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Characterising the nickel isotopic composition of organic-rich marine sediments

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ABSTRACT

New Ni stable isotope data (δ^{60}Ni) determined by double-spike MC-ICP-MS for two geologically distinct suites of organic-rich marine sediments from the Sinemurian–Pliensbachian (S–P) Global Stratotype Section and Point (GSSP; Robin Hood's Bay, UK) and the Devonian–Mississippian Exshaw Formation (West Canada Sedimentary Basin) is presented herein. These sediments yield δ^{60}Ni values of between 0.2‰ and 2.5‰, and predominantly have Ni isotopic compositions that are heavier than those of abiotic terrestrial and extraterrestrial samples (0.15‰ and 0.27‰), and in some cases present-day seawater (1.44‰) and dissolved Ni from riverine input (0.80‰). In addition, the observed degree of isotopic fractionation in the marine sediments is far greater than that of these other sample matrices. However, a strong similarity is exhibited between the δ^{60}Ni values of the organic-rich sediments studied here and those of ferromanganese crusts (0.9–2.5‰), suggesting that factors ubiquitous to the marine environment are likely to play a key role in the heightened level of isotopic fractionation in these sample matrices.

A lack of correlation between the Ni stable isotope compositions of the organic-rich sediments and Ni abundance suggests that isotopic fractionation in these sediments is not controlled by incorporation or enrichment of Ni during sediment accumulation. Further, no relationship is observed between δ^{60}Ni and TOC concentrations or bottom–water redox conditions, indicating that the organic carbon reservoir and levels of oxygenation at the sediment–water interface do not exert a primary control on Ni isotope fractionation in marine sediments. Following examination of these relationships, it is therefore more likely that the heavy Ni isotope compositions of marine sediments are controlled by the weathering environment and the dominant sources of dissolved Ni into the global ocean reservoir.

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1. Introduction

For several decades previous investigations of Ni isotopes have focused predominantly on characterising radiogenic isotopic fractionation in extraterrestrial materials, with a view to enhancing our understanding of planetary processes and the isotopic composition of the early Solar System (e.g. Kohman and Robison, 1980; Morand and Allègre, 1983; Shimamura and Lugmair, 1983; Birck and Lugmair, 1988; Herzog et al., 1994; Xue et al., 1995; Quitté et al., 2006; Cook et al., 2007; Moynier et al., 2007; Chen et al., 2009). Further, the role of Ni as a bioessential trace metal (e.g. Frausto da Silva and Williams, 2001; Cameron et al., 2007, 2009) has led to the recognition that the stable isotopes of Ni may have the potential to be utilised as a powerful biological tool for studies of early life on Earth (Cameron et al., 2009, 2012).

In addition to its role in cosmochemical and biochemical investigations, the potential of Ni to significantly enhance our understanding of organic-rich sedimentary environments and to provide a powerful geological tracer in the petroleum realm has been recognised, following pioneering work by Lewan and Maynard (1982) and Lewan (1984) (e.g. Ellrich et al., 1985; Manning et al., 1991; Alberdi and Lafargue, 1993; López et al., 1995). However, these studies focused on the elemental distribution of Ni rather than on its isotopic characterisation, and as such, no study currently exists that evaluates the behaviour of Ni stable isotopes in organic-rich sediments or indeed within a stratigraphic profile. This can be attributed to Ni being a relatively newly investigated system, together with the difficulty associated with purifying Ni from such complex sample matrices, that has only recently been overcome through advancements in analytical and mass spectrometry techniques (e.g. Quitté and Oberli, 2006; Gall et al., 2012; Cameron and Vance, 2014).

Until now, Ni stable isotope systematics in organic-rich sedimentary matrices have not been investigated. Indeed, it is only recently that the Ni isotopic composition of seawater and the sources of Ni to the

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global oceanic reservoir have been determined (e.g. Gall et al., 2013; Cameron and Vance, 2014). Present-day seawater has an average $\delta^{60}Ni$ value of $1.44 \pm 0.15‰$, with apparent global isotopic homogeneity (Cameron and Vance, 2014). The oceanic residence time of Ni has been calculated as ~30 kyr (Cameron and Vance, 2014), which is significantly longer than the mixing time of the global oceans (~2,000 year; Palmer et al., 1988). This would be sufficient for the ocean to have an isotopically homogenous Ni composition. Cameron and Vance (2014) also demonstrate that draw-down of Ni from the surface to deep ocean during trace metal cycling is not accompanied by isotopic fractionation, thus further suggesting that the modern ocean is isotopically homogenous. In the absence of any Ni isotope studies on banded iron formation and shale datasets, it is difficult to speculate on processes occurring in an ancient ocean. However, examination of Ni/Fe data from banded iron formations and extrapolated maximum dissolved Ni concentration values in sea water through time (Konhauser et al., 2009), demonstrates that dissolved nickel concentrations may have reached present day values by ~550 Ma. As such, given the age of the sediments being studied herein (~190–360 Ma), it is appropriate to use what we know regarding modern ocean circulation and fractionation processes to hypothesise about processes acting in the ancient oceans. The predominant input of dissolved Ni to the oceans occurs via riverine influx, which has been suggested to yield an annual discharge- and concentration-weighted $\delta^{60}Ni$ average of $+0.80‰$ (Cameron and Vance, 2014). Significant variability in the riverine isotopic composition has been observed ($+0.29$ to $+1.34‰$), which has been attributed to isotopic fractionation of Ni during weathering of continental crust, resulting in heavier $\delta^{60}Ni$ values in rivers and seawater. In addition, mineral dust and volcanic ash also contribute to the oceanic Ni budget (Li and Schoonmaker, 2003), as well as hydrothermal vent fluids ($\delta^{60}Ni = 1.5‰$; Gall et al., 2012).

Herein we present the first attempt at creating a Ni isotope stratigraphic profile for an organic-rich sedimentary succession. The marine section across the Sinemurian–Pliensbachian Global Stratotype Section and Point (GSSP), Robin Hood's Bay, UK, is ideally suited to the present study, as it well understood biostratigraphically (Hesselbo et al., 2000; Meister et al., 2006) and has been previously characterised using other isotope stratigraphy techniques, including strontium ($^{87}Sr/^{86}Sr$; Jones et al., 1994; Hesselbo et al., 2000), oxygen ($\delta^{18}O$), carbon ($\delta^{13}C$) (Hesselbo et al., 2000), and Re–Os isotopes (Porter et al., 2013). The section is also consistently thermally immature (the rocks have not been subjected to enough heat or pressure to convert any kerogens present to hydrocarbons), thereby eliminating any potential effects of thermal maturation on the Ni isotope signature. In addition, to draw comparison between the isotopic composition of samples of different depositional ages and environments, we present Ni isotope data from a selection of thermally immature black shale samples from a core of the Exshaw Formation, Canada.

To accurately assess and interpret any stratigraphic variation of Ni isotopes in the Robin Hood's Bay section and Exshaw Formation samples, it is critical to determine whether any fluctuations in paleoredox conditions occur. Nickel primarily occupies one oxidation state in the natural environment (Ni^{2+}), suggesting that it is not redox sensitive. However, its preferential association with redox-sensitive metallo-organic complexes (porphyrins) in organic-rich sediments (Lewan and Maynard, 1982) indicates that certainly within these sample matrices, redox conditions at the time of sediment deposition may directly impact the degree of enrichment or depletion of Ni. Herein, paleoredox conditions have been established for the Sinemurian–Pliensbachian GSSP section and the Exshaw Formation sample suite. Although one previous study (Dewaker et al., 2000) provides a preliminary dataset for the Ni isotope composition of sediments from 3 different basins, our understanding of the behaviour of Ni isotope systematics within organic-rich sediments is currently non-existent. Further, advancements in analytical techniques over the past decade suggest that the methodology employed by Dewaker et al. (2000) may not have been optimal for Ni separation or Ni stable isotope analysis.

This paper presents the first detailed study of nickel stable isotope systematics in organic-rich marine sediments. Analysis of marine sediments of different depositional ages and from two geologically distinct settings, the Sinemurian–Pliensbachian boundary (UK) and the Devonian–Mississippian Exshaw Formation (Canada), yields comparable Ni isotope compositional values for both sites. These samples provide insight into the incorporation of Ni into ocean sediments, and allow evaluation of the contribution of the various dissolved Ni fluxes to the seawater during these time periods.

2. Geological setting

2.1. The Sinemurian–Pliensbachian boundary GSSP, Robin Hood's Bay, UK

The Sinemurian–Pliensbachian boundary, established from the succession's complete ammonite assemblages (Spath, 1923; Dean et al., 1961; Hesselbo et al., 2000; Meister et al., 2006), occurs in the Pyritous Shales of the Redcar Mudstone Formation within the Lias Group at Robin Hood's Bay (Powell, 1984; Fig. 1). At this point in the Early Jurassic, Robin Hood's Bay was positioned on the margins of a shallow epicontinental sea (e.g. Dera et al., 2009) that covered most of Northern Europe, including Britain, during the Mesozoic (Sellwood and Jenkyns, 1975). The facies changes across the boundary, from pale siliceous to finer, more organic-rich mudstones (Fig. 2), indicate an overall relative increase in sea level of at least regional extent (e.g. Hesselbo et al., 2000; Meister et al., 2006; Porter et al., 2013).

The age for the base of the Pliensbachian has been defined by the Geological Time Scale (GTS) 2012 as 189.6 ± 1.5 Ma (Gradstein et al., 2012), derived from cycle-scaled linear Sr trends and ammonite occurrences (as noted above; also includes the lowest occurrence of *Bifericeras donovani*; Gradstein et al., 2012).

2.2. Exshaw Formation, West Canada Sedimentary Basin (WCSB)

The West Canada Sedimentary Basin (WCSB) trends approximately NW–SE between the Canadian Shield to the East and the Western Cordillera to the West (Piggott and Lines, 1992). Within the WCSB lies the Exshaw Formation, a thin but laterally continuous unit (2–12 m thick; Leenheer, 1984; Creaney and Allan, 1991). The Exshaw Formation in south-west and western Alberta (Fig. 3) comprises a lower member of organic-rich mudrocks and black shales which rest with minor disconformity upon Upper Devonian carbonate strata (Richards et al., 1999), and are abruptly to gradationally overlain by bioturbated shelf siltstones (Caplan and Bustin, 1998, 1999; Creaser et al., 2002). The depositional interval of the lower black shale unit is well constrained biostratigraphically; between the *expansa* and *duplicata* zones of Late Famennian to Early Tournaisian time (over a maximum time period of ~363–360 Ma; Caplan and Bustin, 1998). These lower black shales are dark grey, bituminous, relatively thin (consistently between 3 and 5 m; Meijer et al., 1994) and widespread (Meijer et al., 1994). The Devonian–Mississippian boundary (Exshaw-type section at Jura Creek, ~80 km west of Calgary, Alberta, Canada) represents the boundary between the upper calcareous and lower non-calcareous black shale units (Richards and Higgins, 1988). Selby and Creaser (2005) provide an absolute Model 1 Re–Os age for this boundary, and thus the top of the lower black shale unit, of 361.3 ± 2.4 Ma. In addition, U-Pb monazite data from a tuff horizon close to the base of the lower black shale member constrains an absolute depositional age for this unit of 363.4 ± 0.4 Ma (Richards et al., 2002). Deposition at this time represents part of a continent-wide Famennian–Tournaisian black shale event, and in turn, a possible ocean anoxic event (Piggott and Lines, 1992).