

## Cr, Se, and U isotopic fractionation induced by oxidation: A synthesis

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Isotopic fractionations in Cr, Se, and U provide new ways to learn about sources of these contaminants and the redox reactions that control their mobility, and also to track ancient redox conditions. These elements are mobile when oxidized and insoluble when reduced. Fractionations accompanying Cr, Se, and U reduction reactions are fairly well studied and somewhat predictable. Oxidation is less well studied and more complex; this talk will provide a synthesis of theory, lab results, and field measurements.

Laboratory experiments have measured isotopic fractionation when Cr(III)<sub>aq</sub>, Se(IV)<sub>aq</sub>, or U(IV)<sub>aq</sub> is oxidized. Several experiments with oxidation of dissolved Cr(III) by MnO<sub>2</sub> had variable results, with the Cr(VI) product isotopically light, unfractionated, or isotopically heavy, depending on the form of MnO<sub>2</sub> and other variables. Oxidation of U(IV)<sub>aq</sub> by O<sub>2</sub> produced isotopically light U(VI) in one set of experiments. One experiment found no resolvable fractionation for oxidation of dissolved Se(IV) by H<sub>2</sub>O<sub>2</sub>. These variable results reflect inherent complexity with oxidation reactions: Simple kinetic isotope effects change the ratios in one direction whereas equilibrium isotope effects expressed for one or more steps in the overall reaction can have an opposite effect. The net result can be highly variable.

Congruent oxidation of solid phases should produce little isotopic fractionation, as solids must be consumed layer by layer. This was observed in experiments with oxidation of UO<sub>2</sub>. However, long-term contact between U(VI)<sub>aq</sub> and solid UO<sub>2</sub>, or between Cr(VI)<sub>aq</sub> and solid Cr(OH)<sub>3</sub>, has been observed to result in significant isotopic exchange and thus shifts toward isotopic equilibrium. This produces heavy Cr(VI) or light U(VI).

Field data for Cr and Se so far have found oxidized, dissolved weathering products are isotopically heavier than residual solids. Extended contact and isotopic exchange between oxidized and reduced phases and/or partial re-reduction of oxidized weathering products are likely causes. These processes do not appear to affect dissolved U in major rivers, which so far seems to be unfractionated or isotopically heavy relative to average crust. Additional work is needed to better understand how the complexity of oxidation-induced isotopic fractionation plays out in various natural settings.