Ligand control on Zn isotope signatures of marine phytoplankton

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Zinc (Zn) is an essential micronutrient taken up by marine phytoplankton mainly for photosynthesis. Diatoms alone account for as much as 20% of carbon fixation on Earth [1]. The resulting biomass is often characterized by high cellular Zn quotas, in a range also observed for iron (Fe), but rarely for other transition metals. Extreme scarcity of Zn in the euphotic zone, coupled to deep enrichments [2], is consistent with biological uptake at the surface and regeneration at depth. To our knowledge, the diatom *Thalassiosira oceanica* is thus far the only planktonic organism that has been suggested to fractionate Zn isotopes during uptake [3]. Further culturing experiments, elucidating the partitioning of Zn isotopes in well constrained experimental systems, are required.

Consistent with previous work [3], we have cultured diatoms whose biomass contains Zn that is 0.2 to 0.3 ‰ lighter than the culturing medium ($\Delta^{66}Zn_{\text{JMC-Lyon}} = \delta^{66}Zn_{\text{biomass}} - \delta^{66}Zn_{\text{medium}}$). The synthetic chelator ethylene-diaminetetraacetic acid (EDTA) was used in all culturing experiments, and shows a preference for heavy isotopes by about 0.3 ‰. Zn-EDTA equilibrium fractionation in the culture medium leaves the free inorganic Zn pool enriched in light isotopes. All studied organisms take up Zn exclusively from the free inorganic Zn pool. Therefore we suggest that small potential fractionations associated with uptake are superimposed on much larger chelation effects. The conditional stability constant for Zn-EDTA is close to that for natural marine organic ligands, suggesting that ‘apparently’ light signatures in marine biomass are favoured under conditions dominated by abundant, and strong Zn binding ligands. Our findings have important implications for the oceanic realm in that quantity and character of marine ligands are intrinsically tied to our interpretation of biomass associated Zn isotope signatures.

[1] Armbrust (2009), *Nature* **459**, 185-192. [2] Morel & Price (2003), *Science* **300**, 944-947. [3] John *et al*. (2007), *Limnol. Oceanogr*. **52**, 2710-2714.