

Applications of Marcus theory to stable isotope fractionation during chromium(VI) reduction

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Abstract

Metal stable isotope fractionation has emerged as an important tool for tracing redox reactions in natural environments. Nevertheless, descriptions of the fundamental controls on fractionation are sparse, and predicting the magnitude and even the direction of kinetic fractionation remains especially challenging. Marcus theory, which expresses the kinetics of electron transfer in terms of standard thermodynamic quantities, offers a mechanistic framework to interpret kinetic isotope fractionation during electron transfer. Under most conditions, Marcus theory predicts that the magnitude of kinetic fractionation decreases linearly with the standard free energy of reaction and is proportional to equilibrium fractionation. Although Marcus theory has been applied to isotope fractionation during metal electroplating, its potential to quantitatively predict trends in kinetic fractionation in geochemically relevant systems without quantum mechanical computations remains unexplored.

Chromium(VI) reduction was chosen as a model reaction to test the application of Marcus theory due to its tendency to exhibit kinetic chromium isotope fractionation and its environmental importance. Chromium(VI) is a major pollutant that also derives naturally from ultramafic weathering. In the hexavalent state, chromium is toxic and generally soluble; in the trivalent state, chromium is environmentally benign and much less soluble. Chromium isotope fractionation has been proposed as a proxy for chromium(VI) reduction, but its utility is limited by the large variability in kinetic isotope fractionation during chromium(VI) reduction.

We investigated chromium kinetic isotope fractionation during homogeneous chromium(VI) reduction by aqueous iron(II) complexes, which include some of the fastest naturally occurring reductants of chromium(VI). The standard free energy of reaction was varied by changing the ligation of iron(II) (*e.g.*, citrate, nitrilotriacetate). Chromium(VI) reduction was carried out in anoxic, constantly stirred batch reactors, and ⁵³Cr/⁵²Cr was determined using inductively coupled plasma mass spectrometry. Rayleigh fractionation was observed in all reactors, but the magnitude of fractionation varied from -1.7 to -3.4 ‰.

Marcus theory has previously been applied to chromium(VI) reduction by aqueous iron(II) complexes to explain the exponential increase in the rate of reduction as the standard free energy of reaction decreases. Here we show a linear relationship between the kinetic fractionation of chromium(VI) and the standard free energy of reaction, as predicted by Marcus theory. Practical consequences of this linear free energy relationship include the strong pH dependence of the effective fractionation factor for chromium(VI) reduction by aqueous inorganic iron(II), which decreases in magnitude by 2 ‰ in the environmentally relevant pH range of 4-7. Additionally, Marcus theory allows the rate-determining step and mechanistic source(s) of fractionation during chromium(VI) reduction to be probed.

This study not only expands our understanding of chromium isotope fractionation in anoxic settings but also offers a predictive model for kinetic redox fractionation that is more widely applicable to stable isotope systems. Future work includes geochemical modeling of the pH dependence of chromium isotope fractionation in simulated aquifer settings and applying Marcus theory to more complex, heterogeneous systems.