

Cr isotopes as indicators of Cr(VI) reduction and contaminant sources

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Chromium is a common contaminant released from industrial facilities such as plating shops, cooling towers, lumber treating operations, and pigment factories. In many industrial areas, multiple Cr sources exist, and soils derived from ultramafic rocks can also emit Cr, so determining "ownership" of plumes can be difficult. Cr is usually released as Cr(VI), which is soluble and toxic, but is readily reduced by a variety of mechanisms to Cr(III), which is insoluble and less toxic. This reduction often occurs naturally, or it can be induced by a variety of interventions that effectively remediate Cr plumes. Two major goals of forensic Cr geochemistry are tracing plumes back to sources and determining rates of Cr(VI) reduction.

Cr isotope (⁵³Cr/⁵²Cr) measurements show promise as indicators of Cr(VI) reduction. The kinetic isotope effect causes heavier isotopes to become increasingly enriched in the unreacted Cr(VI) with increasing extent of reduction. Two challenges are encountered with this approach: 1) The size of the $\delta^{53}\text{Cr}$ shift for a given extent of reduction is expected to vary if reaction mechanisms vary from site to site, and 2) The original $\delta^{53}\text{Cr}$ of the contaminant must be measured or estimated, and the sources are often gone. We did several laboratory experiments to determine the variability of the kinetic isotope effect. Cr(VI) reduction by *Shewanella oneidensis* MR-1 produces a range of fractionation, but under "lean" conditions similar to those in most aquifers, values of $4.1 \pm 0.2\%$ were observed. Abiotic reduction by Fe(II) and several organic reductants yielded a range of 2.9 to 4.7%, though this work is not yet complete. This range translates into an uncertainty of $\pm 25\%$ in extent of reduction calculated from $\delta^{53}\text{Cr}$ data. Further work is needed to better define the range applicable to actual field sites.

Industrial Cr(VI) supplies probably have Cr isotope compositions close to those of the earth's mantle. However, various plumes may have differing $\delta^{53}\text{Cr}$, depending on factors such as reduction in soils at the spill site. Cr derived from ultramafic rocks may be distinct from anthropogenic sources (Ball et al. talk, this session).

Tracing sources, movement, and fate of hexavalent Cr in ground water using Cr stable isotope variations

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Hexavalent Cr (Cr(VI)) in potable water supplies has become an increased health concern. Cr(VI) in ground water often has had an anthropogenic source. Substantial variations in ⁵³Cr/⁵²Cr ratios occur in nature and may allow identification of sources or chemical processes involving Cr. In waters with high natural background concentrations, Cr isotopes may be used to determine the source of Cr(VI) and to distinguish between anthropogenic and naturally-occurring Cr(VI).

About 200 ground-water samples were collected in the western Mojave Desert in 2001 - 2002. Cr(VI) concentrations in samples from uncontaminated sources ranged from less than the detection limit (0.1 $\mu\text{g/L}$) to about 60 $\mu\text{g/L}$, and were as high as 1,500 $\mu\text{g/L}$ in samples from contaminated sites. Cr(VI) concentrations were less than the detection limit in recharge areas near the front of the San Bernardino and San Gabriel Mountains and in discharge areas near dry lakes with low dissolved oxygen concentrations. The highest Cr(VI) concentrations in uncontaminated water (near 60 $\mu\text{g/L}$) were from wells in the Sheep Creek fan, composed of alluvium weathered from the dark, micaceous schist of the San Gabriel Mountains. Cr(VI) concentrations ranged from 0.9 to 28 $\mu\text{g/L}$ in water from deep wells in the granitic deposits underlying water-supply aquifers near Twenty-Nine Palms, California.

In the Twenty-Nine Palms and Sheep Creek fan areas, ⁵³Cr/⁵²Cr ratios ranged from near 0.0 per mil to +4.6 per mil. The latter value is almost exactly the theoretical maximum expected to accompany oxidation of Cr(III) on MnO_x substrates. Values near zero were from sites known to be contaminated. The ⁵³Cr/⁵²Cr ratios were higher in water from aquifers pumped for water supply and highest in water from the underlying deposits. These waters may be of greater age, thus the ⁵³Cr/⁵²Cr ratios may reflect greater reaction progress. The ⁵³Cr/⁵²Cr ratios from uncontaminated sites can be compared with those from contamination sites and may allow determination of the extent of anthropogenic contamination.