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Kinetic fractionation of stable Cr isotopes between aqueous Cr(III) species: alternative Cr fractionation pathways in Archean environments

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A long-held assumption in the application of stable Cr isotopes as a paleo-redox proxy established from *ab initio* modelling [1] is that isotopic differences and fractionations between Cr(III) species are minor relative to those involving a redox change between Cr(VI) and Cr(III). As such, measurable Cr isotope fractionation in ancient sedimentary rocks have been interpreted as evidence for surficial Cr redox cycling in early Earth's history [2,3]. However, isotope effects associated with Cr(III) reactions (e.g., adsorption, ligand exchange) remain largely untested as an alternative. Moreover, the magnitude of measured variability in Cr isotope values of Archean marine sedimentary rocks is much lower than those from the Proterozoic and Phanerozoic. Accordingly, there is room to accommodate a greater role for isotopic fractionation during aqueous Cr(III) cycling in the more pervasively anoxic environments of the Archean.

This study documents closed-system kinetic isotope fractionation between 3 aqueous Cr(III)-Cl-H_2O complexes during the 2-stage dechlorination reaction from $[CrCl_2(H_2O)_4]^+$ to $[CrCl(H_2O)_5]^{++}$ to $[Cr(H_2O)_6]^{+++}$ at pH 2 and 25°C. These results build on the results of [4] that documented near-equilibrium fractionation of the Cr(III)-Cl-H_2O species in 6 M HCl – conditions where all 3 species are stable. In contrast, at pH 2 only $[Cr(H_2O)_6]^{+++}$ is stable and forced disequlibrium allows documentation of Rayleigh distillation with apparently distinct fractionation factors for each transformation stage, with differences in $\delta^{53/52}$Cr reaching up to ~1‰ between 2 species. The pH conditions of these experiments are argued to be more relevant to natural systems than those of [4] and that the results offer a framework upon which to explore aqueous Cr(III) cycling (e.g., preferential complexation and removal of isotopically light Cr(III)-species in hydrothermal systems) as a viable option for Archean stable Cr isotope reactions.

[1] Schauble et al. (2004). Chem. Geol. 205: 99-114; [2] Frei et al. (2009). Nature 461: 250-253; [3] Crowe et al. (2013). Nature 501: 535-538. [4] Larsen et al. (2016). J Chromatogr. A. 1443: 162-174.