Fractionated Cr isotopes in the late Paleoprotorozoic marine carbonates from the McArthur Basin, Australia: A record of oxic paleo-seawater or a later diagenetic fluid-flow event?

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Reconstructing the redox conditions of the ocean-atmosphere system over geological time is one of the primary research objectives of earth system studies. Thus far, the oxygen levels during the mid-Proterozoic (ca. 1.8 to 0.8 Gyr) remain poorly constrained as different geochemical/isotope proxies allow for a broad range of possible paleo-redox conditions (<0.1 to 10% of present atmospheric O_2 levels [1]). The sedimentary record of marine carbonates and shales deposited in the McArthur Basin in Northern Territory (NT), Australia, provide a unique window into this critical time interval, potentially recording changes in Proterozoic seawater composition and coeval paleo-redox conditions [2].

This study presents high-resolution Cr isotope data ($\delta^{53}Cr$) from late Paleoproterozic carbonates (~1.64 Ga), from two remote and correlative drill cores (Manbulloo and LV09001), which thus potentially represent basin-wide records of paleo-enviromental conditions within the greater McArthur Basin. Acquired $\delta^{53/52}Cr$ trends are complemented by independed paleo-redox (Ce/Ce*) data, and other traditional ($^{87}Sr/^{86}Sr$, $\delta^{13}C$) and novel (Δ47 clumped isotopes) tracers, and micro-scale mineral mapping (Nanomin). Importantly, positively fractionated $\delta^{53}Cr$ data from Manbulloo core, coupled with decreasing Cr concentrations, suggest evidence for a partial-reduction of oxidised Cr(VI) species to Cr(III) in local paleo-seawater, also linked with an increasing abundance of hematite associated with positively fractionated Cr isotopes. However, we also observed abundant chlorite and elevated temperatures of ca. 125-150 °C (Δ47 clumped) associated with fractionated $\delta^{53}Cr$ data, indicating that the latter could be as well a product of later stage fluid-flow alteration event(s). We discuss and critically evaluate these two scenarios, and implications for $\delta^{53}Cr$ paleo-redox reconstructions from ancient carbonate archives.

[1] Ozaki *et al*. 2019, *Geobiology*, Vol. 17, p. 3-11. [2] Cox *et al*. 2019, *Nature Scientific Reports*, 9:5200.