Iron isotope fractionation in a sulfide-bearing subterranean estuary and its potential influence on oceanic Fe isotope flux

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A B S T R A C T

We trace pathways of Fe reactions in the Indian River Lagoon (Florida, USA) subterranean estuary using Fe isotopes to provide new constraints on Fe-isotopic fractionation in a sulfide-bearing subterranean estuary. Porewater δ56Fe values increase from −1.16‰ at 115 cm depth to +0.2‰ at 7 cm depth due to isotope fractionation in three distinct lithostratigraphic zones. The deepest zone contains orange sands with elevated Fe-oxide contents (0.2 wt.%) that dissolve through diagenetic Fe-oxide reduction and elevate Fe concentrations in porewaters (100 to 300 μM/l). This reaction causes porewater δ56Fe values to be ~1‰ lighter than the sediment δ56Fe values. An intermediate zone contains white Fe-poor sands, with Fe-oxide contents ~0.1 wt.% and dissolved Fe concentrations <20 μM/l. This zone is a sink for dissolved Fe through adsorption of isotopically heavy dissolved Fe(II) onto mineral surfaces. This adsorption results in porewater δ56Fe values that are as much as 1.8‰ lighter than sediment δ56Fe values. The uppermost zone contains organic carbon and Fe-sulfide rich black sediments with low dissolved Fe (<1 μM/l) and elevated porewater sulfide (up to 600 μM/l) concentrations. Precipitation of isotopically light Fe-sulfides increases the porewater δ56Fe values as much as 0.68‰ more than corresponding sediment δ56Fe values. The near-surface Fe-sulfide precipitation delivers to the lagoon dissolved Fe with slightly positive δ56Fe values, averaging about +0.24‰, via submarine groundwater discharge (SGD). Iron-sulfide precipitation in sulfide-containing subterranean estuaries thus may result in a previously unidentified source of isotopically heavy Fe to the coastal oceans.

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1. Introduction

Iron is a micronutrient involved in primary productivity in open oceans and coastal waters and thus is important to marine ecosystems (Martin and Fitzwater, 1988; Martin et al., 1994; Hutchins and Bruland, 1998). In coastal waters, Fe concentrations range from a few nanomoles (nM) to tens of nanomoles (Hutchins et al., 1998; Bruland et al., 2001; Lippiatt et al., 2010) and these concentrations are orders of magnitude higher than Fe concentrations in the open ocean, which range from 0.1 to 1.0 nM Fe (Wu, 2007; Lacan et al., 2008). The different Fe concentrations in coastal and open oceans result in part from Fe-oxide reduction and biogeochemical cycling of Fe in continental shelf sediments (Elrod et al., 2004; Chase et al., 2007) and are reflected in distinct isotopic compositions of open oceans, coastal surface waters, and porewaters in shelf sediments (Severmann et al., 2006, 2010; Staubwasser et al., 2006; Rouxel et al., 2008; Homoky et al., 2009).

Coastal zones typically have negative dissolved δ56Fe values with reported values of about −0.9‰ for the surface waters of eastern coastal North America, of −1.3‰ for porewaters from Amazon shelf, and −4.0‰ to −0.7‰ for porewaters from the California–Oregon shelf (Bergquist and Boyle, 2006; Homoky et al., 2009; Rouxel and Auro, 2010; Severmann et al., 2010). In contrast, δ56Fe values are generally slightly positive in open ocean water ranging from +0.02‰ to +0.23‰ in the Atlantic sector of the Southern Ocean (Lacan et al., 2008), up to +0.58‰ in the equatorial Pacific Ocean (Radic et al., 2011), and up to +0.71‰ in the North Atlantic Ocean (John and Adkins, 2010). Isotopically lighter Fe in coastal zones than ocean basins raises the question of what causes the differences in isotopic composition between coastal and open oceans. Positive δ56Fe values occur in river water (δ56Fe values of up to +0.43‰) and these heavy isotope ratios are preserved during estuarine mixing (Escoube et al., 2009).

Dissolved Fe derived from resuspended river sediments have δ56Fe values of about 0.04‰ (Radic et al., 2011). Like surface water runoff, submarine groundwater discharge (SGD) from coastal aquifers (commonly referred to as subterranean estuaries, see Fig. 1a and Moore, 1999) can contribute large amounts of Fe to coastal waters (Windom et al., 2006; Moore, 2010; Roy et al., 2010). This potentially...
increasing the δ supplies DO, SO4 of porewater from wave, tidal pumping and bioirrigation, which between hypoxic fresh groundwater and oxic water column, aeration dissolved organic carbon (DOC), changes in pH, hydrologic mixing further decrease in the dissolved δFe(III)-oxides, which acts as a sink for dissolved Fe(II), resulting in a et al., 2004, 2006; Charette et al., 2005; Meile et al., 2005; Spiteri et al., 2008). At this site, negative porewater sul process common to most subterranean estuaries. Precipitation of Fe-δ values by 4.91‰ were found to result from the combination of two diagenetic pathways: 1) dissimilatory Fe(III)-oxide reduction at the freshwater–saltwater boundary of the subterranean estuary that acts as the major source of dissolved Fe(II) and decreases dissolved δFe values by ~1‰ relative to slightly fractionated groundwater (~0.5‰); and 2) oxidative precipitation of dissolved Fe(II) as solid Fe(III)-oxides, which acts as a sink for dissolved Fe(II), resulting in a further decrease in the dissolved δFe values by ~2 to ~5‰. (Rouzel et al., 2008). Processes that control Fe diagenesis vary from one subterranean estuary to another and thus Fe isotope ratios should differ between subterranean estuaries. These processes include concentrations of dissolved oxygen (DO), sulfate (SO4 2-), sulfide (S2-), dissolved organic carbon (DOC), changes in pH, hydrologic mixing between hypoxic fresh groundwater and oxic water column, aeration of porewater from wave, tidal pumping and bioirrigation, which supplies DO, SO4 2- and lable marine DOC from water column (Martin et al., 2004, 2006; Charette et al., 2005; Meile et al., 2005; Spiteri et al., 2006, 2008a,b; Santos et al., 2008; Beck et al., 2010; Roy et al., 2010).

Waquoit Bay porewaters have little DOC and no SO4 2- reduction, a process common to most subterranean estuaries. Precipitation of Fe-sulfide fractionates lighter Fe isotopes into the solid phase, thereby increasing the δFe values of the dissolved Fe(II) (Butler et al., 2005; Severmann et al., 2006; Bennett et al., 2009; Guilbaud et al., 2011). Consequently, sulfidic subterranean estuaries could contribute heavy Fe isotopes to coastal waters, thereby potentially influencing open ocean δFe values. Both Fe-oxide reduction and Fe-sulfide precipitation can occur in subterranean estuaries so that the δFe values of dissolved Fe(II) would depend on the dominating diagenetic pathway, whereby positive values would occur when Fe-sulfide reaction dominates or negative δFe values would occur when Fe-oxide reduction dominates (Severmann et al., 2006).

We report here δFe values for porewaters and sediments in the subterranean estuary in Indian River Lagoon, Florida. At this location, SO4 2- reduction produces S2-, which reacts with dissolved Fe(II) and precipitates Fe-sulfides (Roy et al., 2010). Iron-oxide reduction produces dissolved Fe(II) below the zone of Fe-sulfide precipitation and this dissolved Fe(II) flows upward with SGD. We use the differences between sediment and porewater δFe values to identify the pathways of Fe diagenesis and isotopic signature of SGD-derived Fe. This study provides new constraints on Fe-isotopic composition of a sulfide-bearing subterranean estuary.

2. Location, sampling and background

Indian River Lagoon is located along the east coast of Florida and the study site (28°08.0’ N and 80°37.5’ W) is in the central part of the lagoon (Fig. 1b). The subterranean estuary of Indian River Lagoon contains sediments representing two distinct depositional environments including estuarine organic matter-rich black sediments near the sediment–water interface overlying fluvial Fe-oxide coated orange sands (Hartl, 2006; Roy et al., 2010, 2011). The change in depositional
condition with transgression results in a reverse diagenetic profile, with \( \text{SO}_2^- \) reduction in estuarine sediments overlying Fe-oxide reduction in the fluvial sediments (Roy et al., 2010).

Much is known of the hydrogeology and Fe diagenesis in the Indian River Lagoon subterranean estuary (Belanger and Walker, 1990; Pandit and El-Khazen, 1990; Cable et al., 2004, 2006; Martin et al., 2004, 2006, 2007; Hartl, 2006; Smith et al., 2006, 2008a,b). Porewater salinity increases gradually from <1 to >30 from the shoreline to about 30 m offshore with a similar increase in chloride (Cl) concentrations. Chloride is conservative and thus we define the freshwater–saltwater boundary of the subterranean estuary to be the 300 mM Cl concentration contour. This geochemical boundary occurred 22.5 m offshore during the sampling time of April 2007 (Fig. 1c). Flow rates of terrestrial SGD (i.e., fresh groundwater from the coastal aquifer) decrease offshore from around 10 cm/day to no flow at the freshwater–saltwater boundary (Martin et al., 2007). Our study area was mainly the freshwater discharge zone of the subterranean estuary where both lateral and vertical flows occur. Considering the relatively longer width (25 m) than the depth of sampling (<2 m), flow is mainly vertical (Martin et al., 2007). Exchange of water across the sediment–water interface by bioirrigation increases offshore and penetrates up to 70 cm deep in sediments at a site located 250 m offshore (Martin et al., 2004, 2006). The pellet number ranges from 1.74 × 10^15 nearshore to 1.25 × 10^11 the seaward edge of the subterranean estuary, indicating solute transportation is dominated by advection (Roy et al., 2011).

Three major lithofacies can be defined based on sediment color. Sediments are orange below about 60 cm below seafloor (cmbsf) and are black above about 40 cmbsf. Intermediate greyish-white sediments occur between the orange and black sediments (Fig. 2a). Based on fossil assemblages, these orange and black sediments were identified to have fluvial (terrestrial) and estuarine (marine) origins, respectively (Hartl, 2006). Thickness of the black marine sediments increases offshore, reflecting about 3 mm/year sea level rise in the study area (Roy et al., 2010). Sediment teaching studies showed that the orange coloration derives from Fe-oxide coatings and the black coloration derives from Fe-sulfide staining (Roy et al., 2010).

Dissolved Fe concentrations vary by three orders of magnitude across the seepage face, with the highest concentrations at the freshwater–saltwater boundary and lowest concentrations at the shoreline. Elevated Fe concentrations are caused by slow flow and elevated marine DOC concentrations at the freshwater–saltwater boundary, resulting in the enhanced Fe-oxide reduction and accumulation of dissolved Fe (Roy et al., 2010). Maxima in dissolved Fe concentrations occur in the orange sediments while Fe minima and dissolved \( \text{S}_2^- \) maxima occur in the shallow black sediments (Roy et al., 2010). Correspondence between dissolved Fe maxima and sediment-bound Fe and S suggests that dissolved Fe is derived from Fe-oxide reduction, and is lost from the porewater through Fe-sulfide precipitation, a hypothesis supported by PHREEQC modeling (Roy et al., 2010). The intermediate white sediments represent a sink for dissolved Fe, although low S contents indicate the sink is not from Fe-sulfide precipitation (Roy et al., 2010, 2011).

## 3. Methods

### 3.1. Samples collection

Details of sample collection and data analysis are available in Roy et al. (2010). In summary, porewaters and sediments were collected from a 30-m shore-perpendicular transect and at a site (CIRL39) 250 m offshore (Fig. 1c). Sampling sites along the transect were separated by approximately 5 m. Near shore sites are named EGN#, where # represents the offshore distance in meters (Fig. 1c). Porewaters were collected from the subterranean estuary between 18 and 22 April, 2007 using “multisamplers,” which are polyvinyl chloride (pvc) pipes that have screened openings (210 µm polypropylene mesh filter) at discrete depths (Martin et al., 2003). Tubing attached to these screened openings was connected to a peristaltic pump and porewater was pumped into an overflow cup, where water quality parameters (conductivity, temperature, and dissolved \( \text{O}_2 \)) were monitored with a YSI model 556MPS multiprobe meter. Once water quality parameters stabilized, three aliquots of samples were collected: 1) 30 ml untreated filtered samples into HDPE bottles for C, \( \text{SO}_4^- \), \( \text{NO}_3^- \) measurements; 2) 10 ml unfiltered samples into scintillation vials for \( \text{S}_2^- \) analysis; 3) 0.45 µm filtered samples for metal and isotope analyses. Samples were filtered with trace metal-clean plastic canister in-line disposable filter cartridges (Wattera FHT-45). The metal samples were immediately acidified to pH <2 using trace metal grade nitric acid and were stored in acid-cleaned HDPE bottles. All unfiltered and filtered samples were stored at 4 °C until analyzed.

Six sediments cores were collected using standard vibracoring techniques at sites EGN0, EGN10, EGN20, EGN22.5, EGN30 in May 2006, and at CIRL39 in October, 2006. At these sites, sediment aliquots were collected at the depths of the porewater samples: 0, 7, 15, 25,
35, 55, 75, 95, and 115 cmbsf at EGN0 to EGN20; 6, 66, 106, 146, and 166 cmbsf at EGN22.5; 10, 30, 50, 150, 190, and 230 cmbsf at EGN 30; and at 10, 20, 30, 40, 60, 110, 140, and 180 cmbsf at CIRL39 (Fig. 1c). Additional cores were collected at EGN0 and EGN30 in October 2006 and at CIRL39 in 2005 (Hartl, 2006) that have identical sedimentary facies distributions as our cores collected in May 2006, reflecting constant sediment geochemistry over the time scale of the study.

3.2. Analytical techniques

3.2.1. Porewater and sediment analyses

Unfiltered samples were analyzed for Cl and SO4 − concentrations using a Dionex ion chromatograph (DX500) with a precision of 3% of the measured value (Roy et al., 2010). For S2− analysis, porewater samples and Na2S standards were treated with mixed diamine reagent immediately after sample collection following the technique described by Cline (1969). Sulfide concentrations of samples and standards were measured at the same time in a Milton Roy Spectronic 401 spectrophotometer within 6 to 10 h of collection. Filtered and acidified samples were measured for dissolved Fe concentrations at the University of Florida using a Finnigan Element II ICP-MS and the reproducibility of measurements was checked against the external standard SRM354, a Canadian river water standard (details are available in Roy et al., 2010).

About 1 g of sediment was sequentially leached at the University of Florida for amorphous and crystalline Fe-oxides using the protocol described by Hall et al. (1996). Sediments were refrigerated and kept in a sealed HDPE container prior to leaching. Sediment samples from all depths were analyzed at EGN20, but only selected samples were measured from the other sites (Table 2). Amorphous Fe-oxides were leached from air-dried sediment aliquots using 0.25 M NH4OH·HCl (hydroxylamine hydrochloride) prepared in 0.25 M HCl matrix and crystalline Fe-oxides were leached by 1.0 M NH4OH·HCl prepared in 25% acetic acid matrix. The sum of amorphous and crystalline Fe-oxides is reported by Roy et al. (2010) as leachable Fe-oxides (Fig. 2). Total S content in sediments was analyzed using a Carlo Erba 1500 CNS Elemental Analyzer with a precision of 0.1% (N = 10 atropine check standard). Because air drying could convert AVS-bound reduced Fe to Fe-oxides, we do not report the KClO3, HCl–HNO3 extraction of air-dried sediments for Fe-sulfides as described by Hall et al. (1996). Instead we report the total S content assuming all sulfides in black sediments are Fe monosulfides.

3.2.2. Iron isotope analysis in porewater and sediments

Iron isotope values were measured by Multicollector ICP-MS (Neptune, Thermo-Element) using the previously reported technique of anion-exchange chromatography (AG1-X8 resin from Bio-Rad) (Rouxel et al., 2008; Escoube et al., 2009). Porewater samples with salinity < 20 and/or Fe concentrations above 100 μM/l were directly evaporated in Teflon beakers and dissolved in 5 ml of 6 N HCl before being processed through AG1-X8 resin for chemical purification. Porewater samples with high salinity (> 20) and low Fe concentrations, were preconcentrated onto nitritolriacetic acid (NTA) chelating resin to remove saltwater matrix interference and then were passed through the AG1-X8 resin (Rouxel and Auro, 2010).

Total sediment-bound Fe was extracted from 1 g of sediments by dissolving the bulk sediment in 10 ml aqua regia (trace metal grade 8 N HNO3 and 3 N HCl) overnight at 80 °C, which removed Fe-oxide and sulfide minerals as well as most poorly crystalline silicates. The solution was evaporated overnight on a hot plate. The dry residue was dissolved in 5 ml of 6 N HCl and the solution was centrifuged to separate insoluble particles. The supernatant leachate was purified onto an anion-exchange column using identical methods to the porewater (e.g., Rouxel et al., 2008; Escoube et al., 2009).

Column yield and external precision of measurements were assessed using an in-house Fe standard (SRM-3149) that was mixed with seawater matrix and processed through the entire purification procedure. The average value of SRM-3149 from all runs (N = 7) gave δ56Fe = 0.43 ± 0.06‰, which is indistinguishable from unprocessed standard value (δ56Fe = 0.39 ± 0.13‰; Rouxel and Auro, 2010). Yield from the column was also tested by using the Ferrozine technique (Stookey, 1970) on sample solutions that were passed through columns, before and after Fe was eluted from the column. In all cases, yield was found to be greater than 98%. The MC-ICP-MS was operated in either medium or high-resolution mode, and we used Ni as an internal standard for mass bias correction (Rouxel et al., 2008; Escoube et al., 2009). Iron isotope values are reported relative to the standard IRMM-14 using the conventional delta notations. All measured δ56Fe and δ57Fe values for porewater and sediment samples (Tables 1 and 2) fell on the mass dependent fractionation line and thus only δ56Fe values are discussed in this paper.

4. Results

4.1. Depth distributions of δ56Fe

Within the subterranean estuary, porewater δ56Fe values and Fe concentrations have distinct trends depending on the lithostratigraphic zones (Figs. 3 and 4). Porewaters in the black sediments have low dissolved Fe(II) concentrations but porewater δ56Fe values are relatively higher compared to the other lithostratigraphic zones. Porewaters from orange sediments have elevated dissolved Fe concentrations and negative δ56Fe values (Figs. 3 and 4a). Only EGN20 has sufficient porewater data from white sediments to discern a trend between dissolved Fe and δ56Fe values, and at this site both porewater δ56Fe values and dissolved Fe concentrations decrease upward in the direction of advection (inset in Fig. 3). In contrast, in the orange sediments, porewater δ56Fe values decrease and dissolved Fe(II) concentrations increase upward (see EGN22.5 and EGN30 in Fig. 4a). Seaward of the subterranean estuary at CIRL39, porewater δ56Fe values are lowest in near-surface white sediments and are greater at depth within black sediments (Fig. 4a).

The relationship between sedimentary and dissolved δ56Fe values changes in the three different lithostratigraphic zones. Because we have a continuous sediment δ56Fe profile only at site EGN 20 (Table 2) we use data from this site to assess the relationship between sedimentary and porewater δ56Fe values in different lithostratigraphic zones (Fig. 3). The sediment δ56Fe values decrease to about −1% from the sediment–water interface to the base of the black sediment, but increase to near zero throughout the white sediments (Fig. 3). In the black sediments, porewater δ56Fe values are up to 0.68‰ heavier than corresponding sedimentary δ56Fe values (Fig. 3). In the white sediments, porewater δ56Fe values are up to 1.8‰ lighter than sedimentary δ56Fe values (Fig. 3). We lack δ56Fe values from the white sediments at other sites, and thus cannot verify whether this relationship occurs elsewhere. The two data points from orange sediments at site EGN20 show porewater δ56Fe values that are isotopically lighter than corresponding sedimentary δ56Fe values (Fig. 3). This relationship also occurs at sites EGN22.5 and EGN30 (Fig. 4a).

4.2. Variations of δ56Fe with salinity

Neither the Fe nor S2− concentrations show conservative mixing between the fresh and salt water within the subterranean estuary, but the δ56Fe values decrease from about 0.5 to −1.5‰ up to a salinity change of about 5 and then increase monotonically with increasing salinity (Fig. 5). Seaward of the subterranean estuary at CIRL39, where all porewaters have marine salinity, S2− concentrations are high (>100 μM) and dissolved δ56Fe values are always positive, averaging about 0.65‰ (Figs. 4, 5b, Table 1). Similarly, at the sediment–water interface of all sites, porewaters have salinity close to
that of the surface water and their $\delta^{56}$Fe values are slightly positive, averaging about +0.24‰ (Table 1). In contrast, where most porewaters are fresh, i.e. at EGN0, porewaters S$^2-$ concentrations are low (<30 μM) and dissolved $\delta^{34}$S values are either negative or near zero (Fig. 4a).

5. Discussion

5.1. Diagenetic controls on Fe-isotopic compositions

The lack of correlation between porewater Fe and S$^2-$ concentrations and salinity suggests that in situ diagenesis is the primary control on their concentrations along with little influence of binary mixing between freshwater and saltwater end-members (Fig. 5). Based on the sediment and porewater Fe(II), S$^2-$ distributions and $\delta^{56}$Fe values, the primary diagenetic reactions appear to be Fe-sulfide precipitation in black sediments and dissolution of Fe-oxides in the orange sediments representing the principle sink and source of porewater Fe, respectively. The white sediment also represents a sink of porewater Fe but the exact nature of the Fe-phase that sequesters dissolved Fe has not been determined (Roy et al., 2011). In the following discussion, we use the isotopic compositions of the dissolved and solid phase Fe to assess diagenetic pathways of Fe in each lithostratigraphic unit and discuss the implications for oceanic $\delta^{56}$Fe values.

5.1.1. Diagenetic reduction of Fe-oxide as source of Fe

Porewater $\delta^{56}$Fe values decrease upward from the orange sediment through the white sediment with little change in the
sedimentary δ56Fe values (Fig. 3), which may reflect the differences in the amounts of Fe in the solid and dissolved phases. Content of sedimentary Fe(III)-oxides is about 4 orders of magnitude greater than corresponding porewater Fe(II) concentrations. Because of the elevated sedimentary Fe content, Fe-oxide isotopic composition would change little from partial Fe-oxide reduction, although minor amounts of dissolution could have a large impact on the isotopic composition of the dissolved Fe. The differences in concentrations of sedimentary and dissolved Fe further suggest that sedimentary Fe-isotopic composition is unlikely to be influenced by transient hydrologic changes that could influence dissolved Fe-isotopic composition, for example during exchange of water across the sediment–water interface during storm events (e.g., Smith et al., 2008a).

Both Fe-oxide reduction and oxidative precipitation of dissolved Fe can produce lighter porewater δ56Fe values (e.g., Bullen et al., 2001; Johnson et al., 2002, 2004, 2008; Skulan et al., 2002; Beard et al., 2003a; Croal et al., 2004). The Indian River Lagoon subterranean estuary is anoxic and contains no NO3− below 100 cmbsf, thus preventing oxidation of porewater Fe(II) within orange sediments, and suggesting that the observed isotopically light δ56Fe values of dissolved Fe within the orange sediments likely result from Fe-oxide dissolution. Although Fe-oxide dissolution could occur through biologic or abiologic pathways, we do not have information to discriminate between these two pathways. Microbial Fe(III)-oxide reduction has been found to cause porewater δ56Fe values to be about 1.25‰ lighter than sediment δ56Fe values in Lake Nyos, Cameroon (Teutsch et al., 2009), where porewaters have low SO42− concentrations and near zero NO3− concentrations, similar to Indian River Lagoon. In addition, Fe(III)-oxides dissolve more slowly via inorganic than microbial pathways (e.g., Lovley et al., 1987; Hyacinthe et al., 2006), suggesting microbial Fe-oxide reduction may dominate in the Indian River Lagoon subterranean estuary. If this is true, Fe-oxide reduction is one of the major pathways of OC remineralization at our site and the isotopically light porewater δ56Fe values are associated with OC diagenesis.

Iron oxides have been shown to dissolve abiologically by ligand bound hydrolysis and by reduction with S2− produced from SO42− reduction in coastal systems (Berner, 1980; Canfield et al., 1992; Brantley et al., 2001, 2004). In the Indian River Lagoon subterranean estuary, microbial SO42− reduction occurs at depths <40 cmbsf and there is no S2− or SO42− below this depth (see EGN 0 to EGN22.5 in Fig. 4b). The calculated peclet number (about 1011 at the fresh–salt water boundary) suggests percolation of dissolved S2− from shallower Fe-sulfide precipitation zone to the deeper Fe(III)-oxide reduction zone is unlikely. Consequently, SO42− reduction (BSR) is restricted to black organic carbon rich shallow sediments at depths <40 cmbsf, while Fe-oxide reduction (possibly microbially mediated) is restricted to Fe-oxides coated quartz sediments at depths >100 cmbsf.

5.1.2. Potential importance of adsorption processes

Decreasing dissolved Fe concentrations in the white sediment suggest they are a sink for dissolved Fe (Fig. 3). The lack of DO indicates the sink is not through oxidative precipitation of Fe(III) oxides and the lack of dissolved and solid sulfides indicate Fe-sulfides are not the sink either. The simultaneous decreases in porewater Fe concentrations and δ56Fe values (Fig. 3) can result from adsorption of dissolved Fe onto Fe-oxides, although we cannot rule out other
mechanisms. Experimental studies show that approximately one-third of dissolved Fe produced by microbial Fe-oxide reduction is re-adsorbed onto the mineral-surface of sedimentary Fe(III) oxides (Icpini et al., 2004). This re-adsorption decreases the dissolved \(\delta^{56}\text{Fe} \) values by about 0.7 to 1.2 \(\text{‰} \) compared to \(\delta^{56}\text{Fe} \) of solid Fe(III)-oxide (Icpini et al., 2004; Crosby et al., 2005). This fractionation during sorption is slightly less than the observed 1.84 \(\text{‰} \) and can be attributed to the difference between closed and open systems. Alternatively, the observed 1.84 \(\text{‰} \) difference between sediment and porewater \(\delta^{56}\text{Fe} \) values reflects a combination of both Fe-oxide

![Diagram](image-url)

**Fig. 4.** Porewater Fe and sulfur distributions. Dark gray zone represents Fe-sulfides rich sediments and light gray zone represents Fe-oxide coated sediments. a. Distributions of dissolved Fe and \(\delta^{56}\text{Fe} \). b. Distributions of sulfide (S\(^2-\)) and sulfate (SO\(_4^{2-}\)).
Heavier than sediment that range from 0 values is shown by decreasing sedimentary Fe isotope fractionation due to Fe-sulfide adsorption resulting from the hydrologic system appears to control isotopically lighter as dissolved Fe adsorbs on to Fe-oxides present which was derived from Fe-oxide reduction in the orange sediments, may re...

Fig. 5. Salinity controls on porewater sulfide, Fe and δ56Fe distributions. a. Variations in porewater sulfide (S2⁻) with salinity. b. Variations in porewater Fe with salinity. c. Variations in porewater δ56Fe with salinity.

5.1.3. Fe isotope fractionation due to Fe-sulfide precipitation

In the black sediments, porewater δ56Fe values are isotopically heavier than sediment δ56Fe values (e.g., Fig. 3), as would be expected from authigenic Fe-sulfide precipitation in organic rich sediments (Severmann et al., 2006; Duan et al., 2010). The increase in δ56Fe values is caused by preferential enrichment of light Fe isotopes in Fe-sulfide mineral phases (Butler et al., 2005; Guibaud et al., 2011). Iron-sulfide precipitation forms porewater with δ56Fe value of about 1.0‰ in Lake Kinneret (Sea of Galilee, Israel) (Sivan et al., 2011), which is slightly heavier than porewater δ56Fe values in the black sediments of Indian River Lagoon. Control of Fe-sulfide precipitation on porewater δ56Fe values is shown by decreasing sedimentary δ56Fe values with increasing S/Fe molar ratios (Fig. 6a). The orange and white sediments are characterized by low S/Fe ratios (~0.2 mol/mol) and have δ56Fe values that range from 0‰ to +0.41‰, while the black sediments have high S/Fe ratios (>0.5 mol/mol) and have δ56Fe values that range from −0.5‰ to −1‰ (Fig. 6a). The maximum difference between porewater and sediment δ56Fe values (Δ56Fe porewater-sediment) is ~+0.68‰ in the black sediments in contrast with a Δ56Fe porewater-sediment of −1.8‰ in the orange sediments (Fig. 6b).

Fig. 6. Sedimentary Fe isotope distribution and its variation with Fe and S content. a. Variation in sedimentary δ56Fe with S/Fe. b. Variation in the differences in porewater and sediment δ56Fe with S/Fe.

5.2. Subterranean estuary: a possible source of heavy Fe isotopes to coastal waters

Two previously identified sources of Fe to the upper oceans are continental shelf sediments and aerosols, which contribute about 2 × 10⁹ mol/year and 0.2–12 × 10⁹ mol/year, respectively (Fung et al., 2000; Elrod et al., 2004) but neither of these sources can explain the slightly positive δ56Fe in ocean water, which ranges from about 0.01 to 0.58‰ (Lacan et al., 2008; John and Adkins, 2010; Radic et al., 2011). Iron-oxide cycling in shelf sediments produces light δ56Fe values of about −3‰, in benthic flux chamber samples (Severmann et al., 2010), while aerosol Fe has δ56Fe that range from about 0.01 to about 0.13‰ (Beard et al., 2003b; Waesles et al., 2007). Aerosol dissolution in the water column likely results in even lower δ56Fe values of dissolved organically bound Fe (Brantley et al., 2001). Dissolved Fe delivered by SGD can be about 10% of the aerosol Fe delivered to South Atlantic Ocean (Windom et al., 2006), which may influence oceanic Fe-isotopic values, depending on the δ56Fe values of the SGD-derived Fe. The SGD-derived δ56Fe values are likely to vary among subterranean estuaries, however, depending on the local hydrogeologic conditions and sediment chemistry (Charette et al., 2005; Windom et al., 2006; Beck et al., 2010; Roy et al., 2010).

Along with isotope variations among subterranean estuaries, the flux of Fe will also vary depending on the redox state of the porewater. Subterranean estuaries, which are oxygenated (e.g., Waquoit Bay, MA) or contain other oxidants with higher energy yields than Fe-oxides (e.g., dissolved NO₃⁻ at Turkey Point, FL), should minimize the amount of Fe mobilized from sediments (Snyder et al., 2004; Santos et al., 2009; Roy et al., 2010). Because of these differences in redox conditions among subterranean estuaries, SGD-derived Fe fluxes and δ56Fe values are poorly constrained. The
dissolved Fe flux from a 240-km long subterranean estuary (Patos Lagoon, Brazil) to South Atlantic Ocean was estimated to be $1.18 \times 10^4$ moles/year, based on using Ra isotopes to estimate SGD coupled with measurements of concentrations of Fe in the groundwater (Windom et al., 2006). The Fe flux from the 250 km long Indian River Lagoon subterranean estuary was estimated to be $7.6 \times 10^4$ mol/year, based on multiple estimates of flow rates and Fe concentrations from porewater profiles (Roy et al., 2010). The difference of nearly four orders of magnitude in these flux calculations could be attributed to differences in sediments chemistry and artifact of methodology.

Regardless of the magnitude of Fe fluxes from subterranean estuaries, the global effect of Fe sources from subterranean estuaries on oceanic Fe isotope composition is unknown. Iron isotopic values ($<0.78\%$) lighter than the open ocean values were observed from Waquoit Bay surface seawater (Rouxel and Auro, 2010), where most of Fe discharge originates from the subterranean estuary, which is characterized by an even lighter isotopic signal (Rouxel et al., 2008). The periodic exposure of the Waquoit Bay subterranean estuary to oxic atmosphere during low tides allows Fe-oxide precipitation and limits Fe-sulfide precipitation (Charette et al., 2005; Rouxel et al., 2008). In contrast to Waquoit Bay, Indian River Lagoon is microtidal, resulting in anoxic conditions that allow Fe-sulfide precipitation and positive porewater $\delta^{56}$Fe values in the near-surface OC-ric black sediments. Sulfidic sediments should occur in most subterranean estuary because exchange across the sediment–water interface would allow reactions between seawater SO$_4^{2-}$ and marine labile DOC. If most subterranean estuaries are sulfidic, similar to Indian River Lagoon, then subterranean estuaries could be a previously unrecognized source of positive Fe-isotopic signal to ocean, although the isotopic ratios of this source would be modified as the dissolved Fe flow offshore in well-oxygenated ocean water.

Sea level rise increases the Fe-sulfide content in Indian River Lagoon sediments as a result of increased deposition of OC-rich marine sediments (Roy et al., 2010) and this sedimentary process shifts porewater $\delta^{56}$Fe values to increasingly positive values offshore. The relationship between porewater $\delta^{56}$Fe and varying Fe-sulfide content (Fig. 6a) suggests that the Fe isotope system is modified in subterranean estuary because of the changes in sediment chemistry caused by marine transgression. Our data shows porewater discharging across the sediment–water interface has slightly positive $\delta^{56}$Fe values, averaging $+0.24\%$ (Table 1). Although Fe and Si$^4+$ reactions are likely to be important in controlling the Fe-isotope composition of water discharging from subterranean estuaries, limited data exists on Fe flux and isotopes in subterranean estuaries. Understanding the influence of subterranean estuaries on oceanic Fe concentrations and isotopic values will require more detailed surveys of dissolved Fe isotope compositions in a variety of subterranean estuaries, as well as coastal and open oceans.

6. Conclusion

Three distinct diagenetic pathways influence the Fe-isotopic composition within different lithostratigraphic units in the Indian River Lagoon subterranean estuary. From bottom to top they are: diagenetic Fe reduction in orange Fe-oxide coated sediments; dissolved Fe adsorption to mineral surfaces on white sediments; and Fe-sulfide precipitation in black OC-rich marine sediments. These diagenetic pathways are likely to occur in most subterranean estuaries, but their relative magnitudes will vary depending on their sediment and hydrogeologic characteristics. Particularly important parameters are the amount of DOC, rates and amount Fe-oxide dissolution, Fe-sulfide precipitation in sediments, and oxygenation of subterranean estuaries caused by periodic exposure of sediments during low tides. In the Indian River Lagoon subterranean estuary, porewaters at the sediment–water interface have positive $\delta^{56}$Fe values, averaging around 0.24$. This value is isotopically heavier than porewaters from deep sediments, which have $\delta^{56}$Fe values of around $-1.8\%$. The increase in $\delta^{56}$Fe values results from precipitation of isotopically light Fe-sulfide minerals during SO$_4^{2-}$ reduction. Our study thus suggests that Fe-sulfide-bearing subterranean estuaries may represent a source of isotopically heavy Fe to coastal waters and possibly to open oceans.

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