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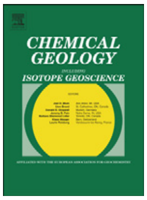

Research paper

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

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ABSTRACT

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 δ^{56}Fe 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 δ^{56}Fe values to be ~1‰ lighter than the sediment δ^{56}Fe 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 δ^{56}Fe values that are as much as 1.8‰ lighter than sediment δ^{56}Fe 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 δ^{56}Fe values as much as 0.68‰ more than corresponding sediment δ^{56}Fe values. The near-surface Fe-sulfide precipitation delivers to the lagoon dissolved Fe with slightly positive δ^{56}Fe 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.

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 δ^{56}Fe values with reported values of about −0.9‰ for the surface waters of eastern coast of 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, δ^{56}Fe 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 δ^{56}Fe values occur in river water (δ^{56}Fe 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 δ^{56}Fe 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

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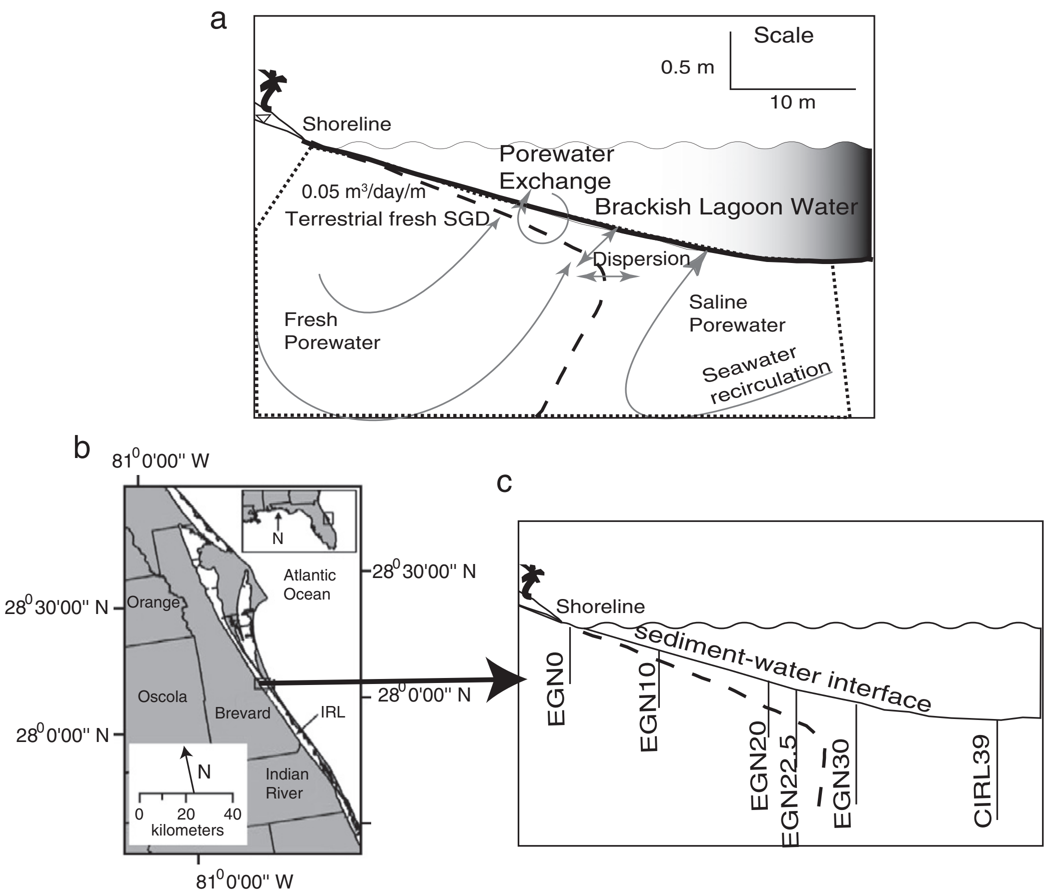

Fig. 1. Location and hydrology of the Indian River Lagoon (Florida, USA) subterranean estuary. a. Hydrology of the subterranean estuary. The black wide dashed line represents the freshwater–saltwater boundary at 300 mM chloride concentrations. Flows of submarine groundwater discharge (SGD) are shown by gray arrows and incorporate terrestrial fresh SGD and marine saline SGD, which includes both recirculated water at the sediment–water interface and recirculated water at the freshwater–saltwater boundary. Mixing between fresh and saline SGD creates the subterranean estuary (area under the dotted line). b. Geographic location of the study site. c. Position and relative lengths of porewater multisamplers in the transect.

large source of SGD-derived Fe to coastal oceans may influence their isotope signatures, depending on the isotope ratios of the Fe flux.

The only previous study of Fe isotope ratios within a subterranean estuary was conducted in Waquoit Bay, Massachusetts (Rouxel et al., 2008). At this site, negative porewater δ^{56}Fe values (down to -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 δ^{56}Fe 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 δ^{56}Fe values by -2 to -5‰ (Rouxel 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 (SO_4^{2-}), sulfide (S^{2-}), 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, SO_4^{2-} and labile 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 SO_4^{2-} reduction, a process common to most subterranean estuaries. Precipitation of Fe-sulfide fractionates lighter Fe isotopes into the solid phase, thereby increasing the δ^{56}Fe 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 δ^{56}Fe values. Both Fe-oxide reduction and Fe-sulfide precipitation can occur in subterranean estuaries so that the δ^{56}Fe values of dissolved Fe(II) would depend on the dominating diagenetic pathway, whereby positive values would occur when Fe-sulfide reaction dominates or negative δ^{56}Fe values would occur when Fe-oxide reduction dominates (Severmann et al., 2006).

We report here δ^{56}Fe values for porewaters and sediments in the subterranean estuary in Indian River Lagoon, Florida. At this location, SO_4^{2-} reduction produces S^{2-}, 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 δ^{56}Fe 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