Chromium Stable Isotope Fractionation During Abiotic Reduction of Hexavalent Chromium

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Chromium, a common surface water and ground water contaminant, occurs as Cr(VI), which is soluble and toxic, and Cr(III), which is insoluble and less toxic. Reduction of Cr(VI) to Cr(III) is often the most important reaction controlling attenuation of Cr plumes, and Cr stable isotope ($^{53}$Cr/$^{52}$Cr) measurements show great promise as indicators of this reaction. Cr(VI) reduction involves a kinetic isotope effect; lighter isotopes react at greater rates and heavier isotopes become increasingly enriched in the remaining Cr(VI) with increasing extent of reduction. If the size of this effect can be constrained well, then precise estimates of reduction are possible. Cr(VI) reduction can be mediated by microbes, or may occur abiotically in the presence of Fe(II) and a variety of organic compounds. A recent study of bacterial reduction of Cr(VI) under low electron donor conditions yielded a Cr isotope fractionation factor of 1000ln$\alpha$ = 4.1 $\pm$ 0.2. A previous study of abiotic reduction indicated a fractionation factor of 1000ln$\alpha$ = 3.4 $\pm$ 0.2, but this work was limited to 3 experiments. The present study provides a more detailed look at Cr isotope fractionation induced by abiotic Cr(VI) reduction by: Fe(II); mandelic acid with alumina and goethite catalysts; and humic substances. Reduction occurred slowly, over days or weeks. The fractionation factor for the organic reductants (all at pH=4), including two surface-catalyzed mandelic acid reactions, two fulvic reactions, and one humic reaction, was 1000ln$\alpha$ = 3.0 $\pm$ 0.4, with no statistically significant differences between experiments. The fractionation factors for the Fe(II) experiments were 4.7 $\pm$ 0.3, 3.7 $\pm$ 0.2, and 2.9 $\pm$ 0.2 for pH = 4, 5, and 6, respectively. Further work is necessary to better constrain this pH dependence and to determine if it occurs with the organic reductants. The overall variability in the size of the Cr isotope fractionation during Cr(VI) reduction translates into a moderate level of uncertainty in Cr/$^{52}$Cr-based estimates of reduction.