Se isotopic tracer of abiotic Se oxidation by Mn-oxides

KATHRIN SCHILLING[1]; THOMAS M. JOHNSON[2]; CELINE PALLUD[1]

[1]Environmental Science, Policy and Management, University of California, Berkeley, USA, kschilling@berkeley.edu
[2]Dept. Geology, University of Illinois, Urbana Champaign, USA

The oxidation state of selenium (Se) regulates its availability as a nutrient as well as its mobility as a contaminant. Biotic and abiotic processes catalyse Se redox transformations. Although Se oxidation is an important process controlling Se fluxes in modern environments, and has been a major Se mobilizing process throughout the geologic history, it is unclear if Se oxidation is mainly driven by abiotic or biological reactions.

Se isotope ratio ($^{82}Se/^{76}Se$) is a powerful indicator, which can help determine the extent of Se oxidation. However, our insufficient knowledge of the magnitude of Se isotope fractionation caused by Se oxidation limits the application of Se stable isotopes. Therefore, we investigated Se isotope fractionation induced by the abiotic oxidation of Se by manganese oxides (Mn-oxides). Mn-oxides are ubiquitous minerals in oxic soils and sediments and known to oxidize $Se^{(IV)}$ to $Se^{(VI)}$.

We conducted batch experiments of $Se^{(IV)}$ oxidation by Mn-oxides under controlled conditions (pH=4 and temp. = 22°C) to investigate the relationship of Se oxidation kinetics and Se isotopic fractionation [$(\varepsilon=1000*(\alpha-1)$; $\alpha = (^{82}Se/^{76}Se)_{Reactant}/(^{82}Se/^{76}Se)_{Product}$].

Our preliminary results show a decrease in $Se^{(IV)}$ concentration by ~40% over 500 hours. It further reveals a small isotopic fractionation of 1.0‰ with $Se^{(IV)}$ as reactant being isotopically heavier relative to the reaction product $Se^{(VI)}$. Any processes other than oxidation can be excluded because (i) sorption on Mn-oxide would lead to a much faster decrease in $Se^{(IV)}$ concentration (time scale of minutes)[1], (ii) $Se^{(IV)}$ reduction would cause larger e (>10‰).[2]

This relatively small fractionation follows the pattern seen for other redox-senstive elements (i.e. S, Cr), which can be fit into the general isotopic theory developed for other elements.

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