

Phase-specific isotopic analysis of dissolved selenium in seawater

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Isotopic measurements of selenium (Se) in seawater have notably lagged behind other trace elements, due to both analytical difficulties and low environmental concentrations. This delay has caused a slow progression of understanding the marine Se biogeochemical cycle in modern environments and also limited the use of Se as a paleo-redox proxy in ancient marine settings. Se is a nutrient element with an active redox cycle and multiple oxidation states (selenate: Se^{6+} ; selenite: Se^{4+} ; elemental Se: Se^0 ; selenide: Se^{2-}). Redox reactions result in large Se isotope fractionations, which could warrant phase-specific Se isotope measurements. However, to date no phase-specific Se isotopic data (and very little bulk Se data) have been generated from seawater. Here we report on the development of new methods for sequential purification of selenate and selenite from seawater for isotopic analysis. We use a thiol resin column procedure for selective purification of selenite. After passing through the column, residual selenate in the matrix is converted to selenite with HCl and passed again through the column for purification. We present a validation of this method using Se-doped seawater with varying proportions of Se^{6+} and Se^{4+} . Finally, we discuss an application of this method to Se isotope variability through the Eastern Tropical Pacific oxygen deficient zone using samples from GEOTRACES cruise GP16 collected in 2013. This study provides a much-needed phase-specific Se isotopic calibration for modern seawater.