Subterranean estuarine influence on molybdenum isotope cycling

E.K. KING[1], T.J. HORNER[1], M.A. CHARETTE[1]

[1]Woods Hole Oceanographic Instutituion, Woods Hole, MA 02543, USA; eking@whoi.edu

Molybdenum (Mo) isotopes are a powerful tracer of marine redox state (*1*). The application of Mo isotopes to trace paleoredox relies on a well-constrained knowledge of both the flux and isotopic composition of Mo delivered to oceans from continents, as well as an understanding of the processes controlling these fluxes (*2*). It has been hypothesized that submarine groundwater discharge (SGD) is a significant flux of Mo to oceans (*3, 4*). However, the evolution of the groundwater Mo flux and isotopic composition during transit from terrestrial to coastal environments is poorly constrained, especially in the geochemically-dynamic subterranean estuary (STE) where terrestrially-derived groundwater and seawater interact (*5*).

Molybdenum geochemistry was monitored over one year in the STE of Waquoit Bay (Cape Cod, USA). This STE is characterized by steep gradients in pH, salinity, and redox state that promote biogeochemical reactions that are predicted to modulate the Mo isotope composition of SGD. Our data suggest that dissolved Mo concentrations are controlled by non-conservative mixing of terrestrial 'fresh' groundwater and seawater. We observe systematic variations in Mo isotope chemistry that can be attributed to mixing between the fresh and marine Mo sources, and adsorption/desorption of Mo onto sediments within the STE. Waters collected in the salt-wedge zone of the STE have low Mo concentrations and are enriched in heavy Mo isotopes up to 2‰ above ambient seawater. The direction and magnitude of Mo isotope fractionation is consistent with progressive Mo precipitation onto iron (Fe)- and manganese (Mn)- (oxyhydr)oxides. Terrestrial groundwaters collected above the salt wedge exhibit low Mo concentrations and highly variable Mo isotopic compositions, again indicating the importance of STE-mediated redox cycling. These results reveal the potential range of Mo isotope fractionation in the STE, which ultimately helps to quantify the role of SGD on the Mo isotope budget of seawater.

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