Iron limited diatoms do not fractionate zinc isotopes: Culturing evidence

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Transition metals, such as zinc (Zn) and iron (Fe), are taken up by marine phytoplankton as essential micronutrients. Extreme scarcity of Zn in the euphotic zone, coupled to deep enrichments [1], is consistent with biological uptake at the surface and regeneration at depth. Recent efforts to unravel the spatial distribution of metal isotopes in the global oceans, reveal a remarkable homogeneity in Zn isotopes beneath the permanent thermocline, with variable signatures confined to the eupothic zone. This isotopic distribution is not easily explained if fractionation of Zn occurs during phytoplankton uptake. Diatoms alone account for as much as 20% of carbon fixation on Earth [2]. To our knowledge, the diatom *Thalassiosira oceanica* is thus far the only planktonic organism that has been shown to fractionate zinc isotopes during uptake [3]. Further culturing evidence elucidating key contolling factors that might potentially cause Zn isotope variability in surface ocean is required.

Here we present the first culturing evidence identifying Fe-limitation as a physiological driver controlling Zn isotope fractionation associated with uptake into marine diatoms. On the basis of four different diatom strains we found that Fe-limitation suppresses δ^{66}Zn isotope fractionation. We identified a threshold concentration of bioavailable Fe in the culturing medium, below which Zn isotope fractionation ($\Delta^{66}Zn_{JMC\text{-}Lyon} = \delta^{66}Zn_{biomass} - \delta^{66}Zn_{medium}$) decreases from variable values in the range of -0.45 and +0.3 ‰ to almost insignificant levels. The range of $\Delta^{66}Zn_{JMC\text{-}Lyon}$ found for Fe-replete conditions is consistent with the only other published dataset on Zn isotope fractionation observed during uptake into a marine diatom [3]. The removal of surface-bound metals from phytoplankton organisms is most critical for the interpretation of any isotope data obtained by culturing efforts. Our well-constrained experimental results allow us to re-address this longstanding debate on metals associated with diatom surfaces.

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