

On the Cr isotopic composition of seawater

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The chromium (Cr) isotopic composition ($\delta^{53}\text{Cr}$) of authigenic marine sediments is increasingly being used to determine past changes in the Cr isotopic composition of seawater. Cr isotopes are fractionated by redox reactions and records of seawater $\delta^{53}\text{Cr}$ have been used to provide important information as to past levels of seawater and atmospheric oxygenation, and in turn their influence on the evolution of life. To date, however, there are only a handful of measurements of $\delta^{53}\text{Cr}$ in the modern ocean and a process-based understanding of the controls on Cr isotopes in seawater is, as yet, intractable.

To fill this gap, we have determined Cr concentrations and $\delta^{53}\text{Cr}$ for a series of well-characterised seawater samples. These include: (i) Continental shelf waters from the Celtic Sea sampled repeatedly during pre-bloom, bloom and post-bloom conditions. (ii) Waters within the sub-tropical Atlantic oxygen minimum zone sampled by GEOTRACES Transect GA06. (iii) Oxidic, anoxic and euxinic waters from the Black Sea taken as part of the GEOTRACES Medblack expedition. We have also determined the evolution of Cr during mixing between riverwater from the River Beaulieu (UK) and adjacent coastal waters.

Our data show that, overall, shelf waters have lower Cr concentrations and higher $\delta^{53}\text{Cr}$ values than adjacent deep waters. We find no evidence for reduction of Cr(VI) to Cr(III) within the sub-tropical Atlantic oxygen minimum zone; the lowest levels of O_2 in these waters are $\sim 50 \mu\text{M}$. However, Cr concentrations are lower in anoxic waters in the Black Sea (0.88 nM) compared to overlying oxidic surface waters (1.02 nM). The anoxic waters have lower $\delta^{53}\text{Cr}$ (1.42 ‰) than oxidic waters (1.69 ‰). Finally, we show that in the Beaulieu estuary, there is a strong correlation between salinity and $\delta^{53}\text{Cr}$ that suggests Cr isotopes behave conservatively during mixing. We also find no evidence for reduction of Cr(VI) during estuarine mixing. The implications of our results for interpretation of $\delta^{53}\text{Cr}$ in ancient marine sediments will be discussed.