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Chemistry, not biology, is the main control on modern ocean transition metal isotope budgets

D. VANCE^{1*}, C. ARCHER¹, S.H. LITTLE², M. KÖBBERICH¹, G.F. DE SOUZA,¹ E.R. CISCATO¹

¹ Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zurich, Switzerland.

(*derek.vance@erdw.ethz.ch)

² Department of Earth Science and Engineering, Imperial College London, UK.

The oceanic cycles of many transition metals are dominated by biological uptake in the photic zone and regeneration at depth, as evidenced by depth profiles in the real ocean, and confirmed by culturing studies. This has led to significant optimism regarding the potential of their stable isotope systems as tools for tracking biological cycling in Earth history, assuming that biological assimilation by phytoplankton is associated with preferential uptake of the light isotopes. Consistent with this idea, the modern oceanic dissolved reservoir is shifted to slightly (Zn) or very (Ni) heavy isotope compositions by an isotopically light output. But, in the modern ocean at least, biological impacts on dissolved isotope compositions are often insignificant, specifically here for Zn and Ni, and redox chemistry is likely to be the dominant control.

Today the biological cycle of Zn is dominated by uptake into diatoms in upwelling zones [e.g. 1]. These organisms undertake most export production and take up an order of magnitude more Zn than other phytoplankton. Constraints from culturing experiments are ambiguous, but real oceanic data demonstrate that no isotope fractionation is associated with this uptake. A growing database for oceanic Ni isotopes shows that modest photic zone depletions *are* associated with an isotope fractionation, but it is very small.

So, the biological output is the most important – perhaps dominant – output vector from the dissolved pool of the modern ocean. But it is not associated with an isotope fractionation. We suggest that it is partial sulphidation of the organic-associated metal inventory in anoxic sediments, analogous to processes within the water column itself in the Black Sea [2], and the transfer back to the oceans of a residual porewater dissolved pool, that drives the modern ocean towards heavy isotope compositions.

[1] Vance, D. et al. (2017) *Nature Geoscience* 10, 202-206.
[2] Vance, D. et al. (2016) *Phil. Trans. Roy. Soc. Lond.* 374, 20150294.