Cr isotope variability in the oceans: Implications for the Cr isotope proxy

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Cr(VI)–Cr(III) interconversions are the principal source of Cr isotopic fractionation in Earth surface environments [1]. Heavy Cr isotopes partition preferentially into Cr(VI), while light Cr isotopes partition into Cr(III). Because Cr(VI) is more soluble than Cr(III), any Cr isotopic fractionation that occurs during continental weathering is transferred to the oceans in runoff, where it has the potential to be preserved in authigenic marine sediment. The mechanistic link between oxidative weathering on the continents and Cr isotope variability in marine sediment is the basis of a technique utilizing Cr isotopes as a tracer of Earth's oxygenation history [2]. Most studies have focussed simply on demonstrating the presence or absence of Cr isotope fractionation in ancient marine sediment. If no Cr isotope fractionation is observed, then oxidative weathering is deemed to be diminished or absent altogether on the continents, with similar implications for atmospheric oxygen levels. Interpretations of δ^{53}Cr in ancient marine sediments make no allowance, however, for fractionation of Cr isotopes by processes internal to the oceans. In this talk, we present measurements of Cr isotopes in seawater that show δ^{53}Cr in the oceans is variable, with values ranging between 0.5 and 1.5‰. The isotopic variations are systematically correlated with total Cr concentration (VI plus III), and are intepreted to reflect redox Cr-cycling in the oceans, specifically fractionation of Cr isotopes associated with reduction and removal fluxes of Cr(VI) and back-mixing of isotopically light authigenic Cr released from particles and sediment. These findings warrant reconsideration of the suggestion in [3] that seawater derived Cr in the anoxic marine sediment of the Cariaco Basin is unfractionated, but supports the findings in [4] that the Argentine Basin is characterized by a low seawater δ^{53}Cr value of 0.5‰. Cr redox cycling in the oceans effectively overprints the isotopic signature of Cr weathering inputs on a global scale. This finding needs to be considered in applications of the Cr isotope proxy to Earth's oxygenation history going forward.

[1] Ellis et al., 2002, *Nature* **295**, 2060–2062; [2] Frei et al., 2009, *Nature* **461**, 250–254; [3] Reinhard et al., 2014, *EPSL* **407**, 9–18; [4] Bonnand et al., 2013, 382, 10–20.