



Natural variations of Fe isotopic compositions of seawater determined by MC-ICPMS

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Considered esoteric only a few years ago, research into the stable isotope geochemistry of iron is moving into the bio-geoscience mainstream. Although initial attention focused on the potential use of Fe isotopes as biosignatures, they are now emerging as powerful oceanographic and paleoceanographic proxies. In particular, Fe isotopes are providing useful information about redox conditions in modern and ancient marine environments, mainly because biotic and abiotic redox processes are among the principal factors that fractionate Fe isotopes. While Fe isotope studies in seawater are still in their infancy, Fe isotope analysis of dissolved Fe in seawater are expected to provide new approaches to important questions concerning Fe sources, Fe speciation and its bioavailability in the ocean.

Here, I report the development of a reliable technique for measuring Fe isotopes in coastal and open seawater at sub-nanomolar level using less than 1 liter sample size. Iron is directly preconcentrated from acidified seawater samples (pH \sim 1.7 with trace H₂O₂) onto a nitrilotriacetic acid (NTA) chelating resin. This method had been already demonstrated to allow high recovery yields at low pH, even in the presence of natural strong iron-binding ligands (Lohan et al., *Anal. Chim. Acta*, 2005). Selected samples obtained after preconcentration were further purified using anion-exchange techniques. However, this additional purification step has proved to be unnecessary due to the excellent sample purity obtained after the NTA resin purification. Preconcentrated Fe is then analyzed using a MC-ICP-MS (Thermo Scientific Neptune) at WHOI coupled to the Apex-Q (Elemental Scientific) introduction system operating at a flow rate of 60 μ l/min. The instrumental mass bias was corrected by the combined approach of "standard-sample bracketing" method and Ni-doping. Procedural blanks have been estimated to be less than 2ng while sample recovery, determined using a standard addition method, was essentially quantitative. The external $\delta^{56}\text{Fe}$ precision is estimated at 0.14‰ (2σ) for total Fe quantity between 20 and 80 ng.

We initially applied this technique to measure Fe-isotope composition of dissolved Fe (<0.2 μ m) from several seawater reservoirs, in particular (1) estuarine waters from Long Island Sound, USA (Connecticut River estuary). For sample salinity ranging from 5 to 25, we obtained $\delta^{56}\text{Fe}$ values of 0.04‰, \pm 0.04 (2σ , n=9) which is similar to river values determined using conventional techniques. These results confirm that Fe flocculation processes in estuary produce minimal Fe-isotope fractionation (Escoube et al., *GCA submitted*). (2) coastal seawater from Waquoit Bay and Vineyard Sound (Cape Cod, USA) where significant groundwater input of isotopically light Fe is expected (Rouxel et al., *GCA* 2008). Results of surface coastal seawater confirm light Fe-isotope composition for dissolved Fe, with $\delta^{56}\text{Fe}$ values ranging from -0.40 down to -0.88‰ for Fe concentrations ranging from 13 to up to 327nM (n=13). (3) open seawater from the Southern Equatorial Atlantic (provided by M. Saito, cruise CoFeMug). Deep water samples (<1000m) with Fe concentrations \sim 0.4nM yielded $\delta^{56}\text{Fe}$ values clustered at 0.24‰, \pm 0.16 (2σ n=4) which compare well with recent Fe-isotope results of Lacan et al. *GRL*, 2009 from the Southern Atlantic.

The preliminary results suggest that iron in coastal seawater, derived from benthic diagenesis and/or groundwater, has a unique (very light) isotope signature that is distinct from other iron sources, such as atmospheric deposition and rivers. Providing that further analysis confirm this hypothesis, then iron isotopes could prove to be a valuable tracer for shelf-derived iron, which has been hypothesized to be an important component for global oceanic iron cycle.