

Chromium Isotopic fractionation during oxidation of Cr(III)-bearing solids by Manganese oxides at circum-neutral pH

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Naturally occurring Cr(VI) contamination of surface and groundwater occurs globally, and is common in the Circum-Pacific region. Cr in mafic and ultramafic rocks occurs as Cr(III), which is sparingly soluble and non-toxic. In the presence of Mn-oxides, Cr(III) oxidizes to Cr(VI), which is soluble, mobile, and highly toxic. Geogenic Cr(VI) tends to have elevated $\delta^{53}\text{Cr}$ values ranging from 0.7 to 5.1 ‰, significantly greater than $\delta^{53}\text{Cr}$ values of the source rocks (Bulk silicate earth ~ -0.14 ‰). The cause of this offset is not understood.

Even though Mn oxides are the major oxidants of Cr(III) in the natural subsurface and play a significant role in the mobilization of Cr(VI) both in modern and ancient environments, isotopic fractionation induced by this reaction remains poorly understood. The goal of this study is to determine the direction and magnitude of Cr isotope fractionation as solid Cr(III) phases are oxidized by solid Mn oxides, and to understand why geogenic Cr(VI) contamination is systematically enriched in heavier isotopes.

Here, we report Cr isotope fractionation factors for oxidation of Cr(III)-bearing solids (chromite, $\text{Cr}(\text{OH})_3$ and $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$) via reaction with synthetic birnessite under circumneutral pH conditions. The laboratory experiments are being conducted under both oxic and anoxic conditions. Results from the oxic experiments indicate that the initial stage of oxidation of Cr(III) solids to Cr(VI) can lead to isotopically heavier products with ϵ reaching up to 0.39 ± 0.09 ‰ ($\epsilon \approx \delta \text{ product flux} - \delta \text{ reactant}$). However, as the reaction progressed, this positive isotopic shift disappeared and $\delta^{53}\text{Cr}$ values of accumulated Cr(VI) approached the initial isotopic composition of the Cr(III) solids. Although we have observed significant isotopic fractionation, this fractionation is not sustained through time and its magnitude is too small to explain the range of $\delta^{53}\text{Cr}$ values reported for geogenic Cr(VI). Thus, our initial findings suggest that, in weathering environments, more complex processes are at play to produce isotopically heavy geogenic Cr(VI).