

The selenium isotope perspective on biogeochemical events in deep time

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Selenium is an essential micronutrient for many organisms and strongly redox sensitive within the stability field of liquid water. The biogeochemical selenium cycle is therefore likely to have responded to redox and productivity changes over Earth's history. The six stable selenium isotopes are primarily fractionated during abiotic and biotic reduction reactions [1], making them ideal tools for tracking perturbations in aqueous selenium cycling. To assess this hypothesis, selenium isotopes were measured in marine black shales across two previously noted event horizons, the Neoproterozoic 'whiff' of oxygen and the Permian-Triassic mass extinction. The Archean section from the Mt. McRae Shale in Western Australia (2.5 Ga) shows a small but statistically significant positive excursion in $\delta^{82/78}\text{Se}$ from background levels around $+0.3 \pm 0.3 \text{‰}$ to a maximum of $+1.4 \pm 0.0 \text{‰}$, which is best explained as enhanced oxidative selenium weathering and isotopic fractionation during transport to the ocean [2]. The Permian-Triassic section from the Western Canada Sedimentary Basin (252 Ma) shows a marked negative excursion from around $0.0 \pm 0.5 \text{‰}$ down to $-1.8 \pm 0.3 \text{‰}$ near the peak extinction horizon, reflecting partial oxyanion reduction and isotopic fractionation at the site of deposition [3]. These results exemplify two critical aspects about the selenium isotope proxy. First, selenium isotopes are sensitive to biogeochemical events down to centimeter-scale. This is likely a reflection of the short residence time of selenium in seawater. Second, isotopic signals appear to be very sensitive to the ratio of oxyanion supply to biological demand. A decrease in the demand under oxic conditions allows for non-quantitative oxyanion reduction and large negative fractionation, whereas a high demand in an anoxic setting leads to quantitative selenium drawdown and the preservation of the source composition. In conclusion, selenium isotopes may allow tracking spatial and temporal heterogeneity in redox and productivity at fine scale and can be powerful addition to the biogeochemical toolbox.

[1] Johnson & Bullen (2004) *Rev. Mineral. Geochem.* **55**, 289-317. [2] Stüeken, Buick & Anbar (2015), *Geology* **43**, 259-262. [3] Stüeken, Foriel, Buick & Schoepfer (2015), *Chem. Geol.* **410**, 28-39.