

## Nickel isotopes in sediment and porewaters from highly productive upwelling margins

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Nickel (Ni) is a bio-essential micronutrient in the ocean with key functions in several enzymes [1]. The element is generally not considered to be bio-limiting in the modern ocean, but culturing studies have suggested that Ni can be a limiting nutrient under certain conditions [2]. Due to the specific biological functions of Ni, variations in Ni availability in past oceans may have also limited or promoted different groups of phytoplankton. Additionally, Ni isotopes are an emerging proxy for past global ocean redox conditions, as the main modern sinks show strongly contrasting isotope compositions. The two dominant outputs of Ni from the modern ocean are those associated with Mn-oxides in pelagic oxic sediments and with organic-carbon burial in continental margin sediments. Here we focus on better quantifying and understanding the organic-rich continental margin sink.

We present a large Ni-isotope dataset from sediments and pore waters from nine different stations from the productive regions of the Namibia Margin, Peru Margin, and Gulf of California. The stations represent a range of depositional redox conditions, from oxic to fully anoxic, allowing evaluation of Ni behaviour in different environments. Under sulphidic conditions light Ni is removed, with fractionation factors approaching those predicted by ab initio calculations for the precipitation of Ni-sulphide complexes, leaving sulphidic pore waters enriched in heavy Ni ( $\delta^{60}\text{Ni} = 1.93 \text{ ‰} \pm 0.33$ , 1SD,  $n = 60$ ) compared to those from non-sulphidic conditions ( $1.43 \pm 0.25$ , 1 SD,  $n = 37$ ). Additionally, pore water Ni concentrations are high implying a benthic source of isotopically heavy Ni from these environments. In the solid phase, the isotope composition of authigenic Ni approaches that of the deep ocean [3,4], such that organic-rich margin derived sedimentary rocks may be used to constrain the past deep-ocean Ni-isotope composition and thereby present a valuable archive for palaeoredox reconstructions.

[1] Ragsdale, S.W. (2009) *J. Biol. Chem.* **284**, 18571–18575.

[2] Dupont, C.L., et al. (2010) *Deep-Sea Res., Part 1, Oceanogr. Res. Pap.* **57**, 553–566. [3] He, Z., et al. (2023) *Geochim. Cosmochim. Acta.* **343**, 84–97 [4] Ciscato, E.R., et al. (2018)

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