

# Redox-independent isotope fractionation during Cr(III) adsorption onto goethite and magnetite

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The previous assumption that Archean Cr stable isotopic variations in the form of <sup>53</sup>Cr-depleted paleosols and <sup>53</sup>Cr-enriched marine chemical sediments is proof for terrestrial oxidative Cr weathering contradicts other geochemical tracers and geological evidence. Chromium isotope studies that proposed Cr(III) oxidation via reactive oxygen species and Mn-oxides as early as 3.7 Ga have far-reaching implications since these reactions would require free atmospheric O<sub>2</sub> availability [1, 2]. Major implications would relate to the redox-evolution of the atmosphere-hydrosphere system and the timing of oxygenic photosynthesis. Inferences of Archean oxidative Cr cycling are underpinned by assumptions that non-redox processes produce immeasurable stable Cr isotope variations in the rock record; however, experimental and empirical investigations of Cr mobility and isotopic fractionation processes of modern oxidized-to-reduced systems remain insufficiently complete to extrapolate results to Archean fully reduced systems.

We developed an experimental setup to shed further light on reaction kinetics, mode (kinetic vs equilibrium), and degree of stable Cr isotopic fractionation during Cr(III) adsorption onto two of the most common reactive Fe minerals in sedimentary environments. Synthesized adsorbent minerals goethite (Fe(III)) and magnetite (Fe(II)/Fe(III)) were characterized and mixed with aqueous Cr(III)-bearing nitric acid solutions at pH 4. The presence of only Cr(III) was confirmed with controlled pre- and post-experiment checks to eliminate the possibility for any interfering redox processes.

Results show initially kinetic adsorption behavior on both minerals before reaching an equilibrium steady-state within days. Upon reaching equilibrium, adsorption of aqueous Cr(III) to both Fe-minerals shows significant non-redox isotopic fractionation, with  $\epsilon^{53/52}\text{Cr}$  ( $\text{CrIII}_{\text{aq}}/\text{CrIII}_{\text{ads}}$ ) of +0.5 to +0.7‰ indicating preferential enrichment of the light isotopes in the adsorbed trivalent Cr.

These results add growing evidence for the possibility of redox-independent Cr(III) isotopic fractionation playing a greater role in natural Cr cycling than previously assumed, potentially including Archean systems [3, 4, 5].

[1] Crowe et al. (2013) Nature 501: 535-538 [2] Frei et al.