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Dissolved Phase-Specific Isotopic Analyses of Selenium from Oxic and Suboxic Waters

LAURA F. PICCIRILLO AND MICHAEL A. KIPP
Duke University

Selenium (Se) is commonly used as a paleo-redox proxy in ancient marine settings because of its sensitivity at high redox potentials. In particular, Se geochemistry has proven to be useful in reconstructing ocean oxygen levels during formative periods of eukaryotic evolution. However, a scarcity of isotopic data for Se in modern seawater has limited its utility as a paleo-redox proxy, as our understanding of the marine Se biogeochemical cycle has lagged behind other trace elements. Selenium is a nutrient element with an active redox cycle, multiple oxidation states (selenate: Se^{6+}; selenite: Se^{4+}; elemental: Se^{0}; selenide: Se^{2-}), and six stable isotopes. Both selenite and selenate are present as dissolved oxyanions in modern seawater, and both are subject to assimilatory and dissimilatory microbial metabolic reactions. Redox transformations of Se occur in the water column and sediments, and result in large Se isotopic fractionations. Additionally, assimilation of inorganic Se by phytoplankton can cause isotopic fractionation of both selenite and selenate, but this has not been constrained in marine settings. To date, no phase-specific Se isotopic data (and limited bulk Se isotopic data) have been generated from seawater.

Here we report validated methods for sequential purification of selenite and selenate from 1L seawater samples for phase-specific isotopic analyses. We use a silica-based thiol resin for selective purification of selenite, after which residual selenate in the matrix is reduced to selenite and passed again through the resin for purification. Selenium isotopes are measured on a Nu Sapphire collision-reaction cell MC-ICP-MS. $\delta^{82/78}$Se values of selenite from oxic waters are >+3‰ at >200m depth, suggesting a large isotopic effect from assimilation in the photic zone. $\delta^{82/78}$Se of selenite decreases with depth upon organic matter regeneration. $\delta^{82/78}$Se of selenate will be studied in upcoming work. We discuss ongoing work to apply this method in the low-oxygen water column of the Tofino Inlet and to seawater from GEOTRACES GP16 through the Eastern Tropical Pacific oxygen minimum zone. This sequential purification can be used in future work to explore different marine settings and employed in tandem with other redox-sensitive tracers.