

## **Twenty years of heavy stable isotopes aimed at redox-sensitive contaminants: Successes, complications, and the road ahead**

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### **Abstract**

Many inorganic contaminants' toxicity arises from chemical reactivity related to oxidation and reduction (redox) reactions. In general, the mobility, bioavailability, toxicity, and environmental impact of these elements are strongly affected by redox reactions. For example, Se, Cr, and U are all mobile and toxic in their hexavalent, oxidized states but immobile and much less dangerous in their reduced valences. Accordingly, detecting and perhaps quantifying redox reactions is critically important in determining impacts of these contaminants on surface water and groundwater resources and/or monitoring remedial actions that involve reduction.

Using a foundation from decades of work on redox reactions involving the stable isotopes of lighter elements (C, H, O, N, and S), about 20 years ago various researchers began to explore stable isotope effects of redox reactions involving heavier elements. Some of these groups aimed their efforts primarily at contamination in the modern world. This presentation will provide an overview of progress to date in developing stable isotope approaches for redox-sensitive contaminant elements heavier than sulfur. The main focus will be on Cr, Se, U, and Hg, but work on V, Ni, Cu, Tl, W, Sb, and Te will be included briefly.

For all of these elements, redox reactions cause major changes to chemical bonds. The differences in bonding between oxidized and reduced forms drive robust equilibrium isotopic fractionations that have been modeled in some cases and measured in a few cases. Nuclear field effects, whereby the different sizes of isotopic nuclei drive fractionation, have been modeled and detected for the very heavy elements Hg, Tl, and U. In many cases, redox reactions tend to be kinetically inhibited: The bonding changes involved tend to make reactions sluggish. As a result, isotopic equilibrium is not readily attained and kinetic isotope effects tend to dominate. Laboratory studies of Cr and U indicate that isotopic exchange and the approach toward equilibrium is important only over many years, except in special cases. Hg isotopic exchange might be faster, but studies under environmentally relevant conditions have not yet been done.

Because reduction reactions involving Cr, Se, U, and Hg are so important, isotopic methods for detecting the reactions have been pursued, and fractionation induced by them has been studied relatively well. In all four elements, reduction consistently leads to isotopic fractionation by abiotic and microbial mechanisms, though in a few unusual cases, fractionation is very weak. Several successful applications, whereby environmentally important reduction reactions have been detected using the resulting isotope ratio shifts, have been conducted: For Cr, U, and Se, isotope ratios in the remaining contaminant change predictably with increasing extent of reduction. Qualitative or semi-quantitative interpretation of field data seems to be very successful so far, but challenges related to variability of isotopic fractionation factors and heterogeneity of natural systems must be overcome to enable quantitative interpretations.

Determination of contamination sources using these isotope ratios seems promising, but has limitations. In several cases, Cr isotope ratios in anthropogenic Cr contaminants have been lower than those of the natural background Cr. However, this type of source tracing is challenging if the potential exists for Cr reduction to alter the "signatures." Hg strongly bound to river sediments seems to maintain a constant isotopic signature over time, and various contaminant sources such as coal ash and metallic industrial Hg may have distinct signatures that can be traced in river systems. In some cases, overlapping and sometimes wide ranges of source isotopic composition preclude effective source tracing.

At present, the isotopic systematics of Cr, Se, U, and Hg are fairly well understood, but important gaps in knowledge remain. For example, oxidation reactions are less well studied and are expected to be

fundamentally more complex than reduction reactions. For the other elements, V, Ni, Cu, Tl, W, Sb, and Te, isotopic systematics are incompletely understood, but are currently under investigation in most cases.

In general, these new isotopic tools rarely provide “magic bullets” that answer major questions unequivocally with simple interpretations. There are simply too many complexities in most natural systems and in the drivers of isotopic fractionation. However, as the new measurements become more widespread and less expensive, they can be more easily combined with other tracers, ancillary geochemical data, and insightful modeling and analysis to serve as key parts of many geochemical studies.