## Rayleigh? Maybe. What controls marine d<sup>53</sup>Cr systematics?

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Chromium (Cr) is a redox-sensitive element whose marine stable isotope distribution is driven by isotope fractionation during the reduction of soluble Cr(VI) to particle-reactive Cr(III). Sedimentary records of Cr stable isotope composition ( $d^{53}$ Cr) have thus been applied to reconstruct past changes in ocean redox state (e.g. Frei et al., 2009, Reinhard et al., 2014), but GEOTRACES-era data have revealed gaps in our understanding of marine  $d^{53}$ Cr systematics.

In the modern open ocean, Cr exhibits a remarkably coherent relationship between the concentration of total dissolved Cr and  $d^{53}$ Cr, which has been interpreted, in the context of classical Rayleigh distillation (Strutt, 1896), to reflect a net isotope effect of around -0.8‰ (e.g., Scheiderich et al., 2015). However, the isotope effect of abiotic Cr(VI) reduction is significantly larger than this, at -1.5‰ to -5.0‰ (Wei et al., 2020 and references therein). Furthermore, the  $d^{53}$ Cr values of co-existing Cr(III) and Cr(VI) are offset by more than 1‰ (Huang et al., 2021). This poses the question of what the apparently simple Rayleigh-like marine  $d^{53}$ Cr systematics really reflects (see also Wang, 2021).

We present results from idealised three-dimensional ocean general circulation model simulations using the Transport Matrix Method (Khatiwala et al, 2005) in which dissolved Cr(VI) and Cr(III) pools, and their stable isotope compositions, are explicitly traced. This allows us to investigate how the physical transport of co-existing, isotopically offset Cr(VI) and Cr(III) interacts with biogeochemical cycling processes, such as isotope fractionation during reduction and scavenging loss of Cr(III), to produce the observed marine  $d^{53}$ Cr distribution, thus elucidating the mechanistic underpinnings of the marine isotope systematics of Cr.

## References

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