Global variations in Ni isotope compositions of ferromanganese crusts: reflecting input sources?

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Abstract

The global distribution of nickel (Ni) isotope values in ferromanganese crusts has been investigated by analysing 24 surface (zero-age) samples of crusts from various oceans by MC-ICPMS, using double-spike for mass bias correction. The isotopic compositions range between 0.9 and 2.5 □ (™60Ni), with □□□□averages □□□□□ for the Atlantic samples □□ permil ± error□□being slightly lighter than the ones at calculated from the Pacific samples (xy permil ± error), although the data show large overlapsre is considerable overlap in the Ni isotope compositions of waters from between all the measured oceans basins mea sured. To complement the crustal surface study also a depth profile through one crust from the Pacific ocean was also analysed. This isotope profile suggest that large variations in nickel isotope composition (1.6□2.3 □) has occurred within this crust throughout the last <70 Myrs, although the mean value is similar to the average isotopic composition for ferromanganese crust surfaces from the Pacific Ocean.

Keywords: ferromanganese crusts, nickel, stable isotopes, ocean biogeochemistry, seawater paleochemistry

1. Introduction

The past decade has seen a rising interest in the use of transition metal isotopes for investigating ocean chemistry and element cycling. As most of the first row transition metals are essential for primary productivity, these elements are especially important forhave particular importance in terms of understanding ocean biogeochemical cycles. Nickel is central to many geologically interesting biological reactions, for example it plays a key role in several enzymes important for the carbon cycle, including uptake of nitrogen in primary productivity (e.g. Ragsdale, 2007; Siegel et al., 2006) and methane production (Cameron et al., 2009). However, very few

studies have to date addressed mass-dependent variations in nickel (Ni) isotopes despiteor the potential of this isotope system to trace biogeochemical processes Ni having a key role in several enzymes important for the carbon cycle, including uptake of nitrogen in primary productivity (e.g. Ragsdale, 2007; Siegel et al., 2006) and methane production (Cameron et al., 2009). Nickel is therefore a necessary element for many geologically interesting biological reactions.

Previous research has shown that hHydrogenetic ferromanganese crusts can be used as□□□□□□□□□□□□□□□□□□□□□□ detailed archives of the □□□□□□□□□□□□isotopic compositions of various elements dissolved in the ocean deep water, due to their natural slow growth (<1mm/Myrs) and their ability to adsorb high concentrations of various metals (e.g. Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003). This study aims to establish the Ni isotopic variation□□□□□□□s in hydrogenetic ferromanganese crusts and determine whether these they can be used as an archive□ for deep water Ni isotope composition. For this purpose both the global variation of isotope ratios in crust surface scrapings and a detailed depth profile through one crust were analysed. Together, these samples record both spatial and temporal variations in the Ni isotopic compositions of ferromanganese crusts and thus provide insights into the biogeochemical cycle of Ni in the ocean.

2. Materials and Methods

2.1. Sample selection

To In order to investigate the Ni isotopic variations in ferromanganese crusts, the top surfaces of 24 globally distributed crusts were analysed (Fig. 1 and Table 1). These sThe selected samples coveramples were selected so as to include all the major ocean basins and have previously been characterised for other radiogenic and stable isotope systems (references). In each case, the most recent growth surface was identified by way-up indicators and the top 0.5 mm of each crust was shaved off using a cleaned scalpel and prepared for analysis. For inter-laboratory comparison also the USGS reference materials of powdered nodules, Nod-A-1 and Nod-P-1, were also analysed. Further details of the samples are provided in Table 1.

The sample chosen for depth profiling, identified as CD29-2 and provided by Jim Hein (US Geological Survey), is a hydrogenetic crust collected during cruise F7-86-HW from a seamount in the central Pacific Ocean (16º42' N, 168º14' W) at a water depth of 1970–2390 m. The average growth rate for this crust is 2.1 mm/Myr (determined from $^{10}Be/^{9}Be$ ratios by Ling et al., 1997), while Os isotope stratigraphy indicates that it started growing at > 70 Ma (Klemm et al., 2005). Furthermore, CD29-2 is well characterised for trace elements having previously been profiled with both radiogenic isotopes (e.g. Christensen et al., 1997; Frank et al., 1999; Lee et al., 1999) and stable isotopes (e.g. Rehkämper et al., 2004; Nielsen et al., 2009). The depth profile through this

crust was sampled using a micro drill, enabling high-resolution profiling with intervals of 0.2 mm between samples. Most samples were passed through an Fe separation column before addition of the Ni-double-spike, as the same sample aliquots were also analysed for their Fe isotope composition (Helen Williams, pers. com.). Nickel yields during this procedure were quantitative and ~~To~~ to ensure that no isotope fractionation occurred during this procedure additional aliquots of the USGS reference materials Nod-A-1 and Nod-P-1 were ~~treated in the exact same way~~processed using the same procedures and analysed alongside the depth profile samples.

2.2. Analytical techniques

The crust samples were weighed in into pre-cleaned ~~savillex~~ Savillex® beakers and dissolved in Teflon-distilled 6M HCl. To separate Ni from the ferromanganese matrix a chemical separation procedure was used comprising three columns and exploiting ~~Ni's~~the ability of Ni to form strong complexes with both ammonia and dimethylglyoxime relative to other elements. The Ni blank from this procedure is xxx ng, which is negligible relative to the quantities of Ni typically processed per sample (xxx ng).

The purified Ni solutions were analysed using a Nu Plasma-HR multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS). Instrumental mass fractionation was corrected for using the double-spike technique, whereby samples were spiked prior to column chemistry in order to resolve any fractionation induced during the chemical separation procedure. (you probably want a quick sentence here about internal standards where you can demonstrate that the double spike corrects for any fractionation during chemistry – I know it's in your methods paper but it's the kind of thing people like to see briefly mentioned in any case) A full description of analytical techniques can be found in Gall et al. (2012).

Nickel has five stable isotopes, ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, and ^{64}Ni, with respective natural abundances of 68.0769%, 26.2231%, 1.1399%, 3.6345%, and 0.9256% Gramlish et al. (1989a). Two of these isotopes (^{61}Ni and ^{62}Ni) were used for the double-spike correction, while the smallest isotope (^{64}Ni) was not measured due to instrumental limitations. All Ni isotope ratios showed here are therefore reported in permil notation as the ratio ^{60}Ni/^{58}Ni relative to the Ni isotope standard SRM 986 (NIST). All samples were analysed between x and y times, and the reported errors are the 2 standard deviations/errors of these values (note if you report standard errors you need to multiply them by the students t-correcting values e.g. for n=3 you multiply the error by 4.3207; you may have already done this, but I wasn't sure from the figures!). Replicate analyses of our internal standard over the last 3 years yield a 60Ni/58Ni value of xxx permil and a long-term reproducibility of xxx permil (2 S.D.) (again, I know it's in the methods paper but good to mention here briefly).

3. Results

Compared to ~~the~~ variation~~s~~ observed in continental rock samples (xxx- xy permil) (Cameron et al., 2009; Gall et al., 2012), the surface scrapings show a very large spread in δ^{60}Ni-values, from 0.88 to 2.47 ‰, with a global average δ^{60}Ni-value of 1.60 ± 0.79 ‰ (2 s.d.). The samples from the Atlantic Ocean have a mean of 1.34 ± 0.73 ‰, whereas those from the Indian and Pacific oceans have higher mean values of 1.58 ± 0.27 ‰ and 1.73 ± 0.84 ‰, respectively. The more restricted range of values in the Indian Ocean may partly be due to the smaller number of samples there.

Resampling of the surface scrapings yields variable sample reproducibilities of between 0.02 to 0.30 ‰, indicating that some crusts may be heterogeneous in Ni isotope composition even in the same surface layer. In Fig. 1 and ~~–~~2, all samples and results are plotted according to their geographical location. In general, ~~lighter values occur in~~ the Atlantic samples display isotopically lighter d60Ni values ~~and~~ whereas heavier values are observed in the Pacific samples, although it not clear whether this represents a real difference between the oceans or whether it is an ~~artefact~~artifact of the number and density of sampling. ~~Furthermore, there~~Furthermore, there ~~is~~ are no correlations of the Ni isotope data with mineralogical parameters (such as Fe/Mn ratio), growth rate or water depth.

The depth profile ~~made~~ though crust CD29-2, from the Pacific Ocean, also displays a large variation in Ni isotope compositions, with δ^{60}Ni values ranging from ~~δ^{60}Ni~~1.60 to 2.27 ‰ (Fig. 3, Table 2). Although ~~it~~the mean d60Ni value of this crust ~~has a slightly higher mean value~~ (1.85 ± 0.36‰) ~~compared to the~~is slightly higher than the surface ~~data~~value (xxx permil), ~~all~~both values fall within the range measured for surface scrapings from similar areas in the Pacific Ocean basin. ~~A plot of the Ni isotope variations within this crust is shown in Fig. 3, while detailed results (labelled by distance in mm from the top of the crust) are given in Table 2.~~ Secondary phosphatization has been recorded in the CD29-2 crust at depths below 52 mm (Ling et al., 1997), making it is possible that the isotope data below this depth could have been affected by remobilisation. ~~The crust's P~~Phosphate concentration~~s~~ in this depth profile ~~is~~are ~~especially~~ particularly high (give range) between 52–62 mm, which correlates with very large fluctuations in Ni isotopes over a this small window in time (would it be possible to make a second panel to Fig. 3, showing phosphate concentration plotted against depth?), indicating that ~~the Ni isotope ratios at this level may not be reliable~~Ni isotopes could be influenced by secondary phosphatisation. However, there is no general correlation between the Ni isotope ratios and P concentration in the rest of this crust and, as for the surface scrapings data, neither are there any clear relations with elemental or mineralogy parameters.

4. Discussion

Comment [HW2]: This section is written well and I think it the right amount of detail – I have just made minor comments

In the absence of published Ni isotope data for seawater, it is ~~difficult to~~presently not possible to establish whether there is a significant isotopic fractionation, or difference between the Ni isotope compositions of seawater and ferromanganese crusts. ~~However, should~~In the absence of any isotopic fractionation between seawater and ferromanganese crusts, the ~~ferromanganese crusts~~isotopic compositions of the latter will directly reflect ~~the~~spatial and temporal variations in the Ni isotopic composition of seawater. Should there be a non-zero, but constant isotopic fractionation between seawater and ferromanganese crusts, then the data will nonetheless provide reliable constraints on the relative variations in the Ni isotope composition of seawater in space and time. ~~, the data presented here show that there have to be significant variations within the deep water.~~ The ~~other~~final possibility is that the fractionation factor between seawater and ferromanganese crusts may be variable due to internal environmental factors.

4.1. Deep water mixing

A possible cause for ~~a~~deep water Ni isotope heterogeneity ~~-~~could be the short residence time of Ni in the ocean. This ~~was~~is estimated to be around 10,000 years, based on sedimentation rates in the open ocean (Sclater et al., 1976). As the total mixing cycle for the world's oceans is estimated to be approximately 1,000 years (Jenkins, 2003), a residence time of 10,000 years would be sufficiently long for Ni to have a homogenous isotopic distribution in the ocean. However, recent literature values for Ni concentrations in pelagic sediments (230 μg/g, Li and Schoonmaker (2003)) and open ocean sedimentation rates (0.22 g/cm2/ky, Rehkämper and Nielsen (2004)) suggest that the residence time of Ni may be as low as 4,000 years. Although this time span is still longer than the ocean mixing time, it has been suggested that the residence times of an element needs to be > 5,000 years for mixing to achieve full homogeneity of elemental concentrations, and isotope ratios, in the deep ocean water (Bruland, 1980). ~~A~~A shorter residence time for Ni is also supported by measurements of seawater Ni concentrations in different basins. Worldwide, this concentration varies from 2–12 nmol/kg with a global average of 8.2 nmol/kg (MBARI, 2012). The highest bottom water concentrations (12 nmol/kg) have been found in the northeast Pacific (Sclater et al., 1976), while the lowest bottom water concentrations (5 nmol) were measured in the north Atlantic (Saager et al., 1997). A plot of sample Ni concentrations shows a similar general trend, with higher concentrations in the Pacific crusts (Fig. 4). However, this variation in sample concentrations does not correlate with the measured isotope ratios, suggesting that the observed isotopic heterogeneity of ferromanganese crusts is unrelated to the incomplete ocean mixing of Ni.

Comment [HW3]: I agree! Very nicely put ☺

Comment on Fig 4 – should be "each sample" rather than "each samples" in caption. The Fig is really nice, how about drawing a field around each ocean to make it easier to compare the relative

differences between them? This might also make Figs 6 and 7 easier to read. You don't have to do this but anything that makes figures easier for reviewers to understand = nicer reviews, if you see what I mean!

4.2. Source variation

If Ni isotopic variations in ferromanganese crusts do not reflect seawater composition, is possible that they result from differences in regional input from continental or hydrothermal sources. The ferromanganese crusts ~~data presented here are isotopically~~ display d60Ni values that are isotopically ~~very~~ heavy compared to continental rock samples (δ^{60}Ni for rock samples is on average only <0.2 □, Cameron et al. (2009); Gall et al. (2012)). As riverine flux to the ocean is considered to be the main source for Ni entering the ocean, riverine input on average should have a Ni isotopic composition of similarly light ratios as the crust□□□□□□□□□□□□□□□□□□□□□ isotope □□□□□□□□□□□□□□ takes place□□□□□□□□□□□□□□□□□□□□□. However, □□□□□□□□□□p□□□□□□□□□□□□□□□□i□,iiiiiie□□□□□□,□□□□□□□□□□~~new~~ Ni isotope data suggest that silicate weathering is accompanied by isotopic fractionation ~~, which could contribute towards the heavy isotopic compositions of ferromanganese crusts~~ (Gall, 2011). Fig. 5 shows how weathering of Ni-silicates in peridotite to Ni-oxides in laterite and further breakdown into Ni-clay minerals results in a fractionation towards lighter isotopic compositions in the weathered material, accompanied by a loss of the heavy Ni isotopes. These data suggest that the heavy isotopes are leached away during silicate weathering and transported to the ocean by rivers. The riverine input of heavy Ni into the ocean will therefore vary regionally, depending on the local geology and the amount of weathering (and accompanying isotopic fractionation) in each catchment. A plot of sample Ni isotope composition against distance from the nearest continental shelf (Fig. 6) does hint that crusts located close to a shelf possess a heavier isotopic composition than crusts growing further away. However, where data were available for the same crusts, radiogenic tracers (Nd and Pb) show no such correlation, implying that Ni isotopes do not purely reflect continental input sources.

The ~~fluid~~ fluxes from ~~hydrothermal~~ vents associated with mid-ocean ridges are estimated to be up to 15×10^{13} L per year (Elderfield and Schultz, 1996). These fluids can contain up to 2.2 μmol/kg Ni (Gaillardet et al., 2003), making hydrothermal fluids the second largest input source of Ni to the ocean. ~~It~~ However, it is generally believed that when the hot fluids come in contact with cold seawater Ni should precipitate out as sulphides. Analysis of ridge sediments supports this theory, as these on average contain 430 μg/g Ni (Li and Schoonmaker, 2003), significantly higher than the average concentration for pelagic sediments (230 μg/g, Bruland and Lohan (2003)), although this may not account for all the hydrothermal Ni entering the ocean. The ferromanganese

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Comment [HW4]: Just to say I really like the way you've put this – I think it's great how you put the idea out there but do not overinterpret the data

One question though – what do you think could happen to Ni isotopes in estuaries?

crust data do not appear to correlate with the distance from the nearest mid-ocean ridge (Fig. 7), although samples growing close to (or on) a mid-ocean ridge cluster around a δ^{60}Ni-value of <1.5 □. It is possible that this value reflects Ni introduced from a hydrothermal source, which would further explain the relative isotopic homogeneity of the Indian Ocean samples, three out of four of which grew close to a mid-ocean ridge. However, there ~~are~~ i□ presently no Ni isotope data □v□□□□□□□□for hydrothermal fluids ~~with which~~that □□□□□□□□□□□□□□□□□□□□□□□□h□□□□□□□□□directly □□□□□□□~~to test this directly~~.

4.3. Other internal processes

The marine geochemistry of Ni was the focus of a detailed study by Sclater et al. (1976), who showed that the concentration of Ni in seawater is strongly correlated with major nutrients such as silicon and phosphorous. These correlations suggest that Ni is a micronutrient in the ocean, consistent with its importance ~~for~~ in several enzymes (e.g. urease) that are utilised during primary productivity. ~~This~~ These observations highlight~~s~~ another possible reason for the extent of Ni isotopic ~~variations~~ variability ~~in of~~ crust samples ~~located far away from~~distal to both continents and mid-ocean ridges: local differences in seawater isotopic composition could be due to isotopic fractionation during biological uptake of Ni. Biological processes are generally thought to be accompanied by a kinetic isotope fractionation where the lighter isotope is preferentially concentrated into biomass ~~that~~, forcing ~~pushes~~ the remaining reservoir towards a heavier isotopic composition. This was demonstrated for the Ni isotope system by experiments performed on *methanogenic archaea* (Cameron et al., 2009), where the observed shift in the isotopic composition of the culture was -0.9 ± 0.5 ‰ relative to the starting medium. ~~During these experiments the cells fractionating Ni isotopes raised their isotopic compositions by~~, which ~~-0.9 ± 0.5 ‰,~~ which in turn would push the ~~remaining~~ residual reservoir towards a significantly heavier Ni isotopic composition.

Another possible explanation for the isotopic variation in ~~FeMn~~ the ferromanganese crust samples, which is not directly connected with hydrothermal or continental inputs, could be differences in the speciation of Ni in seawater and associated equilibrium isotope fractionation between different complexed species. Early literature suggested that the main speciation of Ni in seawater should be the free hydrated ion, Ni^{2+} (e.g. Bruland (1983); Brookins (1988)), but more recent models have shown that > 50% of Ni may instead be accommodated in complexes such as $NiCO_3^0$ and $NiCl^+$ (Calvert and Pedersen, 1993; Glasby and Schulz, 1999). Additionally, Coale and Bruland (1988); Bruland (1989); Bruland et al. (1991); Rue 207and Bruland (1995) and Mackey et al. (2002) have all shown that several transition metals in seawater are mostly organically

complexed, with van den Berg et al. (1991); Xue et al. (2001) and Turner and Martino (2006) suggesting that the majority (< 90%) of seawater Ni is bound to organic ligands rather than to inorganic complexes. Similarly, Sander and Koschinsky (2011) suggested that the flux of metals to the ocean from hydrothermal vents could be significantly higher than previously estimated due to complexation with organic compounds.

Modelling by Fujii et al. (2010) suggested that changes in Ni (inorganic) speciation in seawater should fractionate Ni isotopes, with the heaviest isotopes preferentially being taken up into carbonate ($NiCO_3^0$), followed by sulphate ($NiSO_4^0$) and bicarbonate ($NiHCO_3^+$) complexes, and the light isotopes occurring in hydroxide complexes (e.g. $NiOH^+$). Theoretically, this could cause fractionations of up to nearly 0.8 ‰ between different ~~speciations~~ complexes of Ni in seawater, thereby possibly allowing for local variations in the isotopic composition of Ni available for adsorption onto ferromanganese crusts. (is there data available that would indicate preferential adsorbtion of one complex or another onto the surfaces of the crusts?)

4.4. Isotopic signature due to environmental change?

One reason that CD29-2 was chosen for the isotope profile study was its published growth model, produced using Os isotope stratigraphy by Klemm et al. (2005). In Fig. 8, the Ni isotope compositions through the crust are plotted according to this age model. As previously discussed, the large apparent fluctuation in isotope ratios occurring between 50–45 Ma may result from secondary phosphatization of the crust below this level. The younger part of the crust (< 35 Ma), however, shows no evidence for phosphatization, and its data should be reliable. Fig. 8 show how the isotopic values in the upper part of the crust rise from just over 1.8 ‰ to a maximum of 2.1 ‰ at around 30 Ma, followed by a marked drop of 0.5 ‰ down to 1.6 ‰ at approximately 20 Ma. From 20 Ma until 8 Ma (the youngest age analysed), the isotopic composition steadily rises to 2.0 ‰.

In light of the data from surface scrapings discussed above, interpreting the variations in this depth profile from an environmental point at the moment is difficult. This crust is located in the central Pacific Ocean, far from any continental shelf or mid-ocean ridge. It is however located <800 km SW of the Hawaii island ocean chain, which□s hot spot activity potentially could have influenced the Ni isotopes ratios in this crust with hydrothermal Ni. This makes it is possible that the drop in Ni isotope ratios between 30 to 20 Ma ~~indicate arndicate~~ higher hydrothermal activity and the associated input of isotopically light Ni during this time period.

~~Whether~~ While it is difficult to draw firm palaeoenvironmental constraints from ~~or not the~~the CD29 Ni -isotope profile ~~can be interpreted from an environmental perspective~~ at this point in time, it is ~~anyhow~~ nonetheless interesting that the average $\delta^{60}Ni$ ratio for the upper 40 mm (<35 Myrs) of this crust is relatively close to the average for the Pacific crusts surface scrapings (1.88 ± 0.27 □ and

Comment [HW5]: All your data is "reliable" – it is just whether it is affected by secondary fractionation processes or not! ☺

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1.73 ± 0.84 □, respectively) and □□□□□□□□□□□□□□□□□□□□□ significantly higher than the crustal surface values from the Atlantic (1.34 ± 0.73 □). This could indicate that ferromanganese crusts growing in the Pacific have consistently had a Ni isotopic composition heavier than the crusts growing in the Atlantic over the past <35 Myrs. This apparent inter-ocean basin difference could reflect xxxx, but more detailed studies are required.

Do you think there could be something to do with the age of the water…?

5. Conclusions

A detailed study of the Ni isotope ratios in natural samples of ferromanganese crusts show that these chemical sediments are isotopically heavy and heterogeneous in their Ni isotopic composition. The global variation of crustal surface scrapings is ranges between 0.9 to 2.5 e, while a depth profile through one Pacific crust show a temporal variation of half that range (1.6–2.3 ‰).

6. Acknowledgements

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