

## Earth surface redox constraints from the ancient Cr cycle

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Stable Cr isotope ratios of sedimentary rocks provide a historical record of large kinetic isotope fractionations associated with redox reactions at the Earth's surface. Cr in most igneous phases exists as Cr(III), which remains stable/immobile during terrestrial weathering under reducing conditions. Furthermore, both theoretical and experimental studies indicate that Cr will undergo limited fractionation during non-redox-dependent transformations. In marked contrast to non-redox processes, the oxidation and reduction of Cr induce large isotope fractionations. Therefore, Cr isotopes are ideally suited to track redox processes.

To date, iron formations have been the most utilized Cr isotope archive. Iron formations, as chemical precipitates, have the potential to trap an aqueous Cr isotope signature, rather than carrying a predominantly detrital Cr load. Further, iron oxides sorb significant amounts of Cr. And therefore iron oxide-rich rocks have a much higher potential than other chemical precipitates (e.g., cherts and carbonates) to have Cr isotope signatures that are rock buffered during burial alteration.

Based on previous work and our new results, the Archean iron formation Cr isotope record is generally characterized by near-crustal  $\delta^{53}\text{Cr}$  values suggesting a lack of significant Cr redox cycling. In stark contrast, Neoproterozoic iron formations and Phanerozoic ironstones exhibit large and variable Cr isotope fractionations—a clear signal of substantial Cr redox cycling. Rather surprisingly, we found four mid-Proterozoic ironstones with limited Cr isotope variability despite having significant authigenic Cr enrichments. *In situ* Cr abundance work confirms that Cr in the examined samples is present in depositional phases (e.g., iron ooids) rather than in detrital Cr-rich phases (e.g., chromite). Our new results fill in a previously existing billion-year gap in sedimentary Cr isotope data and suggest that, in the Neoproterozoic, there was a permanent switch to a more oxidative Cr cycle. These results suggest limited Cr isotope fractionations due to low (relative to standard models) environmental oxygen concentrations for intervals of the mid-Proterozoic.

## Modelling scavenged ocean tracers: Rare earth element transport and fractionation

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Insoluble metals such as rare-earth elements (REEs), Al, and Th have not been so widely studied as nutrients or dissolved gases as tracers of ocean process, but are seeing increasing interest driven by extensive new datasets and by a desire to understand the cycling of micronutrient metals (e.g. Fe, Cu) which are critical for biology and have a component of insoluble behaviour. Insoluble tracers have spatial oceanographic gradients dominantly controlled by their propensity to attach to particles (scavenging). In the ocean, REEs are interesting because, when normalized to their source composition (i.e. continental inputs), they show a systematic and relatively smooth (except Ce) progression from the light to the heavy REEs. The shape of this REE-pattern, which is the macro-scale representation of the lanthanide contraction, varies spatially in the ocean as a function of source proximity, water-mass mixing, water mass age and particle concentration. Because source types are similar for most REE (mostly rivers and dust), and REEs do not influence the particle field, the slight differences amongst the source-normalized dissolved REE concentrations in the ocean interior reflects the balance between physical transport and scavenging. Light REE (LREE) scavenge more readily than heavy REE (HREE) so HREE are more sensitive to transport than LREE.

In this study we exploit the LREE-to-HREE progression and explore the value of a new tracer (REE\*) defined by the incremental differences between REEs in the pattern. We first present the large scale distribution and mean gradients of REE from the analysis of a global REE data set assembled from published historical values and new GEOTRACES measurements. Secondly, we discuss results from a set of sensitivity modeling experiment, based on the transport matrix formalism, designed to better understand controls on the distribution of REE in the ocean, the potential value of REE\* as a water mass tracer, and the use of REEs to understand scavenged elements more generally.