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Nickel and its isotopes in organic-rich sediments: implications for oceanic budgets and a potential record of ancient seawater

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ABSTRACT

Nickel (Ni) is a biologically active element that displays a nutrient-like depth distribution in the modern oceans. Recent studies of Ni isotopes have highlighted the fact that, in common with many other transition metals, the Ni stable isotope composition, expressed as δ^{60}Ni, of the dissolved phase is heavier than the inputs, at +1.3 to +1.7‰. The sedimentary outputs that control the high δ^{60}Ni of the ocean, coupled with records for past seawater, could potentially yield new information on the past Earth system, but these are currently not well understood. Here we present the first Ni abundance and isotope data for a key output, that associated with Ni uptake into organic matter, at productive upwelling regions and elsewhere. We investigate the distribution of Ni and its isotopes in two fractions separated from the bulk sediment, an HF-digestible fraction, extracted with HF–HCl, and an organic-sulphide-rich fraction. The organic-sulphide fractions exhibit a range in δ^{60}Ni, from +0.86 to +1.83. Systematic relationships between Ni concentrations, total organic carbon and Ni isotopes suggest that the organic-sulphide fraction originates in the photic zone, and is delivered to the sediment as a closed system, despite the possibility of transfer of Ni to sulphide within it. Authigenic Ni in the bulk sediment is dominated by the HF-digestible fraction which, in Ni-enriched sediments where the detrital correction is small, is very close to the modern deep ocean, at $\delta^{60}\text{Ni} = +1.2$‰. These data suggest that organic-rich sediments beneath upwelling zones, while they are an important output flux of Ni from the oceans, do not solve the isotope balance problem because their δ^{60}Ni is almost identical to modern seawater. On the other hand, the approach adopted here involving the analysis of the two fractions, both traces the fractionation imparted by biological uptake as well as recording the δ^{60}Ni of contemporary seawater, suggesting potential for understanding the past oceans.

1. Introduction

Nickel (Ni) is a bioessential trace metal, characterized by a nutrient-type depth profile in the modern ocean, with dissolved Ni concentrations reaching 11 nM in the deep Pacific and values as low as 2 nM in many parts of the photic zone (e.g., Sclater et al., 1976; Bruland, 1980; Mackey et al., 2002; Lai et al., 2008). The role of biological processes in the oceanic cycling of Ni is confirmed by strong correlations between Ni concentrations and those of the major nutrients like phosphate and silica (Sclater et al., 1976; Bruland, 1980). The specific biological roles of Ni have been reviewed by Ragsdale (2009). Nickel is an essential component of at least seven enzymes involved in the biological cycling of carbon, nitrogen, and sulphur. A further two are of key importance for the metabolism of methanogens, which may have played a prominent role on the early Earth (e.g., Kasting, 2005; Konhauser et al., 2009).

In addition to its clear biological cycling, there are two other important processes that control the marine geochemistry of Ni. First, like many other transition metals, sorption to particulate Fe–Mn oxides represents an important output from the dissolved pool in settings where oxygen is plentiful (e.g., Shaw et al., 1990; Peacock and Sherman, 2007; Gall et al., 2013). On the other hand, Ni is also highly reactive towards dissolved sulphide (e.g., Landing and Lewis, 1991). Thus, in the deep Black Sea sulphidation of dissolved Ni, coupled to either scavenging of particle reactive sulphidised species or to sulphide precipitation, also removes it from solution to sediment (e.g., Landing and Lewis, 1991; Vance et al., 2016).

These aspects of the oceanic Ni cycle represent different outputs from the oceanic dissolved pool – uptake into cells and burial of organics, sorption to Fe–Mn oxides and sedimentation under oxidising conditions, removal to particulate sulphide and

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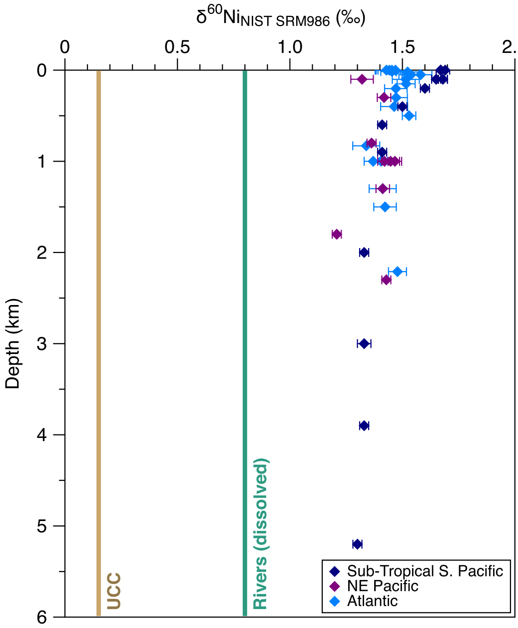

Fig. 1. Published Ni isotope data for seawater compared to that of the discharge weighted average for the dissolved phase of rivers (turquoise line) and to that of the upper continental crust (UCC, brown line). Data from Cameron and Vance (2014) and Takano et al. (2017). (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

sedimentation under reducing conditions – whose relative importance now and in the past is controlled by key aspects of the Earth's surface environment, including biological productivity and oceanic redox state. Previous work has highlighted the utility of metal isotope studies in quantifying both the relative importance of these sinks in the modern ocean (e.g., Siebert et al., 2003; Little et al., 2014; Andersen et al., 2014), and for understanding the environmental drivers of fluctuations in these sinks throughout Earth history (e.g., Arnold et al., 2004; Pons et al., 2013). For nickel, isotope data published to date for the oceanic dissolved pool (Fig. 1, Cameron and Vance, 2014; Takano et al., 2017) show two key features. Firstly, the δ^{60}Ni (defined as $[((^{60}\text{Ni}/^{58}\text{Ni}_{\text{sample}})/(^{60}\text{Ni}/^{58}\text{Ni}_{\text{NIST SRM986}})) - 1] \times 1000$) of the water column is relatively homogeneous, though there is a subtle shift towards heavier Ni isotopes as Ni is drawn down in the photic zone (Archer et al., 2017; Takano et al., 2017). Secondly, the nickel isotope composition of the dissolved pool is significantly heavier than the main input, the dissolved load of rivers, itself heavier than the best estimate of the upper continental crust (UCC; Cameron and Vance, 2014; Gueguen et al., 2013). This latter feature is common to a number of transition metals (e.g., Arnold et al., 2004; Little et al., 2014), and requires that: (a) the oceans are not in steady-state for Ni and its isotopes; (b) there is an uncharacterized heavy input that dominates over rivers or; (c) that the outputs from the dissolved pool are isotopically light.

The first two potential explanations remain possible, though evidence has been previously marshaled against them (Gall et al., 2013; Cameron and Vance, 2014; Gueguen et al., 2016), and we return to this issue in the discussion in the light of new data presented in this study. Here, we focus on the third possible explanation for the apparent imbalance in the marine isotope budget of Ni. Two outputs from the dissolved pool have been characterized for Ni isotopes. The first is that associated with particulate Fe–Mn oxides (Gall et al., 2013; Gueguen et al., 2016), whose surface layers cluster between δ^{60}Ni $= +1.6$ and $+1.9$, with most ($n = 22$ out of 26) heavier than the modern water column. This finding thus worsens the isotopic mass balance problem (Fig. 1). Secondly, isotopically light Ni is preferentially removed to sediment in sulphidic basins like the Black Sea (Vance et al., 2016). This finding is consistent with the reactivity of Ni towards dissolved sulphide (e.g., Landing and Lewis, 1991), the fact that such aqueous sulphide species are particle reactive (or perhaps precipitated as sulphide minerals), and that aqueous sulphide species prefer the light isotopes of Ni (Fujii et al., 2014).

Extraction of light Ni from seawater in euxinic water columns is important to the oceanic isotope budget, but this output is almost certainly insufficient to quantitatively solve the balance problem. Here, we quantify a sink that has not yet been characterised for Ni isotopes, but that is well known to be a major output flux of Ni from the dissolved pool of the oceans (Böning et al., 2015) – that associated with cellular uptake in the photic zone and enhanced organic matter preservation beneath productive upwelling zones. In addition, we investigate the degree to which the contemporary seawater signal can be extracted from organic matter in sediments, not only in the organic-rich sediments deposited beneath productive upwelling zones, but also in organic-lean sediments such as carbonate. In contrast to traditional bulk sediment digests, we measure Ni abundance and isotope composition in an HF-dissolvable fraction and an "organic matter plus pyrite" fraction, with the aim of learning more about the location and isotope composition of different isotopic pools of Ni within sediments.

2. Setting

2.1. Peru Margin

The Peru Margin was chosen as the principal focus for this study, as it offers the opportunity to investigate organic-rich sediments deposited at sites with a range of bottom-water oxygen (O_2) concentrations, and thus different sedimentary redox states. The Peru–Chile margin is considered as the most productive upwelling system in the world ocean (Fuenzalida et al., 2009). The high productivity of this region results in the permanent eastern South Pacific oxygen minimum zone (OMZ), which has its core located between 5 and 13°S. The seafloor below the OMZ and along the margin is dominated by two main sedimentary facies: (i) a lens-shaped, up to 100 m thick, diatomaceous (opal up to ~16 wt.%), organic-rich mud at depths between 50 and 500 m at 11–14°S; and (ii) a coarser-grained, less organic-rich, calcareous mud on the shallow shelf at 8.5°S and 15–17°S (Suess et al., 1987). Thus, the most organic-rich sediments are deposited between 11 and 14°S, which are the latitudes targeted here.

Peru Margin sediment cores were recovered as box cores and multicores in October–November 1992 during a cruise of *R/V Seward Johnson*, and as multicores in October–November 2005 during cruise 182-9 of *R/V Knorr*. Upon recovery, all cores were immediately sliced at 0.5–1.0 cm intervals, stored in glass jars or plastic sampling bags, and frozen. In this study we focused on core-tops recovered by *R/V Seward Johnson* and multiple down-core samples from three of the cores recovered by *R/V Knorr* (Fig. 2a, b), in order to cover a range of redox conditions and organic matter contents. Following Böning et al. (2004), the samples can be subdivided into three groups based on their location with respect to the OMZ (see Supplementary Information for precise locations): (i) upper edge of the OMZ, where O_2 is recorded to be <10 μM but may fluctuate to higher values during El Niño years; (ii) lower shelf and upper slope, within the OMZ where O_2 is at or below 5 μM; (iii) lower continental slope, below the OMZ.

2.2. Lagoa Salgada

The Lagoa Salgada site was chosen to investigate whether its carbonate-rich (34–75%) sediments, although only moderately organic-rich, also offer the possibility for isolating an authigenic