”, by definition, contain dissolved H$_2$S) (Canfield et al., 1996; Lyons, 1997; Wijsman et al., 2001; Raissel and Anderson, 2005; Lyons and Severmann, 2006).

Identification of Fe shuttling in ancient basins, together with the spatial scale of Fe transport and the related mass balance relationships, is important to understanding Fe cycling in ancient oceans (Raissel, 2006b). For example, oxygenation would lower the stability of dissolved Fe$^{2+}$aq in the water column and hence the system’s capacity to transfer isotopically light Fe to deep ocean basins. As a result, the efficiency of the Fe shuttle may be linked inversely to the presence of dissolved O$_2$ in the water column, favoring higher Fe export in an Archean ocean, prior to the rise of O$_2$ in the atmosphere and ocean (Raissel, 2006a; Severmann et al., 2008).

In sediments of the modern Black Sea, the isotopic expression of the Fe shuttle can be seen in the correlation of $\delta^{56}$Fe with reactive Fe enrichment (Fig. 1) (Severmann et al., 2008). Here we seek to identify the isotopic fingerprint of Fe cycling and specifically the Fe shuttle as expressed in ancient rocks by investigating Fe isotope systematics in two organic carbon-rich black shale units of mid-to-late Devonian age. The Oaktree Creek Formation (OCF) and the younger Genesee Formation (GF) were deposited in the Appalachian basin; the paleogeography, specific depositional settings and redox chemistry of this basin through time are well characterized from previous work, providing a rich geochemical context for the interpretation of the Fe isotope variations (Murphy et al., 2000; Werne et al., 2002; Sageman et al., 2003).

2. Background

2.1. Reactive iron enrichment and isotope expression in the modern Black Sea

Reactive Fe is defined as being reactive toward dissolved sulfide on early diagenetic time scales (years to thousands of years). Operationally, reactive Fe includes amorphous and crystalline Fe-oxides, pyrite, FeS and other pyrite precursors, and the portion of silicate-bound Fe that is reactive in the presence of sulfide (Raissel et al., 1988; Canfield, 1989). Measures of reactive Fe enrichment, derived from speciation studies of sediments accumulated under diverse depositional conditions (Canfield et al., 1996; Raissel and Canfield, 1996, 1998; Poulton and Canfield, 2005; Lyons and Severmann, 2006), include (1) the reactive Fe enrichment factor (the ratio of highly
reactive Fe to total Fe, Fe_{HR}/Fe_T) (Raiswell and Canfield, 1998; Anderson and Raiswell, 2004), (2) the degree of pyritization (DOP, the ratio of pyrite Fe to total reactive Fe) (Berner, 1970; Raiswell et al., 1988), and (3) the total Fe-to-Al ratio (Fe_T/Al) (Wilkin and Arthur, 2001; Lyons and Severmann, 2006). In the Black Sea and other modern euxinic basins, these proxies reveal elevated concentrations of reactive Fe in euxinic sediments relative to their nearshore oxic counterparts (Canfield et al., 1996; Raiswell and Canfield, 1998; Hurtgen et al., 1999; Warning and Brumsack, 2000; Wijisman et al., 2001; Anderson and Raiswell, 2004; Lyons and Severmann, 2006).

Iron isotope compositions of sediments from the Black Sea demonstrate that the high Fe_T/Al ratios in euxinic sediments coincide with isotopically light Fe, while δ^{56}Fe values are comparatively heavier in oxic shelf sediments where Fe_T/Al ratios are lower, close to the ratios for bulk continental weathering products (Fig. 1) (Severmann et al., 2008). This negative correlation of δ^{56}Fe values with Fe_T/Al is interpreted as a fingerprint of reactive Fe enrichment and specifically the Fe shuttle (Severmann et al., 2008).

2.2. Geological setting

Iron speciation and isotopes were examined in two organic carbon-rich black shale units of mid-to-late Devonian age. The samples were taken from the Akzo Nobel drill core #9455, western New York State, located at 42°44′54.140″N, 77°46′38.368″W (Fig. 2) (Werne et al., 2002; Sageman et al., 2003). The OCF and GF are two stratigraphic units among a series of organic carbon-rich intervals deposited successively in the central Appalachia basin. These shales have been interpreted to represent deepening events that correlate with the mid-to-late Devonian record of eustatic sea-level (Sageman et al., 2003). It is generally agreed that nutrient supply, primary production, bacterial decomposition, water column stagnation and bulk sedimentation rate affected the extent of bottom water anoxia and the rate of organic carbon accumulation in these black shale units, although the relative importance of these factors is debated (Murphy et al., 2000; Sageman et al., 2003; Meyer and Kump, 2008). Independent of this debate, however, duration and spatial extent of anoxia are commonly estimated from geochemical indicators, such as total organic carbon contents (TOC), DOP, trace metal enrichments and organic biomarkers (Murphy et al., 2000; Sageman et al., 2003). DOP values are overall high (0.52–0.95) in the OCF, while the values from the GF are significantly lower (0.15–0.45) (Sageman et al., 2003). Based on the empirically derived classification of DOP (Raiswell et al., 1988; Raiswell and Canfield, 1998; Sageman and Lyons, 2003; Lyons et al., 2009), high DOP values of the OCF unequivocally point to persistently euxinic deposition (DOP > 0.75), whereas lower DOP values of the GF indicate a less reducing depositional environment (DOP < 0.42). Intermediate DOP values (0.45–0.75) in OCF could reflect increased siliciclastic flux beneath euxinic bottom waters (Canfield et al., 1996; Lyons, 1997; Werne et al., 2002; Lyons and Kashgarian, 2005; Lyons and Severmann, 2006). These potential ambiguities in the DOP proxy can be overcome by integrating additional proxies such as Fe_T/Al, TOC and trace metal enrichments. Molybdenum enrichments, in particular, are observed in sediments overlain by euxinic bottom waters (Emerson and Huested, 1991; Crusius et al., 1996; Algeo and Lyons, 2006). In the OCF, high DOP values coupled with high TOC (typically above 5 wt.% and as high as 17.3 wt.%) and pronounced Mo enrichments with Mo/Al ratios (expressed as ppm/wt.%) of up to 59 (compared to average continental crust ratios of 0.19; Taylor and McLennan, 1995) suggest that these shales were deposited beneath a euxinic water column (Werne et al., 2002; Sageman et al., 2003). In the GF, in contrast, low to intermediate DOP values combined with low TOC contents (0.48 wt.% to 6.40 wt.%) and moderately elevated Mo/Al ratios (up to 4) imply a suboxic to intermittently euxinic depositional environment (Murphy et al., 2000; Werne et al., 2002; Sageman et al., 2003; Gordon et al., 2009).

3. Methods

Ten black shale samples from an 8 m interval of the OCF and 11 samples from a 10 m interval of the GF were cut from the core and powdered in the Department of Earth and Planetary Sciences.
of Northwestern University using procedures described in Murphy et al. (2000) and Werne et al. (2002). A standard multi-acid (HNO₃–HF–HCl) digestion was employed for bulk sample analysis, using multiple steps until the samples were dissolved completely. In parallel, a sequential extraction was carried out to quantify the following three individual Fe pools of pyrite (Raiswell et al., 1988; Canfield, 1989; Huerta-Diaz and Morse, 1990; Raiswell et al., 1994): (1) Fe₅₆IRMM: extracted using 12 N boiling HCl for 1 min to target all Fe oxides and some of the Fe in clays, followed by (2) Fe₅₄: 10 N HF for 16 h to extract all residual aluminosilicate Fe and (3) Fe₅₇: 16 N HNO₃ for 2 h to extract all pyrite Fe.

Values for DOP were calculated as Fe₅₆pyrite/(Fe₅₆pyrite+Fe₅₄HCl), as defined by Berner (1970). DOP values were determined for most (but not all) of the samples as part of previous studies (Werne et al., 2002; Sageman et al., 2003) using the standard chromium reduction technique to quantify pyrite-S; pyrite-Fe was calculated assuming an FeS₂ stoichiometry. In this study, Fe₅₆pyrite was measured directly using the modified procedure of Huerta-Diaz and Morse (1990). To fill remaining data gaps and for consistency, we calculated DOP values for all our samples using our Fe₅₆pyrite and Fe₅₄HCl data and compared them with those in Sageman et al. (2003) and Werne et al. (2002). Iron concentrations in pyrite extracts were determined colorimetrically using 0.02% Ferrozine reagent with 1% hydroxylamine-hydrochloride buffered to pH 8 (Stokey, 1970).

For isotopic analyses, Fe extracts were purified by anion exchange chromatography using Bio-Rad AG MP-1 resin following procedures described in detail by Arnold et al. (2004). Yield were determined by comparing Fe concentrations measured colorimetrically with Ferrozine at 562 nm in aliquots taken before and after chromatography. We rejected any samples with yields less than 95%, because lower yields could induce isotopic artifact larger than ~0.15‰ (Anbar et al., 2000). Isotope measurements were conducted in duplicate or triplicate using multi-collector ICP-MS (MC-ICP-MS; Thermo Scientific Neptune, ASU) for each solution. We used the medium and high mass resolution modes of the instrument to resolve the isotopes of interest from the polyatomic interferences from ArN⁺, ArO⁺ and ArOH⁺ (Weyer and Schwieters, 2003; Arnold et al., 2004). The sample-standard-bracketing (SSB) method was used in combination with an internal Cu “element spike” to correct for systematic variation in mass bias (Weyer and Schwieters, 2003; Arnold et al., 2004).

Isotope data are reported using the δ notation relative to the international Fe standard IRMM-14 which is a synthetic standard supplied as metallic Fe (Taylor et al., 1992):

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

We only accepted instrument runs when Cu-normalized δ⁵⁶FeIRMM values were within 0.5‰ from non-normalized values. All accepted runs yielded agreement between δ⁵⁶FeIRMM and δ⁵⁶FeIRMM within 0.05‰ on a per amu basis. Natural standards, as well as gravimetrically prepared standards, were measured together with samples to monitor measurement accuracy. Long-term reproducibility of IRMM-14 standards was 0.02 ± 0.05‰ (1-SD) in δ⁵⁶FeIRMM based on 43 measurements over 7 months.

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

In Table 1 we report δ⁵⁶FeIRMM as well as isotopic ratios normalized to average igneous rocks (δ⁵⁶FeIRGG) which have a mean value of 0.09±0.05 (1-SD) relative to IRMM-14 and have been used as the terrestrial baseline for Fe isotopes (Beard et al., 2003b). In all the plots and the following text, δ⁵⁶Fe refers to δ⁵⁶FeIRGG, this choice allows for direct comparison to detrital input, which is the dominant Fe source for most marine sediments. Analytical uncertainties were determined from repeated MC-ICP-MS measurements of each solution.

Sequential Fe extractions can introduce analytical bias, for example, if there is isotopic fractionation associated with the extraction and the recovery of the targeted Fe pool is not quantitative. To test for such isotope effects during our extraction procedures we have measured the isotope compositions of total digests of pure mineral phases and compared these to sequential extractions of the pure minerals, as well as synthetic mineral composites (Table 2). All pure Fe minerals were derived from commercially available hand specimens of natural samples. The pure mineral phases were treated in the same manner as our Devonian shale samples and ground in a ball mill prior to chemical treatment. Our results show that goethite, siderite and pyrrhotite were extracted quantitatively within error using the boiling 12 N HCl extraction, and the δ⁵⁶Fe of the pure mineral bulk digest agrees within error with the sequential extraction step that targets that specific mineral or mix of minerals. As expected, the two silicate materials (chlorite and basalt) were partially extracted by boiling HCl, but neither phase shows significant isotopic fractionation during boiling 12 N HCl or 10 N HF extraction. Further, the δ⁵⁶Fe value for the boiling 12 N HCl extract of the two composite samples is elevated relative to the isotopic composition of goethite, the major phase extracted by 12 N HCl because most of the isotopically heavier chlorite was also extracted with this step. The lighter values for the 10 N HF extract of the composites relative to pure chlorite may be due to contributions from residual Fe oxides following the HCl extraction. Importantly, the δ⁵⁶Fe value for the 16 N HNO₃ extract of the sequentially extracted composites is analytically indistinguishable from the pure pyrite. Therefore, Fe isotopes measured on HNO₃ extraction should truly reflect the isotope composition of pyrite Fe.

4. Results

4.1. Iron content, speciation, and proxies

The OCF has a variable total Fe content ranging from 1.9 wt.% to 7.1 wt.% and an average Fe₅₇ of 4.5 ± 1.7 wt.% (1-SD; Table 1; Fig. 3). Total Fe contents for the GF vary from 2.6 wt.% to 4.3 wt.% with a lower average of 3.2 ± 0.5 wt.% (1-SD; Table 1; Fig. 3). Normalizing Fe₅₇ to Al to assess Fe enrichment corrects for dilution by biogenic components. The average Fe₅₇/Al ratio of 0.67 in the OCF is elevated relative to the upper continental crust value of 0.48 (Rudnick and Gao, 2003), indicating significant Fe enrichment. The ratio of 0.47 for the GF is essentially indistinguishable from average weathering input (Table 1; Fig. 3).

In the OCF shales, the dominant Fe phase is Fe₅₆pyrite, accounting for 35 wt.% to 81 wt.% of total Fe with an average of 63 ± 16 wt.% (1-SD); Fe₅₆HCl is mostly a minor Fe pool (Table 1; Fig. 3). In almost all the GF samples, in contrast, Fe₅₆HCl is the largest fraction, suggesting that unsulfidized Fe oxides and HCl-extractable Fe-silicate phases (such as clays) are the dominant reactive Fe pool, reaching up to 58 wt.% of the total Fe. The remaining Fe fractions, Fe₅₄ and Fe₅₇, are present in about equal amounts in the GF (Table 1; Fig. 2). These data are consistent with DOP values for the OCF samples varying from 0.43 to 0.92 with an average of 0.77 ± 0.15 (1-SD) and much lower values for the GF samples — 0.19 to 0.48 with an average of 0.35 ± 0.10 (1-SD; Table 1; Fig. 3). DOP values reported here and those from Sageman et al. (2003) are in strong agreement despite the different methods used for determining Fe₅₆pyrite, with <0.1 offset for the majority of
### Table 1

Iron content, proxies, speciation, and Fe isotope composition.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Content</th>
<th>Iron proxies</th>
<th>Speciation</th>
<th>Isotope composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Depth</td>
<td>Fe&lt;sub&gt;T&lt;/sub&gt;</td>
<td>TOC&lt;sup&gt;c&lt;/sup&gt;</td>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Basalt (BIR)</td>
<td>162.72</td>
<td>43 ± 1.8</td>
<td>1.7</td>
<td>0.48 ± 0.62</td>
</tr>
<tr>
<td>Chlorite</td>
<td>163.7</td>
<td>3.0</td>
<td>0.5</td>
<td>0.38 ± 0.04</td>
</tr>
<tr>
<td>Pyrite</td>
<td>164.7</td>
<td>3.0</td>
<td>5.8</td>
<td>0.38 ± 0.04</td>
</tr>
<tr>
<td>Average</td>
<td>3.2</td>
<td>0.35</td>
<td>0.47</td>
<td>46 ± 25</td>
</tr>
</tbody>
</table>

### Table 2

Isotope compositions of pure minerals and mineral composites for total digests and sequential chemical separations demonstrate the robustness of the extraction procedures at sampling the intended Fe pools.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Total digest</th>
<th>Boiling 12 N HCl</th>
<th>10 N HF extraction</th>
<th>16 N HNO&lt;sub&gt;3&lt;/sub&gt; extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ&lt;sup&gt;56&lt;/sup&gt;Fe</td>
<td>2-SD&lt;sup&gt;e&lt;/sup&gt;</td>
<td>δ&lt;sup&gt;56&lt;/sup&gt;Fe</td>
<td>2-SD&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Goethite</td>
<td>-0.52</td>
<td>±0.06</td>
<td>97</td>
<td>-0.55</td>
</tr>
<tr>
<td>Siderite</td>
<td>-0.36</td>
<td>±0.00</td>
<td>102</td>
<td>-0.33</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.11</td>
<td>±0.06</td>
<td>90</td>
<td>0.16</td>
</tr>
<tr>
<td>Basalt (BIR)</td>
<td>-0.05</td>
<td>±0.07</td>
<td>61</td>
<td>-0.18</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>-0.45</td>
<td>±0.13</td>
<td>98</td>
<td>-0.45</td>
</tr>
<tr>
<td>Pyrite</td>
<td>-0.39</td>
<td>±0.13</td>
<td>0.2</td>
<td>n.d.</td>
</tr>
<tr>
<td>Composite A</td>
<td>72</td>
<td>±0.26</td>
<td>2.7</td>
<td>±0.08</td>
</tr>
<tr>
<td>Composite B</td>
<td>70</td>
<td>±0.28</td>
<td>1.5</td>
<td>±0.32</td>
</tr>
</tbody>
</table>

Samples (17 out of 18). Taken together, the Fe<sub>T</sub>/Al and DOP data confirm the distinctly different depositional redox conditions for two black shale units inferred previously from Fe geochemistry as well as sediment fabric, TOC contents, redox-sensitive elemental enrichments (Mo, V + Cr and Mn) and S isotope compositions (Sageman et al., 2003). The OCF was deposited beneath a dominantly euxinic water column associated with reactive Fe enrichment in the sediment, whereas the GF was formed in a basin that was less reducing and most likely intermittently euxinic (Sageman and Lyons, 2003).
4.2. Iron isotope compositions of bulk black shales and pyrite

Ten bulk black shale samples from the OCF display relatively variable bulk Fe isotope compositions, covering a ∼0.5‰ range from −0.44‰ to 0.03‰ (Table 1, Fig. 3). Eleven samples from the GF have dominantly positive δ56FeT values, falling into a narrower range from −0.09‰ to 0.12‰ (Table 1, Fig. 3). To examine the effect of depositional conditions on Fe isotope compositions, δ56FeT values are plotted versus FeT/Al and DOP (Figs. 4a and 5, respectively). δ56FeT values for OCF samples display strong co-variation (except the samples 329.48 and 334.63) with both FeT/Al and DOP — i.e., δ56FeT values decrease with increasing FeT/Al and DOP, while these correlations are not apparent for GF samples (Figs. 4a and 5).

All extracted pyrite samples from both formations yield δ56FePyb < 0‰, lighter than average igneous rocks and bulk weathering products (Table 1; Fig. 3). δ56FePy cover a similar range for both units, −0.57‰ to −0.03‰ for the OCF and −0.66‰ to −0.12‰ for the GF (Table 2, Fig. 3).

5. Discussion

Four major observations emerge from the above relationships. First, nine out of ten bulk samples from the OCF and all pyrite extracts from both formations have light Fe isotope compositions relative to average terrestrial igneous rocks (δ56FeT = 0.00 ± 0.05‰, n = 46; Beard et al., 2003b) and the average continental weathering flux (δ56FeT = 0.02 ± 0.07‰, n = 61; Beard et al., 2003a). Second, bulk isotope compositions of the OCF (mean δ56FeT = −0.18 ± 0.15‰, 1-SD) are isotopically light relative to the average continental weathering flux and span a range of ∼0.5‰, similar to observations in the Black Sea (Fig. 3). In contrast, bulk δ56Fe of the GF are relatively heavy (mean δ56FeT = 0.04 ± 0.06‰, 1-SD) compared to those of the OCF and span a range of only ∼0.2‰. Third, δ56FeT and FeT/Al are for the most part negatively correlated for the OCF samples, while the GF samples cluster at high δ56FeT and low FeT/Al values (Fig. 4a). We observe a similar negative correlation for δ56FeT and DOP (Fig. 5). Fourth, pyrite isotope data span similar ranges for both formations, although δ56FePy correlates well with δ56FeT in the OCF but not in the GF (Fig. 6).
Below, we consider whether these observations are consistent with the Fe shuttle hypothesis, using the Fe isotope systematics of the Black Sea as a modern analog. In particular, we discuss (1) the production of light Fe isotope signatures in the euxinic OCF and their coupling with FeT/Al and DOP and (2) the processes responsible for the variable and light Fe isotope signature in the pyrites from the GF, particularly as compared to the more homogenous and heavier δ⁵⁶Fe values in the GF bulk rock.

5.1. Controls on bulk Fe isotope composition

Notable correlations between bulk δ⁵⁶Fe and paleo-redox Fe proxies (FeT/Al and DOP) in the OCF suggest that the Fe isotope signatures are related to the processes that control FeT/Al and DOP (Figs. 4a and 5). The elevated FeT/Al ratios and DOP values provide strong evidence for Fe enrichment in euxinic black shales in the OCF, presumably through the addition of reactive Fe (Wijisman et al., 2001; Anderson and Raiswell, 2004; Lyons and Severmann, 2006). Here, we propose that the light Fe isotope signatures in bulk sediments of the OCF are the result of a shelf-to-basin Fe shuttle, as seen in the modern Black Sea (Severmann et al., 2008).

Sedimentary pore fluids, which are considered the primary source of shelf-derived benthic Fe flux, have a distinctly light isotope composition with δ⁵⁶Fe values as low as −3.4‰ (Bergquist and Boyle, 2006; Severmann et al., 2006; Homoky et al., 2009). These light values are interpreted to be the product of extensive sedimentary Fe redox recycling during early diagenesis, where low δ⁵⁶Fe pore fluids generated during microbial and/or abiotic Fe reduction are shifted to even lighter values as bioturbative injection of oxic seawater causes partial re-oxidation of porewater Fe²⁺(aq), preferentially removing heavy Fe isotopes into ferrihydrite (Severmann et al., 2006; Homoky et al., 2009). Some of the dissolved Fe²⁺(aq) that escapes from the shelf sediments above the chemocline would re-precipitate at the sediment–water interface, causing a further depletion in δ⁵⁶Fe of the residual dissolved Fe²⁺(aq) (Bullen et al., 2001; Severmann et al., 2008). Stabilization of the residual benthic Fe efflux by ligands or transport as very fine-grained Fe-oxhydroxides facilitates the lateral transport within the chemocline and in the upper water column over hundreds of kilometers (Santana-Casiano et al., 2000; Wijisman et al., 2001; Lam et al., 2006; Nishioka et al., 2007). Hence, reactive Fe transported laterally from anoxic or suboxic continental shelf is very likely to have an Fe isotope signature at least as light as that seen in pore waters of suboxic sediments (Lyons and Severmann, 2006; Severmann et al., 2008), although the Fe isotope composition of the benthic Fe flux from sediments to oxygen-deficient bottom waters has so far not been measured directly.

We hypothesize that a similar shelf-to-basin Fe transfer process might have occurred along the oxic shelf and basin contemporaneous with OCF deposition. The Bell Shale of Ontario, west of the OCF, has been attributed to a broad expanse of shallow “shelfal” deposition (Desantis et al., 2004), providing geological evidence for an oxic shelf analogous to that along the margin of the modern Black Sea. Under the inferred euxinic conditions, the flux of reactive Fe export was likely incorporated near-quantitatively into syngenetic pyrites (i.e., forming in the water column) followed by settling to the seafloor. The relatively depleted and uniform δ⁴⁴S/⁴⁴S pattern in OCF pyrites and high DOP values (with the majority greater than 0.75) are consistent with open-water, Fe-limited formation of syngenetic pyrites, providing an efficient trapping mechanism (Lyons, 1997; Raiswell and Canfield, 1998; Werne et al., 2002). Isotopically light reactive Fe is transferred by the “shuttle” from the shelf to the deep basin, causing an increase in FeT/Al, a decrease in δ⁵⁶Fe of bulk sediments, and thus an overall negative correlation between FeT/Al and δ⁵⁶Fe values (Fig. 4a). The correlation is roughly linear when plotted as δ⁵⁶Fe versus Al/FeT, as expected from a simple two-component mixing relationship between isotopically light shuttle Fe and heavier detrital Fe (Fig. 4b); the correlation between δ⁵⁶Fe versus FeT/Al for the OCF samples presumably reflects a mixing hyperbola (Fig. 4a). The correlation between δ⁵⁶Fe and DOP can be interpreted similarly, because DOP and FeT/Al are generally correlated under euxinic condition (except for sample 329.48; Fig. 5). We note that the OCF samples 329.48 and 334.63 fall off the general δ⁵⁶Fe versus Fe proxy trends (Figs. 4 and 5). Re-extraction and re-analysis of a duplicate of one of these two samples (334.63) yielded the same isotope value within error, arguing against an analytical artifact. The explanation for these outliers is unknown.

Another way to generate light sedimentary Fe isotope compositions, independent of the shuttle, is through hydrothermal input. Hydrothermal Fe has been observed to have isotope compositions ranging from −0.7‰ to −0.2‰ in modern deep-sea systems, with most values close to −0.3‰ (Sharma et al., 2001; Beard et al., 2003a; Severmann et al., 2004). However, light Fe isotope compositions in the OCF are not easily explained by such Fe sources. Although tectonostratigraphic models for deposition of black shales in the GF and OCF argue for basin deepening events that occurred during periods of tectonic activity in the foreland orogenic belt (Ettensohn et al., 1988), there is no evidence for hydrothermal activity in the basin. Furthermore, deposition of the OCF probably occurred during one of the most restricted periods in the basin’s history. Therefore, even if enhanced hydrothermal activity occurred in some areas of the Devonian ocean, it is difficult to envision this having a strong influence on Appalachian basin waters during deposition of the OCF.

Assuming two-component mixing between light Fe (presumably from the shuttle source) and heavier detrital Fe, we can estimate the isotopic composition of the light Fe component on a sample-by-sample basis using the method described in Severmann et al. (2008):

\[
\delta^{56}\text{Fe}_{\text{Ex}} = \delta^{56}\text{Fe}_{\text{T}} \times \left[ \frac{\text{Fe}_{\text{T}}}{\text{Fe}_{\text{Ex}}} \right]
\]

where FeT is the benthic export Fe flux. This flux can be determined by:

\[
\text{Fe}_{\text{Ex}} = \text{Fe}_{\text{T}} - \text{Al} \times \left( \frac{\text{Fe}_{\text{T}}}{\text{Al}_{\text{detri}}} \right)
\]

where FeT and Al are total Fe and Al contents measured in each sample, and (FeT/Al)detri is the assumed total Fe-to-Al ratio for detrital material entering this basin. We further assume a δ⁵⁶Fe value of 0‰ for the detritally derived Fe, i.e., average weathering flux, consistent with Beard et al. (2003b), and use the average FeT/Al of the GF bulk samples, 0.47, as the most likely FeT/Al to Al ratio for (FeT/Al)detri. This FeT/Al value is very close to the continental FeT/Al value of 0.48 (Rudnick and Gao, 2003). The calculations yield a predicted mean δ⁵⁶Fe for the light component of −0.73 ± 0.35‰ (1-SD; excluding the sample 334.63 and two samples showing no reactive Fe enrichments), compared to igneous rocks and average weathering products.

![Fig. 6. Relationship between δ⁵⁶Fe and δ⁵⁶Fe in the Geneseo Formation (GF) and in the Oatka Creek Formation (OCF).](image)
This simple two-component mixing model also demonstrates that hydrothermal efflux with a mean value close to $-0.3\%\text{o}$ would not be sufficiently light to explain the observed shift in the bulk isotope compositions of the OCF deposits. Instead, the mean estimated $\delta^{56}\text{Fe}_{\text{ex}}$ value is in the upper range of values measured for porewater $\text{Fe}^{2+}_{\text{aq}}$ in modern, bioturbated suboxic continental shelf sediments ($-3.4\%\text{o}$ to $-0.5\%\text{o}$; Severmann et al., 2006; Homoky et al., 2009). Our $\delta^{56}\text{Fe}_{\text{ex}}$ value for the Appalachian basin is $-0.5\%\text{o}$ heavier than the isotope composition of the light Fe flux estimated in the modern Black Sea ($-1.3\%\pm0.3\%\text{o}$; Severmann et al., 2008). The isotope composition of the light, exported Fe end member is a function of multiple factors that may vary among basins, including the $\delta^{56}\text{Fe}$ value of the pore fluids on the shelf and the fraction of porewater-derived Fe that undergoes re-oxidation and precipitation during efflux and transport to the deep basin. Coupling of DIR with an effective oxidation mechanism, which may generally be considered to vary with the degree of bioturbation and injection of $\text{O}_2$ to the sediments, is required for sufficient redox recycling to generate such low isotope signatures in the shelf porewaters (Severmann et al., 2008). However, the intensity and penetration depth of bioturbation in the Devonian are both considered to have been lower (Thayer, 1982). The absence of evidence for significant bioturbation and benthic fauna in the Appalachian basin during the late Devonian (Thompson and Newton, 1987; Sageman et al., 2003) suggests that redox recycling during that time period may not have been as vigorous as that of the Black Sea today, resulting in a smaller isotope fractionation in $\delta^{56}\text{Fe}$ of pore fluids on the shelf during the deposition of the GF and the OCF. Consequently, the isotope composition of shelf-derived Fe reaching the deep basin would not have been as light in the Devonian as today, even if the export efficiency for reactive Fe was comparable.

In contrast to the OCF, the overall moderate Fe$_2$/Al ratios and DOP values in the GF indicate that Fe enrichment did not occur during deposition of the GF. The absence of an efficient Fe shuttle may point to a reduced benthic Fe flux from the shelf sediments during that time. Bottom water oxygen concentrations on the shelf may affect the flux of Fe(II) out of the sediments, as well as the kinetics of Fe(II) oxidation within the bottom boundary layer, which ultimately determines the magnitude of the Fe export flux (Lohan and Bruland, 2008). It is also possible that, even if there was a similar Fe redox cycle on the shelf and a significant Fe export flux, such Fe failed to be efficiently trapped in the deep basin due to the absence of dissolved water column $\text{H}_2\text{S}$ and syngentic pyrite formation, just as sediments in the modern deep oxic ocean do not show reactive Fe enrichments (Lyons and Severmann, 2006). Consistent with this argument, the bulk Fe isotope compositions in the GF average $-0.04\%\pm0.06\%\text{o}$ (1-SD), approximating the detratically derived Fe source into the basin. These data constitute the source end member for the trend line defined by $\delta^{56}\text{Fe}_{\text{py}}$ versus Fe$_2$/Al (Fig. 4a).

Overall, the consistency of our $\delta^{56}\text{Fe}_{\text{t}}$ data with other sedimentary Fe proxies demonstrates that Fe isotopes could tie Fe enrichments in ancient shales and oceans to the shuttle mechanism. Hence, the bulk Fe isotope signature may be used in ancient rocks to reflect system-wide Fe cycling and repartitioning, and to distinguish between different depositional redox environments.

5.2 Controls on pyrite Fe isotope compositions

In contrast to the good correlation between $\delta^{56}\text{Fe}_{\text{t}}$ and $\delta^{56}\text{Fe}_{\text{py}}$ in the OCF, we find no correlation in the GF (Fig. 6), suggesting different processes control pyrite versus bulk isotope compositions in the two formations. These observations can be explained if Fe isotopes in pyrite reflect either the isotopic composition of the reactive Fe source or a fluid-mineral fractionation factor expressed during pyrite formation, or some combination. Which behavior dominates depends on the extent to which reactive Fe is converted to pyrite, which in turn depends on water column redox conditions as discussed below.

The $\delta^{56}\text{Fe}_{\text{py}}$ values of the OCF most likely record the isotope composition of the source as a result of quantitative transfer of Fe from solution to minerals under persistently euxinic and therefore Fe-limited conditions (Raiswell and Berner, 1985; Lyons and Berner, 1992). The close correlation between $\delta^{56}\text{Fe}_{\text{t}}$ and $\delta^{56}\text{Fe}_{\text{py}}$ is indicative of the coupling of pyrite Fe isotope compositions with Fe proxies, which we consider as a further fingerprint for the Fe shuttle. We concluded in Section 5.1 that bulk sediments preserve the Fe shuttle signature by syngentic pyrite formation as an efficient trapping mechanism, and it is logical therefore to expect pyrite alone to carry this signature.

In contrast, we propose that the $-0.5\%\text{o}$ variation of $\delta^{56}\text{Fe}$ recorded in the GF pyrite is due to mineral-fluid isotope fractionation during pyrite formation in a suboxic or intermittently euxinic marine environment. Under these conditions, most of the pyrite was likely formed in the sediment during early diagenesis, and the rate of pyrite precipitation was probably limited by the availability of $\text{H}_2\text{S}$ rather than of reactive Fe as is consistent with low DOP values. Pyrite isotope compositions therefore express the fluid-mineral isotope fractionation factor to varying extents during incomplete conversion of the reactive Fe to pyrite.

Unfortunately, the fractionation factors in the Fe–S system are currently not well known. Theoretical calculations predict that $\delta^{56}\text{Fe}$ of pyrite should be heavier than that of coexisting $\text{Fe}^{2+}_{\text{aq}}$ (Polyakov and Mineev, 2000; Polyakov et al., 2007). This prediction has not been verified experimentally. However, an experimental study of Fe isotope fractionation during precipitation of synthetic mackinawite (FeS), which forms as a natural precursor mineral to pyrite (Berner, 1970; Rickard, 1975), shows that FeS is isotopically light relative to the Fe$^{2+}_{\text{aq}}$ source. The isotope fractionation factor ($\Delta\delta^{56}\text{Fe}_{\text{py}}$) is reported to be $-0.3\%$, when approaching isotopic equilibrium and could be as high as $-0.8\%$ when FeS precipitation is rapid and kinetic isotope effects dominate (Butler et al., 2005). A recent study of a seafloor hydrothermal vent reveals that the $\delta^{56}\text{Fe}$ of hydrothermal pyrite is lower than associated hydrothermal fluids by $-0.91\%$ (Rouxel et al., 2008), consistent with the isotope trends for Fe observed by Butler et al. (2005).

We may assume that dissolved Fe$^{2+}_{\text{aq}}$ for pyrite formation was generated first via either DIR or abiotic processes (i.e., sulfidization). In either case, light Fe isotopes would most likely be enriched in the resulting Fe$^{2+}_{\text{aq}}$ (Beard et al., 2003b), although isotope fractionation during abiotic processes remains to be tested. Fe$^{2+}_{\text{aq}}$ then could combine $\text{S}^{2-}$ to form Fe-sulfide (initially as FeS, which is subsequently converted to pyrite). This would result in a lighter isotope composition in the sulfide phase owing to the mineral-specific isotope fractionation ($\Delta\delta^{56}\text{Fe}_{\text{py}}$) inferred from the experiment discussed above and non-quantitative Fe transfer under Fe-replete condition. Therefore, negative $\delta^{56}\text{Fe}$ values in pyrite are to be expected, consistent with our observation that $\delta^{56}\text{Fe}$ in pyrite from the GF is uniformly lower than average igneous rocks and weathering products (Fig. 2). Light Fe isotope signatures in pyrites have been reported previously for modern environments. For example, the isotope studies of two modern suboxic to anoxic continental shelf sediments off central California reveal the average $\delta^{56}\text{Fe}$ values of sedimentary pyrites to be $-0.78\%\pm0.15\%$ relative to terrestrial igneous rocks (Severmann et al., 2006). This relationship has been attributed to the isotopically depleted Fe$^{2+}_{\text{aq}}$ produced by DIR and the fractionation during pyrite formation (Severmann et al., 2006). Further mechanistic research into isotope fractionation would allow more definitive interpretations of the light Fe isotope compositions in sedimentary pyrites.

6. Conclusions and implications

The Fe isotope compositions of black shales from two formations deposited in the same basin have contrasting patterns that correlate with differing depositional redox environments inferred
independently for two deepening events. In the more reducing Oatka Creek Formation, the relationships between Fe isotope variation and sedimentary Fe proxies are similar to those reported recently for the Black Sea, suggesting a shared mechanism (Severmann et al., 2008).

The overall low $\delta^{56}{\text{Fe}}$ of bulk black shales is in accord with the reactive Fe enrichment suggested independently by the Fe redox proxies — DOP and Fe/Al ratios — and is consistent with a shelf-to-basin Fe shuttle accompanied by a net addition of isotopically light Fe to the euxinic sediments.

Because pyrite formation under euxinic bottom water conditions is typically Fe-limited, the pyrite isotope compositions of the OCF ($\delta^{56}{\text{Fe}}_{\text{py}} = -0.57\%$ to $-0.03\%$, relative to average igeneous rocks) are inferred to approach the isotope composition of the reactive Fe source. By contrast, $\delta^{56}{\text{Fe}}_{\text{py}}$ values from the Geneseo formation ($\delta^{56}{\text{Fe}}_{\text{py}} = -0.66\%$ to $-0.12\%$, relative to average igeneous rocks) mostly likely reflect incomplete reactive Fe consumption and mineral-specific isotope fractionations during early diagenetic, Fe-replete pyrite formation. Therefore, despite the apparently similar ranges in pyrite isotope compositions in the two formations, when we take sedimentary Fe proxies that indicate different depositional redox into account, they are interpreted to represent different Fe cycling mechanisms and pathways of pyrite formation.

Our results capture for the first time the isotopic fingerprint of a shelf-to-basin Fe shuttle in an ancient marine depositional system. This shuttle is a little known but likely central player in the global Fe cycle, particularly at times of widespread oxygen deficiency in the ocean. Hence, the Fe isotope proxy, when used in concert with other geochemical indicators, holds great potential for fingerprinting Fe sources, the persistent coupling of biotic or abiotic Fe reduction with oxidation mechanism and therefore the extent of redox cycling in ancient geological settings.

Late Archean black shales generally display much more variable and negative isotope compositions than their Phanerozoic counterparts (e.g., Rouxel et al., 2005; Yamaguchi et al., 2005; Johnson et al., 2008a). The Fe chemistry of the Archean ocean and the possible operation of an Fe shuttle during that time await further exploration. More studies of the type undertaken here, in combination with complementary work in modern oxygen-deficient basins, will better resolve the link between environmental redox and Fe cycling and will expand and strengthen the utility of Fe isotopes in studies of ancient ocean chemistry.

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