Applications of Marcus theory to stable metal isotope fractionation during redox reactions

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Stable isotope fractionation is a powerful tool for tracing redox reactions in complex natural systems, yet mechanistic descriptions of the underlying controls on fractionation are rare. Predicting the direction and magnitude of kinetic fractionation is especially difficult. Marcus theory, which relates electron transfer kinetics to standard thermodynamic quantities, offers a framework to interpret kinetic isotope fractionation during electron transfer. Under most conditions, Marcus theory predicts that more thermodynamically favorable electron transfers are faster and produce less kinetic fractionation.

We investigated the ability of Marcus theory to quantitatively predict kinetic fractionation during homogeneous chromium(VI) reduction by aqueous iron(II) complexes. Chromium(VI) reduction is an important control on the fate of Cr(VI), a water-soluble carcinogen and pollutant. The standard free energy of reaction ($\Delta G°$) was varied by changing the ligation of Fe(II) (*e.g.*, citrate, salicylate, 2OH). Marcus theory has previously been applied to this model system to explain the increase in the rate of Cr(VI) reduction with increasing $\Delta G°$. Here we demonstrate that $\Delta G°$ also affects the kinetic fractionation of Cr. Deprotonation of aqueous Fe(II) makes Cr(VI) reduction more thermodynamically favorable and results in less kinetic fractionation of Cr, causing the effective fractionation of Cr(VI) during reduction by aqueous Fe(II) to vary with pH. We model the experimental results using Marcus theory to gain a mechanistic understanding of Cr isotope fractionation.

This study not only improves our understanding of Cr isotope fractionation in anoxic settings but also provides a new predictive model for kinetic redox fractionation that is widely applicable to stable isotope systems.