



Large Scale Iron Isotope Fractionation in Subterranean Estuaries

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Dissolved Fe concentrations in subterranean estuaries, like their river-seawater counterparts, are strongly controlled by non-conservative (removal) behavior during mixing of groundwater and seawater in coastal aquifers. The recent discovery of an "Iron Curtain" in the subterranean estuary of Waquoit Bay on Cape Cod, USA demonstrates extensive precipitation of groundwater-borne dissolved ferrous iron and subsequent accumulation of iron oxides onto subsurface sands. Here, we report Fe isotope compositions ($\delta^{56}\text{Fe}_{IRMM-14}$) of iron-coated sands and porewater in the intertidal zone of Waquoit Bay measured using high mass resolution MC-ICP-MS (Neptune) and Ni for mass bias correction .

The distribution of pore water Fe shows two distinct sources : one source resides in the upward rising plume of Fe-rich groundwater ($[\text{Fe}] \sim 100\mu\text{M}$) and the second source lies in the salt-wedge zone of pore water ($[\text{Fe}]$ up to $400\mu\text{M}$). Both end-members have $\delta^{56}\text{Fe}$ values varying between 0.3 to -1.3 permil consistent with Fe isotope fractionation by dissimilatory Fe reduction. Since pore water data suggest minor sulfate reduction, sulfide precipitation is negligible in this system.

A series of sediment cores, ranging from 1.1 to 2.0m in length were collected and display various abundances of ferrihydrite, goethite and lepidocrocite. Fe concentrations in Core#2 range from 500 to 8000 ppm and $\delta^{56}\text{Fe}$ values decrease upward from ~ 1.5 permil at 140 cm to 0 permil near the surface. The strong $\delta^{56}\text{Fe}$ gradient over only 2m of section is remarkably similar to the Fe concentration gradient. Similar feature has been observed in Core#5 whereas in Core#3, minimum $\delta^{56}\text{Fe}$ values occur at mid-depth (down to ~ -2 permil) with maximum $\delta^{56}\text{Fe}$ values (~ 0 permil) occurring at the top and bottom (120cm) of the core. The relationship between Fe concentration

and $\delta^{56}\text{Fe}$ values of Fe oxides can be modeled by incremental processes (distillation) during the progressive precipitation of Fe-oxides in the subterranean estuary. Estimated fractionation factors indicate that the $\delta^{56}\text{Fe}$ value of precipitated Fe-oxides is enriched in heavy isotopes by ~ 1.2 permil relative to dissolved Fe(II) which is consistent to those obtained in experimental studies.

The results demonstrate a large-scale Fe isotope fractionation (up to 3.5 permil) associated with the formation Fe oxide in the subterranean estuary of Waquoit Bay. Hence, any coastal aquifer bearing high concentrations of dissolved ferrous iron that intercepts surface water are expected to produce a significant Fe(II) flux to coastal seawater characterized by very low $\delta^{56}\text{Fe}$ values. These results have also broader implications for the utility of Fe isotopes to trace Fe redox cycling in larger scale and ancient aqueous systems as suggested previously for Archean environments.