Zn isotopes as a new tracer of metal micronutrient usage in the oceans

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Many transition metals are essential micronutrients for marine phytoplankton and the expectation is that biological processes play an important role in their marine geochemistry. This raises the prospect of using isotope records to track metal usage in the past, of importance to the efficiency of the biological pump and atmospheric CO_2. The characterisation of trace metal isotopic fractionations associated with marine primary productivity is thus a key scientific goal. Here we report isotopic fractionations associated with Zn uptake by diatoms and relate them to water column data for a trace-metal limited region of the ocean.

Cultures were established in artificial seawater media and the cultures filtered to separate diatom material from residual media for analysis for Zn concentrations and isotope composition. The diatom organic material shows small but resolvable fractionations relative to the starting medium. Initial experiments with inadequate EDTA control on free Zn^{2+} concentrations resulted in heavy Zn being sequestered by the diatoms, a result we attribute to preferential surface adsorption of the heavier isotopes. Subsequent experiments, with EDTA demonstrate preferential uptake (by about 0.4 per mil for $\delta^{66}Zn$) of light Zn isotopes that is most pronounced at low free Zn^{2+}. Seawater measurements, from the NE Pacific HNLC zone show that the deep ocean Zn inventory is un-fractionated with respect to the continental input at around +0.3 per mil relative to the Lyons JMC standard. However, the upper water column is much more variable, with $\delta^{66}Zn_{JMC}$ up to +1 per mil at the surface. This is complemented by enrichments in lighter isotopes ($\delta^{66}Zn_{JMC}$ = -0.1 per mil) relative to the input at around 100m.

Taken together, these data suggest preferential uptake of light Zn isotopes by phytoplankton at the surface and significant recycling of that pool of Zn by regenerative processes in the thermocline. The data put constraints on the rate of recycling of trace metals in the upper water column and suggest that records of Zn isotopes in sediment may shed light on the operation of these processes in the past.