

## Usefulness and limitations of stable oxygen isotopes in application to selenium oxyanion biogeochemistry

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Stable selenium isotope systematics within the Se redox cycle has been well characterized within the literature, however concomitant oxygen isotope systematics requires further investigation. This work describes how  $\delta^{18}\text{O}$  values in selenate ( $\text{SeO}_4^{2-}$ ) may be useful in describing selenate reduction or formation. Selenate reduction experiments revealed a kinetic O isotope effect in selenate, with abiotic selenate reduction by chloride green rust producing a larger enrichment ( $\epsilon_o \sim 22\%$ ) [1] compared to biotic reduction with bacterium *Sulfurospirillum barnesii* SES-3 ( $\epsilon_o$  1.5-5.8%) [2].  $\delta^{18}\text{O}$  values potentially could be used to distinguish abiotic and biotic selenate reduction processes in nature, so long as they are not masked by mass transfer limitations in pores. Potential selenate formation pathways in surface waters were probed by oxidizing selenite with hydroxyl radicals, hydrogen peroxide, and ozone using  $^{18}\text{O}$  to trace selenite oxidation to selenate. Comparing  $\delta^{18}\text{O}$  in  $\text{SeO}_4^{2-}$  and  $\text{H}_2\text{O}$  indicates that all three oxidants yielded selenate that was assembled using three O from selenite (originally from  $\text{H}_2\text{O}$  after complete O mixing) and the fourth O from the oxidant. These results suggest the  $\delta^{18}\text{O}$  signature of natural selenate depends on the  $\delta^{18}\text{O}$ - $\text{H}_2\text{O}$  and the specific oxidation pathway. For sampling natural waters, the  $\delta^{18}\text{O}$ - $\text{SeO}_4^{2-}$  measurement method is limited by the need to concentrate selenate typically 1,000-fold greater than that found in nature, and to remove potentially interfering oxyanions.

[1] Schellenger & Larese-Casanova (2013), *Environ. Sci. Technol.*, **47**, 6254–6262. [2] Schellenger et al. (2015), *Appl Geochem.* **63**, 261-271.