

Pseudo-redox control on the oceanic budget of Zn and Zn isotopes

Susan H. Little^{1*}, Derek Vance², Corey Archer², Michael Köbberich²

¹ Department of Earth Science and Engineering, Imperial College London, London SW7 2BP, UK

² Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland

*Corresponding author email address

Zinc (Zn) is a key micronutrient, utilized in over one hundred Zn-specific enzymes across all five kingdoms of life, and cellular uptake by phytoplankton sets oceanic dissolved Zn distributions (e.g., Bruland et al., 2014). As a result, it was anticipated that Zn stable isotopes would offer potential as a tracer of past ocean productivity. However, recent analytical advances allowing precise measurement of Zn isotopes in seawater suggest that biological uptake may not be a key control on Zn isotope distributions in the ocean (e.g., Vance et al., 2016). Instead, the oceanic budget of Zn isotopes and the Zn isotope composition of seawater ($\delta^{66}\text{Zn}_{\text{seawater}}$ of about +0.5‰, relative to JMC-Lyon) appear to reflect a balance of the removal of Zn into distinct 'oxic' and 'reducing' sedimentary sinks.

Zinc is a group 12 element in the periodic table. It has only one important oxidation state, +2, in which it has a stable d10 electronic configuration. As a result, Zn does not exhibit genuine redox-related stable isotope fractionation. Instead, Zn isotope fractionation in the aqueous environment reflects one or more of a) adsorption, b) ligand exchange or c) kinetic effects. One key output of Zn from the modern ocean is sorption on Fe-Mn oxides, found dispersed throughout sediments deposited under normal oxic marine conditions. This oxic output flux is isotopically heavy (at about +1‰; Maréchal et al., 2000; Little et al., 2014a) compared to the known Zn input fluxes (including rivers, aerosols, and hydrothermal Zn, all at about +0.3‰; Little et al., 2014a), consistent with experimental and theoretical predictions of the preferential sorption of heavy Zn isotopes on Fe-Mn oxides (Little et al., 2014b; Bryan et al., 2015). In order to balance this isotopically heavy oxic output flux, and to drive seawater isotopically heavy relative to the Zn inputs, another Zn sink must be isotopically light.

New Zn isotope data from the water column of the Black Sea and from organic-rich continental margin sediments indicate that this missing light Zn pool may reside in sulphides. Zinc sulphide species are insoluble in aqueous solution, and complexation by sulphide ligands is predicted to favour light Zn isotopes (e.g., Fujii et al., 2014). Consistent with these predictions, removal of Zn from the water column of the euxinic (sulphide-containing) Black Sea is near complete, with a small (<5%) residual dissolved pool that is isotopically heavy (Vance et al., 2016). While the Black Sea is quantitatively unimportant in the global mass balance of Zn, light Zn isotope signatures have also recently been reported for organic-rich continental margin sediments beneath open ocean upwelling zones (Little et al., 2016). We suggest that these signatures reflect the partial sulphidisation of Zn in organic material in these anoxic settings, rather than a light isotope signature of biological origin.

In conclusion, the modern oceanic mass balance of Zn reflects removal in oxic (heavy isotopes) and reducing (light isotopes) settings. While isotope systematics driven by sulphide complexation and Fe-Mn oxide adsorption likely exclude the use of Zn isotopes as a paleoproductivity tracer, this model does open up new and exciting potential for their use to interrogate past ocean redox.

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