

Chromium isotope fractionation during oxidation of Cr(III) by manganese oxides

DANIEL J. BAIN AND THOMAS D. BULLEN

U. S. Geological Survey, Menlo Park, CA, USA.
(djbain@usgs.gov; tdbullen@usgs.gov)

Early investigation of environmental chromium (Cr) fractionation has focused on natural processes attenuating anthropogenic hexavalent chromium (Cr(VI)) contamination. Reduction of mobile, toxic Cr(VI) to immobile trivalent Cr (Cr(III)) preferentially reduces lighter Cr isotopes, resulting in light Cr(III) and heavy Cr(VI) near Cr(VI) contamination sites. However, environmental interactions between Cr(III) and manganese oxides can generate significant quantities of Cr(VI) without human activity. The oxidation of Cr(III) is not well understood, yet is potentially important to Cr isotopic systematics. Initial laboratory investigations of Cr(III) oxidation by birnessite (δ -MnO₂) demonstrated wide variation in the isotopic composition of the developing Cr(VI) pool ($\delta^{53}\text{Cr} = -2.5$ to $+0.7$ ‰, relative to NIST 979). Further, variation in isotopic composition continues after net Cr(VI) production ceases. These observations suggest that multiple oxidation mechanisms are present, even in simple systems, and individual mechanisms are discriminating against both heavy and light isotopes.

Understanding fractionation during oxidation of Cr(III) requires elucidation of the oxidation mechanisms. For example, the range of $\delta^{53}\text{Cr}$ observed thus far in high Cr(VI) groundwaters is from 0 to $\sim+4.4$ ‰. The data are not consistent with simple Cr reduction, suggesting that dilution or other processes are also important in cycling. In particular, Silvester *et al.* (1995) suggest that reaction rates in Mn oxide limited systems are controlled by production of the Cr(IV) intermediate species. If the associated reprecipitation of Cr(IV) (i.e., $3\text{Cr(IV)} \rightarrow 2\text{Cr(III)} + \text{Cr(VI)}$) imparts the theoretical maximum fractionation between Cr(VI)O₄²⁻ and Cr(III)(H₂O)₆³⁺ predicted by Schauble *et al.* (2002), $\delta^{53}\text{Cr}$ of the resulting Cr(VI) should be $\sim+4.4$ ‰ and that of Cr(III) ~-2.2 ‰. Improved understanding of this mechanism may be key in allowing differentiation between anthropogenic and “natural” Cr(VI) and provide a powerful probe for investigation of the Cr cycle.

References

- Schauble, E.; Rossman, G. R.; Taylor, H. P., Jr. (2004) *Chem. Geol.* **205**, 99-114.
Silvester, E.; Charlet, L.; Manceau, A. (1995) *J. Phys. Chem.* **99**, 16662-16669.

Copper isotope fractionation at high temperature: Investigating copper mineralization at Corocchohuayco, Perú

KIERRAN C. MAHER¹ AND PETER B. LARSON²

¹Washington State University, Webster 1228, Pullman, WA 99164 (kmaher@wsu.edu), ²(plarson@wsu.edu)

Copper isotopes from mineralization in the high temperature hydrothermal skarn system at Corocchohuayco, Perú, show a range in $\delta^{65}\text{Cu}_{\text{NIST SRM 976}}$ from -1.29 to +1.17 per mil (± 0.08 ‰, 2σ). These analyses come from vein and disseminated chalcopyrite and bornite. Locally the copper isotopes are strongly zoned from isotopically light in proximal/early mineralization to heavy in distal/later mineralization. The fractionation mechanism proposed by Marechal and Albarede [1] at low temperatures between different copper complexes may be applicable at higher temperature. Isotopic fractionation between copper complexes of different thermodynamic stabilities would lead to isotopic differences between early and later mineralization produced from the same fluid. Geologic constraints indicate the hydrothermal fluids responsible for mineralization at Corocchohuayco were high salinity brines (ave 43 % wt NaCl eq) that precipitated copper sulfides between 300-350° C. Mineralization is initiated by thermodynamic instability of one of the copper complexes [2], leading to instability of the other important complexes and massive precipitation. Early mineralization would receive its isotopic signature from the first unstable copper complex and later mineralization would be characterized by the isotopic composition of the remaining complex(es). If copper is significantly fractionated between different copper complexes (“ligand-choice”) in higher temperature hydrothermal solutions then an “apparent” Rayleigh-style fractionation trend should be expected in the resulting mineralization. The large fractionation observed at Corocchohuayco is likely produced by both a true Rayleigh-type fractionation mechanism (related to differing stabilities of ⁶³Cu and ⁶⁵Cu in the same complex) and the “ligand-choice” mechanism. This “ligand-choice” fractionation mechanism would be most important in those hydrothermal systems where more than one important copper complex is present.

References

- [1] Marechal, C. and Albarede, F., (2002), *Geochim. Cosmochim. Acta*, **66**, 1499-1509.
[2] Liu W., Brugger, J., McPhail, D. C. and Spiccia, L., (2002), *Geochim. Cosmochim. Acta*, **66**, 3615-3633.