Negligible Ni isotope fractionation associated with phytoplankton uptake in the South Atlantic Ocean

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Many transition metals have important roles in ocean biogeochemistry. These roles are played out through photosynthetic carbon fixation by marine phytoplankton, during which many of these metals have essential biochemical functions (e.g. Fe, Zn, Cd, Ni, and others) [1]. Dissolved Ni typically displays a "nutrient-type" vertical profile in the ocean (e.g. [2]), with lower concentrations in the surface and higher concentrations at depth. Despite these strong concentration gradients, and the metabolic requirement of phytoplankton for Ni [3], Ni appears to be homogenous in its isotopic composition throughout the ocean [4].

Much of our recent understanding of the role of trace metals in the oceans is due to the work of the international GEOTRACES programme. Here we report full vertical profile Ni data from samples collected as part of two UK-GEOTRACES South Atlantic Ocean cruises along a transect at 40°S. At all stations, Ni decreases in concentration from ~6-7 nM at depth to \sim 2 nM at the surface. In contrast to previous findings, this depletion is associated with an isotopic fraction, with δ^{60} Ni increasing from a constant value of ~1.3‰ below the thermocline to values as heavy as 1.75‰ at the surface. The interpretation of this fractionation as a simple signature of phytoplankton uptake is complicated however by two factors. Firstly, this isotopic pattern is not seen at all stations, with one station displaying no isotopic variation throughout the water column, despite similar concentration profiles. Secondly, a survey of all available Ni data in the oceans suggests a concentration minmum of ~2 nM, as seen here in the S. Atlantic. We suggest that in fact virtually all of the bioavailable Ni is consumed by phytoplankton within the surface zone, and by inference the fractionation involved with this process is very small, an emerging observation with other key micronutrients e.g. Zn [5] in the oceans.

[1] Morel, F.M.M et al. (2003) Science, **300**. 944-947. [2] Bruland. K.W. (1980) *Earth Planet. Sci. Lett* **47**, 176-198. [3] Twining, B.S. et al. (2012) *Glob. Biogeochem. Cycles* **26**, GB4001. [4] Cameron V. and Vance D. (2014) *Geochim. Cosmochim. Acta* **128**, 195-211. [5] Vance D. et al., (2017) *Goldschmidt Subm.*