Thermodynamic controls on kinetic stable isotope fractionation: chromium(VI) reduction by iron(II)

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Stable isotope fractionation caused by changing redox conditions records the oxygenation of Earth's atmosphere and evolution of life as well as modern biogeochemical cycles. Quantitative understanding of the fundamental chemical controls on redox-driven fractionation may improve the reliability of fractionation models in natural systems, which are currently hindered by unexplained variability in fractionation factors. Here we develop a mechanistic framework for kinetic isotope effects associated with redox reactions. The model relates isotopic signatures to reaction pathways and environmental conditions and can be applied to all redox-sensitive stable isotope systems.

We evaluate the framework experimentally using the model system of Cr(VI) reduction. Chromium stable isotope fractionation is an important proxy for paleo-redox conditions because reduction of mobile Cr(VI) to immobile Cr(III) induces kinetic fractionation documented as positive isotopic excursions in banded iron formations and marine carbonates. One of the most common reductants of Cr(VI) is Fe(II). We measure chromium isotope fractionation during reduction by both aqueous Fe(II) species and an Fe(II/III)-bearing clay mineral. Aqueous Fe(II) is one of the fastest reductants of Cr(VI) at circumneutral pH. Iron(II/III)-bearing clay minerals are ubiquitous in anoxic environments and similarly fast reductants of Cr(VI) at high Fe(II)/Fe(total) ratios. We investigate the effects of pH, ligation of aqueous Fe(II), and the Fe(II)/Fe(total) ratio in the nontronite. The reaction mechanism and rate law of Cr(VI) reduction are consistent with the mechanistic framework. This model may explain some of the diversity in reported Cr(VI) fractionation factors and ultimately increase the utility of stable isotopes to studying geochemical systems past and present.