

Sources and biogeochemical cycling of Iron isotopes in marine environments

OLIVIER ROUXEL

Marine Chemistry & Geochemistry Dept., Woods Hole Oceanographic Institution, Woods Hole, MA02543, USA (orouxel@whoi.edu)

Considered esoteric only a few years ago, research into the stable isotope geochemistry of iron is moving into the biogeochemistry 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 still present a challenging analytical problem, Fe isotopes provide a new approach to important questions concerning Fe sources, Fe speciation and its bioavailability in the ocean. Here, I will review and present new results of Fe isotope systematics in modern marine environments, in particular: (1) riverine input to the ocean, which has been generally considered to have low $\delta^{56}\text{Fe}$ values (down to -1%). Our recent study of two estuaries along US East coast suggests that flocculation processes produce minimal Fe-isotope fractionation. However, we also found that dissolved Fe flux to the ocean may be characterized by more positive $\delta^{56}\text{Fe}$ values (up to 0.3%) relative to the crust than previously reported; (2) redox cycling of Fe in subterranean estuaries and shelf sediments, which can result in very light Fe-isotope composition in surface pore waters (down to -5%); (3) atmospheric Fe sources to the open ocean, with crustal $\delta^{56}\text{Fe}$ values. Our recent time-series study of marine particulates from the Sargasso sea (sediment traps) yielding $\delta^{56}\text{Fe}=0.07\pm 0.03\%$ (1σ , $n=36$) confirm such assumptions; (4) hydrothermal Fe sources from mid-oceanic ridges, back-arc systems and volcanic seamounts, which are shifted to low $\delta^{56}\text{Fe}$ values from 0.0 down to -1.8% compared to igneous rocks. Additional Fe-isotope fractionation may be also produced in hydrothermal plumes through the water column during partial sulfide precipitation and Fe oxidation and stabilization of Fe in seawater by organic-ligands.

Further advances will focus on the direct determination of Fe-isotope compositions in seawater in order to provide new constraints on the oceanic sources and cycling of Fe, an element that is essential for ocean biogeochemistry.

Measurement of Germanium isotope composition in marine samples by hydride generation coupled to MC-ICP-MS

OLIVIER J. ROUXEL¹, RAPHAELLE ESCOUBE^{1,2} AND OLIVIER F.X. DONARD²

¹ Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA02543, USA (orouxel@whoi.edu)

² IPREM, U. Pau et Pays de l'Adour, CNRS UMR 5254, Hélioparc 64053 Pau, France

Germanium (Ge) is a trace metalloid in seawater that is of particular interest in marine biogeochemistry because of its strong chemical similarity to silicon. In addition, Ge stable isotope ratios in biogenic silica may have strong potential as paleoceanography proxies. We recently reported Ge-isotope composition of igneous rocks and deep-sea clays and defined a bulk Earth $\text{[}^{74/70}\text{Ge]}$ value of 0.5% (relative to NIST3120a). Based on $\text{[}^{74}\text{Ge]}$ values of modern marine sponges, it has been also suggested that Ge-isotope composition of seawater is enriched in heavy isotopes relative to the crust ($\text{[}^{74}\text{Ge]}$ around 2.2%).

Here, we report the development of a new technique to measure Ge isotope composition in seawater. Ge is co-precipitated with magnesium at $\text{pH}\sim 9\text{-}10$ and Mg precipitates are filtered and dissolved in 0.25N HNO_3 . The samples are then analyzed using a continuous flow hydride generation system coupled to a MC-ICP-MS (Thermo-Finnigan Neptune) operating at WHOI. The instrumental mass bias was corrected by the "standard-sample bracketing" method.

We initially applied this technique to measure Ge-isotope composition in seafloor hydrothermal fluids. Ge isotopic composition of low temperature ($\sim 50^\circ\text{C}$) hydrothermal fluids from Loihi Seamount in the Pacific Ocean show systematically positive $\delta^{74}\text{Ge}$ values $\sim 1.5\%$. In contrast, $\delta^{74}\text{Ge}$ values of associated hydrothermal deposits, composed essentially of Fe-oxyhydroxides, range from -0.7 to 0.6% . The enrichment of light Ge-isotopes in Fe-oxyhydroxide precipitates at Loihi relative to the fluid (up to 2.5%) is consistent with previous experimental study of Ge-isotope fractionation during Ge-sorption onto Fe-oxyhydroxides (goethite). These results suggest that seafloor hydrothermal fluids may represent a source of isotopically heavy Ge in the ocean and that this isotope signature may be affected by Ge precipitation upon mixing with seawater. Additional studies will focus on Ge-isotope systematics in rivers and deep seawater in order to establish a reliable isotope mass balance of Ge in the ocean.