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Tracking seawater chemistry over the last 3.2Ga: a Ni stable isotope perspective

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Nickel (Ni) is an important metal in the modern biosphere, and perhaps played a key role in the early evolution of the biosphere. In the modern ocean Ni behaves like a nutrient, being depleted in the photic zone, and it may have limited methanogenesis in the Archean-Proterozoic [1]. Our current knowledge of the biogeochemical behaviour of Ni is still at its infancy, as of all of the transition metals it is perhaps the one for which we know the least in terms of its inputs and outputs to the ocean. Early work, however, has highlighted a key observation: the oceanic dissolved pool is at about 1.44 ± 0.15‰ in δ^{60}Ni, while the rocks of the continental crust are at ~0.15‰ [2,3]. With the aim of better charaterising the geochemical signatures of Ni in sediments, as well as probing its applicability as a potential biosignature and chemical tracer, we present phase-specific and bulk geochemical analyses of Ni in mostly organic-rich sediments.

We have developed an acid digestion methodology that enables us to separate a ‘Pyrite + organics’ fraction from an ‘HF extractable’ fraction, to then determine their respective authigenic trace metal inventories. In organic-rich (TOC of 1-16 wt%) sediments from the Peru Margin, both these phases are within uncertainty of data for the modern oceanic dissolved pool, after the ‘HF-extractable’ fraction is corrected for detrital inputs using Ni/Al systematics. In moderately organic-rich (TOC of 3-6 wt%) carbonate sediments from a modern hypersaline lagoonal setting, the signature of the modern dissolved oceanic pool is also preserved in the ‘Pyrite + organics’ fraction, while the ‘HF-extractable’ fraction records signatures with δ^{60}Ni of about 0.0-0.4‰, hence closest to the typical detrital input.

Our findings clearly suggest that isotopic analyses of organic-rich sediments, as well as the ‘Pyrite + organics’ fraction extracted from less organic-rich sediments, represent a promising tool to investigate past ocean Ni isotope geochemistry. Hence, we subsequently apply our approach to a suite of sediments from the geological record and construct a δ^{60}Ni record for the last 3.2 billion years. We observe a preferential preservation of δ^{60}Ni lighter than modern seawater throughout most of the record, with an especially confined range of variability just before the GOE and in the late Paleoproterozoic.

[1]Konhauser K.O., et al. (2009) *Nature* **458**, 750-753
[2]Cameron V. and Vance D. (2014) *GCA* **128**, 195-211
[3]Cameron V., et al. (2009) *PNAS* **106**, 10944-10948