

Rapid-throughput MC-ICPMS techniques for analysis of multiple transition metal isotope ratios in seawater, and case studies from recent GEOTRACES cruises

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Transition metals play key roles in marine systems, acting to limit growth of phytoplankton in the oceans, and thus influence patterns of marine primary productivity and the global carbon cycle over a range of timescales. In recent years, high-resolution sections of trace metals in the oceans have been produced as part of the GEOTRACES program, revolutionising understanding of marine trace metal cycling¹. However, these concentration sections alone are often unable to provide enough information to discriminate between a range of competing biogeochemical processes. It is here that stable isotope ratios of the transition metals offer promise.

Such ideas have motivated a number of research groups to develop techniques to measure the seawater-dissolved stable isotope ratios of the transition metals (e.g. $\delta^{56}\text{Fe}$, $\delta^{65}\text{Cu}$, $\delta^{60}\text{Ni}$, $\delta^{66}\text{Zn}$, $\delta^{114}\text{Cd}$). Making these measurements is not simple however, due to the vanishingly-low concentrations of these metals in seawater ($\sim 0.00001 - 10 \text{ nmol kg}^{-1}$) compared to both the seasalt matrix and a need for high precision analysis. As a result, groups often require large volumes of seawater (up to 20L) for single isotope system measurements, prohibiting the widespread application of these tracers.

To address this paucity of field data, we have developed two rapid-throughput methods for the determination of 1) $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ in a single litre of seawater and 2) $\delta^{65}\text{Cu}$, $\delta^{60}\text{Ni}$ and $\delta^{66}\text{Zn}$ in 1-2 L samples utilising Nobias PA-1 and AGMP-1 resins and high-precision double-spike Neptune MC-ICPMS². Subsequently, we have generated a number of high-resolution GEOTRACES sections in both the Atlantic and Pacific Oceans, generating large datasets of dissolved $\delta^{56}\text{Fe}$, $\delta^{66}\text{Zn}$ and $\delta^{114}\text{Cd}$ (>1000 data per element). In this talk, we present these methods, together with several examples where high-resolution isotope sections or multiple-element isotope profiles have led to new insights into the contrasting behaviour of metals in the oceans.

[1] Mawji *et al.* 2015. *Marine Chemistry*. **177**(1). 1-8.

[2] Conway *et al.* 2013. *Analytica Chimica Acta*. **793**. 44-52.