Journal Article

Heavy nickel isotope compositions in rivers and the oceans

Author(s):
Cameron, Vylinniskii; Vance, Derek

Publication Date:
2014-03-01

Permanent Link:
https://doi.org/10.3929/ethz-b-000080377

Originally published in:

Rights / License:
Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International

This page was generated automatically upon download from the ETH Zurich Research Collection. For more information please consult the Terms of use.
Heavy nickel isotope compositions in rivers and the oceans

V. Cameron¹,* and D. Vance¹,²

¹Bristol Isotope Group, School of Earth Sciences, University of Bristol, Wills Memorial Building, Bristol, BS8 1RJ, UK.

²Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, NW D81.4, Clausiusstrasse 25, Zürich 8092, Switzerland.

*Corresponding author. e-mail: glxvc@bristol.ac.uk; tel: +44 1173315037; fax +44 117 9253385.

9400 words in main text
9 figures
2 tables

Keywords: nickel, stable isotopes, rivers, seawater, biogeochemistry, chemical oceanography
ABSTRACT

Nickel is a biologically-active trace metal whose dissolved concentration depth profiles in the ocean show nutrient-like behaviour. If the pronounced removal of nickel from the dissolved phase in the surface ocean, and its return in the deep, is associated with an isotopic fractionation nickel isotopes may be able to yield constraints on the precise biogeochemical processes involved. Here we present the first nickel isotope data for seawater along with data for the dissolved phase of rivers, one of the principal sources of nickel to the oceans.

The dissolved phase of rivers exhibits substantial variability in both Ni concentration and $\delta^{60}$Ni: from 2.2 to 35 nmol kg$^{-1}$ and $+0.29$ to $+1.34\%$, respectively. The most striking result from the nickel isotope analyses of rivers is that they are substantially heavier (by up to $1\%$ for $\delta^{60}$Ni) than the range for silicate rocks on the continents, a finding that is analogous to that for other transition metal isotope systems. If the data presented here are close to representative of the global riverine flux, they suggest an annual input of Ni to the oceans of $3.6 \times 10^8$ moles, and a discharge- and concentration-weighted $\delta^{60}$Ni average of $+0.80\%$. The relationship between Ni isotopes and concentrations shows similarities with those for other transition metal isotope systems, where the main control has been suggested to be isotopic partitioning between the dissolved phase and particulates, either in the weathering environment or during transport.

In stark contrast to the rivers, the dataset for seawater is very homogeneous, with 2SD of the entire dataset being only twice the analytical reproducibility. The second main feature is that seawater is distinctly heavier in Ni isotopes than rivers. The average $\delta^{60}$Ni is $1.44\pm0.15\%$ (2SD), and only 2 of the 29 seawater analyses have a Ni isotopic composition that is lighter than the heaviest river. The lack of an isotopic shift associated with the drawdown of nickel concentrations in the surface ocean suggests that the cycling of nickel between the surface and deep ocean is not associated with a pronounced isotopic fractionation. The isotopic data also present a mass balance problem. The main
output of nickel from the oceans (sorption to Fe-Mn oxides) appears to be similar in isotopic composition to the dissolved phase, yet the riverine input is lighter than the dissolved pool. This observation either requires other inputs that are isotopically heavy, or an output that is isotopically light. Further large inputs, over and above the dissolved riverine source, appear to be required by what we know of the elemental budget, but the isotopic mass balance suggests that such an input needs to be isotopically much heavier than both the riverine dissolved load and the lithogenic isotopic composition of nickel.
1. INTRODUCTION

Nickel (Ni), like other transition metals, is a biologically-active element (Frausto da Silva and Williams, 2001; Ragsdale, 2009). It has long been known (Sclater et al., 1976; Bruland, 1980) that dissolved Ni concentrations in the modern ocean show a “nutrient-like” distribution with depth. Thus Ni concentrations show depletions in the photic zone that are suggestive of biological uptake. In addition, concentration increases with depth follow the regeneration of major nutrients like phosphate and silica, and the slopes of Ni-phosphate and Ni-silica correlations for dissolved concentrations are similar to those for the Ni-Si-PO$_4$ inventories of oceanic phytoplankton (e.g. Lai et al., 2008; Twining et al., 2012). Nickel may have had a more fundamental role in the biogeochemistry of the early Earth (e.g. Williams and Frausto da Silva, 2003; Domagal-Goldman et al., 2008). Methanogens have an absolute requirement for Ni, through the Ni cofactor in methyl-coenzyme reductase (MCR), which catalyses the terminal step in methanogenesis and may also be involved in methane oxidation (e.g. Thauer, 1998; Kruger et al., 2003; Shima et al., 2012). Methane is a favoured candidate for the dominant greenhouse gas in the anoxic Archean atmosphere (e.g. Kasting, 2005), and it has recently been suggested (Konhauser et al., 2009) that a nickel famine in the late Archean ocean might have precipitated the dramatic rise in atmospheric oxygen that has become known as the Great Oxidation Event (GOE).

The isotope systems of the transition metals are increasingly being developed to investigate both the modern oceanic cycling of the transition metals (e.g. Bermin et al., 2006; John et al., 2010; Abouchami et al., 2011; Little et al., 2013; Zhao et al., 2013) and to understand the biogeochemistry of the past Earth (e.g. review by Anbar and Rouxel, 2007). Nickel stable isotopes have been slower to develop than some others. Cameron et al. (2009) presented the first data for terrestrial materials, specifically loess, river sediments and basalts, which had an average $\delta^{60}$Ni (= $(^{60}$Ni/$^{58}$Ni)$_{\text{sample}}$(^{60}$Ni/$^{58}$Ni)$_{\text{NIST986}}$ -1)x1000) = 0.15±0.12 (1SD, n = 16). These authors also
showed that, in contrast to this homogeneity, methanogens grown in culture take up Ni that is about 1‰ lighter than the culture medium. More recently, Gall et al. (2013) have presented data for hydrogenous Fe-Mn crusts which have $\delta^{60}\text{Ni} = 0.9\text{-}2.5\%$. Gueguen et al. (2013) reported data for basalts, Mn nodules and organic-rich rocks and suggested a value for the bulk silicate Earth of +0.05‰ while Hofmann et al. (2013) showed enrichment of light Ni isotopes in magmatic sulphides, with $\delta^{60}\text{Ni}$ at -0.28 to -0.47‰ ($n = 6$). A single study (Fujii et al., 2011) has used both a theoretical and experimental approach to suggest that the Ni isotope compositions of different aqueous species of Ni could be as great as 2.5‰.

Clearly, nickel isotopes are significantly fractionated by Earth surface processes, and thus have some potential in attempts to understand modern and ancient biogeochemical processes. However, there are currently no data for the isotopic composition of dissolved Ni in the modern oceans. Here we report such data, for samples from the Atlantic, Pacific and Southern Oceans, including three depth profiles that cover all or a substantial portion of the water column. We also report the first data for the dissolved load of rivers, to characterise one of the inputs to the oceans. We use the data to discuss the controls on nickel isotope cycling in the hydrosphere and, with recent data for the principal Fe-Mn oxide output (Gall et al., 2013), to discuss the mass balance of Ni and its isotopes in the modern ocean.

2. BACKGROUND: OCEANIC BIOGEOCHEMISTRY OF NICKEL

In the oceanic realm nickel exhibits many biogeochemical features that, qualitatively at least, are common to other transition metals (see review in Bruland and Lohan, 2003). Beginning with the pioneering studies of Sclater et al. (1976) and Bruland (1980), measurements of dissolved nickel distributions have revealed “nutrient-like” profiles. Surveys of the dissolved concentrations of bioactive metals in the oceans have typically found close associations between the depth
distributions of these metals and individual major nutrients, such as that of Zn with silicate (e.g. Bruland, 1980; Lohan et al., 2002) and Cd with phosphate (e.g. Boyle et al., 1976; Bruland, 1980; Norisuye et al., 2007). Ni appears to be re-mineralised in close stoichiometry with phosphate in the upper water column, but with silicate (Si) in the deep ocean (Sclater et al. 1976; Bruland 1980). The association with phosphate in the upper ocean implies a sizeable inventory associated with more labile organic matter in phytoplankton. The association with Si in the deep ocean is common to Zn, and is expressed in the longer lengthscale of remineralisation of Si, Ni and Zn relative to the labile nutrients and Cd. Though this finding also suggests an association with diatom opal, the very low Zn content of diatom opal itself (e.g. Ellwood and Hunter, 2000; Andersen et al., 2011) means that it cannot be the dominant regenerative source of Zn. Such considerations may also be relevant to Ni. Twining et al. (2012) have shown that cellular Ni in diatoms collected in the field and grown in culture is split approximately equally between frustule and organic material, and that cellular Ni/Si ratios are comparable to the slopes of dissolved Ni-Si relationships in the oceans. In the upper water column of the Southern Ocean, Lai et al. (2008) find slopes for dissolved Ni-PO$_4$ and Ni-Si correlations that are both close to stoichiometric ratios for individual plankton cells observed during Southern Ocean fertilization experiments (Twining et al., 2004).

There are also some key differences between the oceanic biogeochemistry of Ni and that of other bioactive trace metals. Thus, unlike Cd and Zn, concentrations of Ni are never reduced to near zero in the euphotic zone, and in fact never descend beneath about 1.5-2 nM (e.g. Bruland, 1980; Boyle et al., 1981; Bruland and Franks, 1983; Yeats and Campbell, 1983; Morley et al., 1993; Yeats et al., 1995; Saager et al., 1997; Mackey et al., 2002; Bowie et al., 2002; Norisuye et al., 2007; Ellwood, 2008). Moreover, the increase in concentrations as deep water ages between the Atlantic and Pacific, at factor 1.8, is smaller than for Zn and Cd, at factor 4-5 (Sclater et al., 1976; Bruland, 1980; Bruland and Franks, 1983). Finally, Ellwood (2008) finds little seasonal variation in surface
Ni concentrations in the Subantarctic Zone of the Pacific, despite large changes in Cd and Zn correlated with the summer algal bloom and with phosphate depletion.

In terms of specific biochemical functions, the identification of nickel-containing metalloenzymes has developed more slowly than for some other metals (see review by Ragsdale, 2009). There have been three biochemical roles identified for Ni that are important in the marine microbial realm, and to its biogeochemical cycling. The importance of Ni in enzymes involved in methane cycling, such as MCR, is well established (e.g. Thauer, 1998; Kruger et al., 2003). Though likely much more widespread on the early Earth (e.g. Kasting, 2005), this metabolism is only relevant to restricted anoxic basins or sediments of the modern ocean, and to life associated with hydrothermal systems (e.g. Kelley et al., 2002). In the modern oxic oceans the most commonly cited role of Ni is in urease, by which phytoplankton hydrolyse urea to yield ammonia (Frausto da Silva and Williams, 2001). Thus cultures of diatoms (Price and Morel, 1991) and cyanobacteria (Dupont et al., 2008a) grown on urea as the sole source of nitrogen are limited by Ni, and Ni-N co-limitation of phytoplankton is deemed likely in some oceanographic regimes (Price and Morel, 1991). Culturing studies have also found that cyanobacteria are limited by Ni even when grown on nitrate (Dupont et al., 2008a), consistent with the suggestion that these organisms contain a Ni superoxide dismutase, Ni-SOD, an enzyme which catalyses the breakdown of toxic superoxide (Dupont et al., 2008a,b).

Concentrations of total dissolved Ni that are never beneath about 1.5-2 nM in the euphotic zone are not consistent with the suggestion, for example, that Ni-N co-limitation may occur in some oceanographic regimes, unless only a small fraction of the dissolved pool is bioavailable (c.f. Mackey et al., 2002). This brings up another feature of Ni’s oceanic biogeochemistry that is common to other transition metals. It is commonly assumed that only free metal ions are available for uptake into phytoplankton cells. But for many metals a large proportion of the dissolved pool (operationally-defined as the material passing through a 0.45 μm filter) is bound in complexes with organic ligands. It appears that this may be the case for Ni too (van den Berg and Nimmo, 1987;
Donat et al., 1994; Xue et al., 2001; Turner and Martino, 2006), though estimates of the portion of
dissolved Ni that is organically-bound (in complexes with conditional stability constants between
$10^{12}$ and $10^{17}$) varies from 25 to 99.9%. There is also some debate over the extent to which these
results reflect the slow kinetics of exchange of these Ni-organic complexes (Xue et al., 2001), as
opposed to their thermodynamic stability (Gerringa, 1991; Mackey et al., 2002).

In terms of whole ocean mass balance, Sclater et al. (1976) suggested a residence time of Ni on the
order of 10 kyr, with the dissolved load of rivers as the major input. More recently, Gall et al.
(2013), on the basis of revised values for the output to pelagic sediments, have calculated a shorter
residence time of 4 kyr. It appears that dust and hydrothermal fluids are minor inputs in comparison
with some other metals (Sclater et al., 1976; Bruland, 1980; Bowie et al., 2002), while Danielsson
et al. (1985) and Bowie et al. (2002) document evidence for a source of Cu and Fe, but minimal Ni,
from sediment. Sclater et al. (1976) also suggested that scavenging by Fe-Mn oxides is the major
output. There is no impact on Ni concentrations of the intense oxygen minimum zone of the NW
Indian Ocean (e.g. Saager et al., 1992), and Ni concentrations in the deep sulphidic Black Sea are
not drawn down by reaction with H$_2$S, as they are for many other metals (e.g. Haraldsson and
Westerlund, 1988), suggesting that suboxic-anoxic or euxinic sediments may not be as important a
sink for Ni as they are for many other metals (e.g. Tribovillard et al., 2006). Ni is actually mildly
enriched in euxinic Black Sea sediments relative to upper continental crust, but is much more
strongly enriched in non-sulphidic open ocean settings that are characterised by intense upwelling
such as the Peru Margin (Boning et al., 2004). This, along with the ubiquity of lowered dissolved Ni
concentrations in the photic zone, might suggest that transfer in organic matter is a significant
sedimentary sink for Ni (c.f. Tribovillard et al., 2006).

The above relatively simple picture may, however, be complicated by a major apparent imbalance
in the oceanic Ni budget. Krishnaswami (1976) used measurements of the authigenic output of Ni
to pelagic Pacific sediment, as well as the little that was known about the dissolved riverine input at
that time, to suggest that the total output of Ni is up to six times greater than the dissolved riverine input. We return to this issue in the Discussion section with the additional constraints that derive from the data presented here.

3. SAMPLES AND METHODS

3.1 River samples

Details of the river samples and their collection can be found in Vance et al. (2008) and Archer and Vance (2008), where data are reported for Cu and Mo isotopes, respectively, on these samples. In addition, Zn isotopic data for many of them can be found in Little et al. (2013). All river samples were collected from close to the bank into pre-cleaned, low density polyethylene bottles after pre-rinsing with the sample 2-3 times. The Amazon, Brahmaputra, Nile and Chang Jiang samples were immediately passed through a pre-cleaned cellulose nitrate 0.2 μm filter using a pre-cleaned plastic filter holder and reservoirs, pre-rinsed with filtered sample before final filtrate collection, then decanted into a new pre-cleaned low density polyethylene bottle. The Kalix, Missouri and Tocantins samples were filtered in the same manner up to 2 weeks after collection, on return to the laboratory. All samples were acidified to pH 2 after filtration with concentrated twice-distilled HCl. Samples were pre-concentrated prior to column chromatography and mass spectrometry (see section 3.3) by drying down, treatment with concentrated nitric acid (containing a small amount of H₂O₂) to oxidise organics, and re-dissolution in a few ml HCl before chromatographic separation of Ni (see section 3.3). Following Cameron et al. (2009) mass bias correction for Ni was achieved using a mixed ⁶¹Ni-⁶²Ni double spike (details in section 3.3) and samples were spiked before being dried. Ni concentrations of river samples were first measured by ICPMS to allow accurate spiking (though all concentrations reported here are from the isotope dilution analysis via the double-spike analysis).
3.2 Seawater samples

Samples from the Iceland Basin were collected in August 2010 by E. Achterberg (NOCS, UK) on cruise 354 of the RRS Discovery. The cruise was primarily aimed at investigating high-latitude Fe limitation. The single depth profile measured here for Ni and its isotopes is from Station 28. Samples were collected using a trace metal clean titanium CTD frame fitted with 10 L trace metal clean Teflon coated OTE (Ocean Technology Equipment) bottles, and were filtered under pressure using 0.2 μm pore size cartridge filters (Sartobran P-300, Sartorius). Samples were acidified to pH 1.9 upon return to the Bristol laboratory, and equilibrated with the added acid for weeks before analysis for Ni isotopes. Water depth at this site was 2229 m, so that the profile presented here covers the entire water column.

The single 1000 m sample from the sub-tropical North Atlantic site was collected during the June 2008 US-Geotraces Intercalibration cruise (IC1) aboard R/V Knorr to the Bermuda Atlantic Time Series (BATS) site. The sample was collected with the US GEOTRACES 24-sample 12-L trace element General Oceanics GO-Flo Rosette system deployed on a Kevlar cable. The sample was filtered through 0.2 μm Pall Acropak capsule filters in the GEOTRACES clean van, and acidified with 2 mL distilled 6N HCl per liter of sample. Further details of sampling, as well as data for other trace metal systems, can be found in Boyle et al. (2012). The water depth at this site is approximately 4680 m so the sample reported here is from well above the bottom.

Samples from the Southern Ocean, including 4 surface transect samples and one depth profile through the upper 1500 m of the water column, were collected during Polarstern cruise ANT-XXIV/3 (Feb-April 2008) in the Atlantic sector of the Southern Ocean as part of the International GEOTRACES program and a contribution to the International Polar Year (IPY). Surface samples were collected at 2-5 m using an IFISH torpedo sampler with an all-Teflon pump. The depth profile was sampled using the TITAN frame (de Baar et al., 2008). Samples were filtered on board in a class 100 clean room environment through 0.2 μm filter capsules (Sartobran-300, Sartorius) under
slight nitrogen pressure and collected into acid-cleaned Nalgene high density polyethylene (HDPE) bottles and canisters. Acidification was done onboard to pH=2 with 12 N HCl (Baseline, Seastar). The water depth at the depth profile station PS71-104 was 4202m – thus well below the deepest sample reported here for Ni isotopes. These samples have been the subject of studies for both Cd (Abouchami et al., 2011) and Zn isotopes (Zhao et al., 2013).

Samples from the Juan de Fuca Ridge, NE Pacific, were collected in June 2009 by V. Cameron on cruise AT15-47 of the R/V Atlantis. The EAGER (Endeavour-Axial Geochemistry and Ecology Research) Program involved a suite of research activities focussed on several of the hydrothermal vent sites along the Endeavour Segment and at Axial Volcano. Samples for the single depth profile reported here represent off-axis (background) seawater, collected with the Sea-Bird SBE-911plus CTD system fitted with a 23 bottle 10-L Niskin rosette. Filtration was done on board using 0.2 µm filter units (Pall VacuCap 60) connected with Teflon tubing, into acid-cleaned Nalgene HDPE bottles. In-line filters were pre-cleaned plastic holders with 0.2 µm cellulose nitrate filters. Samples were stored double-bagged in plastic boxes and, immediately on return to Bristol, were acidified to pH 2 with double-distilled HCl. The water depth at this site is no greater than 2400m.

Samples from the NE Pacific were supplied by M.C. Lohan (University of Plymouth, UK), and were collected either in 1999 or 2001, originally for Zn concentration analysis (Lohan et al., 2002). Samples C1000 and E1000 were collected to investigate trace metal concentrations at the centre and edge of Haida eddies. Sample 26P1000 is from Ocean Station Papa. The three samples were collected by the C.S.S. John Tully with acid-cleaned 30-L Teflon-coated Go-Flo bottles attached to a Kevlar line and closed with Teflon messengers. The samples were filtered through 0.4-µm acid-cleaned polycarbonate membrane filters and acidified to a pH of 2 with sub-boiling quartz-distilled HCl on return to the UK. For the decade after collection and until the Ni isotope analyses presented here were performed, the samples had been stored double-bagged in plastic boxes. The water depth at these locations is in excess of 4000m, thus well below the depth at which all three NE Pacific
samples analysed here were collected.

All seawater samples were pre-concentrated by co-precipitation with Al(OH)$_3$, using an approach identical to that used previously for zinc and described in detail in Zhao et al. (2013). Briefly, the acidified sample was spiked (see section 3.3) and doped with an aluminium solution pre-cleaned of nickel. Seawater concentrations were known well enough from previous work to allow appropriate spiking. Following at least 24 hours equilibration, the pH was raised to 8.5-8.8 to produce an Al(OH)$_3$ precipitate. This precipitate was centrifuged, the supernatant poured off and a volume of MQ adjusted to a similar pH, was added. The mixture was again centrifuged and the supernatant removed; this washing process was repeated once more. The precipitate was finally dissolved in 7M HCl and purified for Ni isotopic analysis as described in section 3.3. The nickel yield from this procedure was 40-90%, as obtained by comparison of the signal size for a spike-free isotope with that of a standard, versus the result for Ni abundance from isotope dilution. Because the double spike is added before pre-concentration, 100% yields are not necessary for the accuracy of either Ni concentrations (by isotope dilution) or isotopic composition (from the double spike reduction).

Total analysed amounts of Ni were 110-680 ng, while total procedural blank for the Ni procedure was 11 ng, half of which comes from the aluminium solution. Thus, blank corrections to these samples would be 0.02-0.16‰, given a likely $\delta^{60}$Ni of around 0‰. As will be seen later, the dataset presented here is very homogeneous in Ni isotopes, and there is no correlation at all between Ni isotopic composition and the amount of Ni analysed so that these small blank corrections were not applied.

### 3.3 Chemical purification and mass spectrometric analysis of nickel

Separation and purification of nickel was carried out as described in detail in Cameron et al. (2009) with the exception of one additional column step. Briefly, spiked co-precipitated seawater and river samples (see section 3.1) in 7M HCl+H$_2$O$_2$ were loaded onto a first ion-exchange column in which the anion resin AG MP-1M (Bio-Rad) is used to remove Fe and Zn. The dried samples are then
taken up in 1M HCl/1M ammonium citrate, and the pH adjusted to 8-9 before loading onto columns filled with Ni resin (Eichrom Technologies). This is a reversal of the column procedure outlined in Cameron et al., (2009) as we discovered that the seawater samples would precipitate (most likely due to the heavy solute load) when adjusted to the high pH values required for the Ni column. After oxidation to remove Ni-bound DMG, the samples are finally put through a third column, which is a repeat of the first anion column, to clean up any residual Fe and Zn. This last column was deemed necessary as $^{56}$Fe after the Ni-resin column was significant. Given the initial anion column, and given the low Fe concentrations in seawater, this post-Ni-column Fe is presumably blank addition. In any case, it was monitored in all samples measured for Ni isotopes, as detailed below.

All isotope analyses were performed at low mass resolution on a ThermoFinnigan Neptune multicollector ICPMS, with samples introduced in 2% nitric acid via a CPI PFA nebuliser (50 µl/minute) attached to an Aridus desolvating nebuliser system (Cetac, Omaha, NE, USA). Signals were monitored at masses 58, 60, 61, 62 and 64. The latter has a potential $^{64}$Zn interference but is not used here. For some types of samples an isobaric interference from residual sample $^{58}$Fe is a potential problem at mass 58. This was dealt with by manual checking of the $^{56}$Fe/$^{58}$Ni ratio in high resolution prior to the Ni isotopic analysis and applying a correction to the 58 signal. However, this correction was insignificant, e.g. relative to the propagated internal uncertainty on $\delta^{60}$Ni, except for two samples. In the case of sample Kx4 it resulted in an upward correction of 0.38‰, and the corrected value is identical to that obtained for sample Kx5. In the case of sample Negro3 it resulted in an upward correction of 0.17‰, and the corrected result is identical to sample Negro2. The other potentially problematic interference is the $^{40}$Ar$^{18}$O molecular at mass 58, given that these samples were measured in low resolution. This was reduced to levels of $1-2 \times 10^{-14}$A compared with $^{58}$Ni signals in the $10^{-10}$A range for all samples, by the addition of a small amount of N$_2$ to the Aridus sweep gas. The size of the $^{58}$Ni molecular, and those of the background signals on all measured Ni masses, was monitored by the measurement of on-peak zeros (aspirating 2% nitric) prior to each
sample or standard. The “blank” values obtained were subtracted from sample signals before double-spike reduction.

A potential issue with double spike analysis was raised by Bermin et al. (2006) for Zn. The isotopic composition of the double-spike used here is referenced to the following isotope ratios for SRM986: $^{61}\text{Ni}/^{58}\text{Ni} = 0.016744$, $^{60}\text{Ni}/^{58}\text{Ni} = 0.385202$ and $^{62}\text{Ni}/^{58}\text{Ni} = 0.0533939$. The first of these ratios is assumed. The other two are obtained by mass-bias correction of measured ratios for pure SRM986 obtained during the session in which the spike was calibrated, using an exponential law.

Small deviations in the behaviour of the instrument after this session, on any subsequent day when spiked samples and standards are analysed, can arise through, e.g. deviations from the exponential mass bias law used in data reduction or changes in cup efficiencies. These can propagate through to inaccuracies in the $\delta^{60}\text{Ni}$ of the sample. Following Bermin et al. (2006) this is dealt with here using multiple measurements of pure NIST SRM986 during each analytical session to monitor variations in instrument behaviour. The normalised $^{60}\text{Ni}/^{58}\text{Ni}$ and $^{62}\text{Ni}/^{58}\text{Ni}$ ratios obtained are compared to those listed above, and adjustment made to raw isotope ratios of the spike-sample and spike-standard mixtures to take them into account, before any double-spike reduction is done. The success of this approach is demonstrated by the accuracy and reproducibility of spike-standard mixtures.

For the period Aug 2007 until July 2012, mixtures of NIST SRM986 (treated in this case as an unknown) and double-spike with std-spike ratios of 0.1-4 and run during each analytical session gave $\delta^{60}\text{Ni} = 0.06\pm0.08$ (n = 184). All sample/spike ratios for samples analysed here were between 0.5 and 2.5.

A further test of accuracy can be obtained by comparison of our nickel isotope data with those obtained independently in other laboratories. There are very few published studies of nickel isotopes, but Gall et al. (2012) recently reproduced two USGS basalt standards for which data were published in Cameron et al. (2009) to $\leq0.05 \%$. Gall et al. (2013) and Gueguen et al. (2013) also report $\delta^{60}\text{Ni}$ for two Fe-Mn nodule reference materials. They obtain $+1.08\pm0.07$ and $+1.03\pm0.06$
respectively, for Nod A-1 versus values of +1.13 and +1.06 obtained in this laboratory. They also
obtain $\delta^{60}\text{Ni} = +0.40\pm0.10$ and $+0.36\pm0.07$ respectively, for Nod P-1 whereas we have obtained two
values at +0.41.

4. RESULTS

4.1 The nickel concentration and isotopic composition of rivers

All the data obtained here, for rivers and seawater, are shown as a histogram in Fig. 1. The river
data are presented in Table 1 and displayed in Fig. 2. The dissolved phase of rivers exhibits
substantial variability in both Ni concentration and $\delta^{60}\text{Ni}$: from 2.2 to 35 nmol kg$^{-1}$ in Ni
concentration and from +0.29 to +1.34‰, respectively.

There are no previous data for nickel isotopes in rivers, but the concentrations reported here can be
compared with published data. The lowest Ni concentrations overall are for the Negro, a tributary of
the Amazon that drains the lowland regions of the Amazon Basin, and the Kalix, a small river in
Arctic Sweden. The range of nickel concentrations found here for the Kalix of 4.1-5.6 nM is within
the published range of 2-6 nM (Pekka et al., 2004; Dahlqvist et al., 2007). There are no published
nickel data specifically for the Negro, nor for the other major tributary that joins the Negro at
Manaus, the Solimoes, but Boyle et al. (1982) document a concentration of 4-5 nM for the riverine
end-member at the mouth of the Amazon. The value reported here for the Tocantins, another major
river that debouches into the Atlantic alongside the Amazon at Belem, is 4.5 nM. Reported Ni
concentrations for the Chang Jiang at its mouth (2-3 nM; Edmonds et al., 1985) are lower than the
6-8 nM found here at, or upstream of, Wuhan. Measurements up to 400 km inland of the mouth,
however, are closer to those found here, at 4-5nM (Koshikawa et al., 2007), so there may be a real
increase upstream. Nickel data have been reported for the Ottawa, and the St. Lawrence system
generally (Rondeau et al., 2005). The reported concentrations for the Ottawa show significant inter-
annual variability (6-14 nM) while those at the mouth of the St. Lawrence are temporally constant at 12-13 nM. Both of these are consistent with the value of 12.3 nM reported here. Finally, our concentration for the Missouri at Columbia of 35 nM is just slightly higher than the range previously reported for the Missouri and the Mississippi system generally, at 30-32 nM (Shiller and Boyle, 1987; Shiller, 1997).

The most striking result from the nickel isotope analyses is that only two rivers, the Negro and the Brahmaputra, have isotopic compositions that overlap with the range for silicate rocks and sediments reported in Cameron et al. (2009). All other rivers are heavier, with $\delta^{60}\text{Ni}$ up to about 1‰ heavier than the “lithogenic” value for the Chang Jiang, a finding that is analogous to that for Cu (Vance et al., 2008) and Mo (Archer and Vance 2008). In fact, the relationship with Ni concentrations bears some similarity with these other systems and will be returned to in the discussion. Different analyses of the same river, collected at close to the same location but collected, filtered and stored in separate bottles, are all analytically the same (given the long-term reproducibility of standards). There is also very little difference, in either concentration or isotopic composition, between the dry and wet season Nile samples.

### 4.2 Nickel concentrations and isotopic composition in seawater

The data for seawater samples is reported in Table 2 and displayed as depth profiles in Fig. 3-5. Concentrations for these samples range from 3.1 to 11.2 nmol kg$^{-1}$. The first striking feature of the isotopic data is its homogeneity: the average and 2 standard deviations for the entire dataset is 1.44±0.15‰, compared to our estimate of the reproducibility based on repeat analyses of standards of 0.08‰. The second is that seawater is distinctly heavier in Ni isotopes than rivers. Only 2 of the 29 seawater analyses have a Ni isotopic composition that is lighter than the heaviest river.

As with rivers, there are no published data on nickel isotopes in seawater, but our data for concentrations can be compared with literature values, though this is not always easy because
locations of previous work are not exactly the same and some of the older concentration datasets
have many outliers due to the difficulties with clean sampling and analysis at the time. Despite this,
our dataset as a whole for the North Pacific is clearly identical to that of Bruland (1980), with
agreement all the way down the depth profiles to a small fraction of a nmol kg\(^{-1}\) (Fig. 6). This is all
the more remarkable given that the various stations in Fig. 5 are spread across 35 degrees of latitude
and over more than 20 degrees of longitude. Our data for the Iceland Basin in the North Atlantic are
similar to those for two nearby stations analysed previously (Yeats and Campbell, 1983; Danielsson
et al., 1985), and the same is true for our partial depth profile in the Polar Front Zone of the
Southern Ocean (Löscher, 1999), though the latter two datasets are rather noisy compared with the

Comparison can also be made between relationships between Ni concentrations and the major
nutrients, for the data presented here and published previously. Fig. 7 shows this relationship for
phosphate, with the same datasets from the North Pacific and North Atlantic that feature in Fig. 6
plotted for comparison. It has long been recognised (Sclater et al., 1976; Bruland, 1980) that Ni and
phosphate are regenerated in a similar fashion in the upper water column so that concentrations, as
expected, are strongly correlated there. Beneath the mid-depth phosphate maximum, however,
nickel concentrations continue to increase to a maximum (if present) at much deeper levels, so that
deep nickel concentrations are better correlated with silica. This is clearly seen on Fig. 7 for the
highest Ni concentrations, which are from depths beneath 1000-1200m, and which lie increasingly
off the Ni-PO\(_4\) correlation at greater depth. Nearly all the data presented here, for which we also
have phosphate data, are for the upper 1500m of the water column, so that the relationship with
phosphate (Fig. 7) holds for the entire dataset. The best-fit line yields a slope of 0.0022 (mol/mol),
with an R\(^2\) of 0.93. This compares with slopes of 0.0014-0.0027 for data in the literature (Sclater et
al., 1976; Bruland, 1980; Bruland and Fanks, 1983; Yeats and Campbell, 1983; Danielsson et al.,
1985; Mackey et al., 2002; Norisuye et al., 2007; Lai et al., 2008).
5. DISCUSSION

5.1 Controls on the dissolved nickel isotope composition of rivers

As noted previously, the key feature of the riverine isotopic data is that all but two rivers are distinctly heavier than silicate rocks and sediments. It has also been noted that this same feature has been seen for Mo and Cu isotopes in rivers (Archer and Vance, 2008; Vance et al., 2008). In these previous studies the possibility that the isotopic compositions of these different metals are lithologically-controlled was discussed and dismissed. For Ni, Gueguen et al. (2013) report $\delta^{60}$Ni for coal and shale at $+0.5$ to $+0.6\%$ and it is possible that variably heavy Ni isotope compositions in the dissolved phase in rivers can be explained by variable contributions of Ni from these lithologies. However, for Mo and Cu, this does not explain the relationship between isotopic compositions and reciprocal concentration, which are much more readily explained in terms of weathering processes.

The similarities between the Cu and Ni systems are emphasised in Fig. 8, where the Ni isotope data are plotted versus $\delta^{65}$Cu where the two are available for the same samples. For most of the data the river samples extend along a positive array to heavy Ni and Cu isotopic compositions and away from a value close to the “lithogenic” isotopic composition for both systems. With the exception of the Brahmaputra sample, which has an anomalously light Ni isotope composition given its $\delta^{65}$Cu, the $R^2$ for the data in Fig. 8 is 0.75.

The exception already mentioned is the Brahmaputra, but there are no Cu isotope data for the Negro samples which, like the Brahmaputra, have Ni isotopic compositions close to the lithogenic value. For Cu there is a general tendency for the isotopic composition to get heavier as riverine Cu concentrations decrease, and this is also mostly the case for Ni (Fig. 2). But the Brahmaputra is clearly different, and despite the fact that the Negro has the lowest Ni concentration of any river measured here its Ni isotopic composition is close to the value for silicate rocks and sediments (Fig.
1) There is one clear and well-established characteristic of the Negro that probably explains its behaviour. The River Negro is the archetypal transport-limited river of Stallard and Edmond (1983), who noted its low total cation load (c.f. Ni) and cation ratios close to those of substrate rocks (c.f. Ni isotopes). Of all the Amazonian rivers, the Negro drains the most intensely-weathered terrain. Thus it seems likely that the Negro represents an end-member river composition that is close to isotopic equilibrium with its source rocks, in a terrain that is so intensely-weathered on a time-integrated basis that the modern supply rate of many cations, including Ni, is slow. It is not clear whether this explanation could apply to the other exception, the Brahmaputra, as well.

In this view, the remaining Cu-Ni isotope data would be explained in terms of variations in weathering intensity in terrains that, unlike the Negro, have not experienced intense time-integrated weathering, and thus have not lost a lot of their nickel. Thus, the data for both isotopic systems are consistent with decreasing modern weathering intensity along the array, providing opportunity for isotopic compositions in the dissolved phase of rivers that are increasingly out of isotopic equilibrium with the rocks they drain. We note that this explanation is similar to that advanced for Mo isotopes and concentrations in Archer and Vance (2008), but is different from that put forward for Cu in Vance et al. (2008). In the latter study, particulate analyses were also available for one river, and this particulate load contained the isotopically light counterpart of the dissolved Cu load.

It was suggested that the Cu isotope data could be explained by equilibrium partitioning, during transport, of Cu isotopes between a heavy dissolved load that was predominantly bound to organic ligands and a light particulate load. In the absence of data for the particulate load of Ni in rivers, this is also a tenable explanation for the Ni data, though the explanation in terms of weathering has the advantage that it has an obvious rationale for the Negro data too. On the other hand, another characteristic of the Negro is its high load of dissolved organic (humic) material (Stallard and Edmond, 1983), perhaps allowing the organic complexation of all of its small load of Ni and little partitioning into the solid phase.
This discussion is of general importance to the characteristics of transition metal isotope systems in rivers, but its resolution must await further, more detailed, studies of river systems.

5.2 The dissolved riverine input of nickel and its isotopes to the oceans

Overall, if the data presented here are close to representative of the global riverine flux, the Ni concentration data combined with the water discharges suggest an annual flux of Ni to the oceans of 3.6x10⁸ moles. This is very close to the estimate of 3.2x10⁸ moles yr⁻¹ made by Sclater et al. (1976), though both are below the Gaillardet et al. (2003) estimate of 5.2x10⁸ moles yr⁻¹. However, the latter was based solely on an early measurement of the Amazon, whereas roughly half of the Ni discharge we have measured is also from the Amazon, so this estimate could change with the addition of further data. Boyle et al. (1992) and Edmond et al. (1985) show that the mixing of freshwater and seawater in the Amazon plume and the Chang Jiang estuary are both close to conservative for nickel, so that, at least based on these estuaries, this estimate is not likely to be significantly modified by estuarine processes. In terms of isotopes, the discharge- and concentration-weighted average δ⁶⁰Ni for this group of rivers is +0.80‰, about 0.6-0.7‰ heavier than the “lithogenic” value.

An initial question that is relevant to our overall aim to use these data as an estimate of the input of Ni and its isotopes to the oceans, is whether this flux and its isotopic composition is representative of the long-term global flux, particularly in the light of potential anthropogenic perturbation. This question is very difficult to address unequivocally. Generally speaking there does not seem to be a strong correspondence between high Ni concentrations and polluted river systems. For example, the Solimoes and Negro at Manaus, relatively undisturbed rivers, have Ni concentrations that bracket those of the Tocantins at Belem, likely more polluted. This range for the two Amazon tributaries also encompasses the measured concentrations in the Chang Jiang and Brahmaputra, and these are all similar to the likely pristine Kalix (e.g. Pekka et al., 2004). The Nile and Ottawa concentrations are higher at 12-13 nM, but again the Nile in Sudan, where these samples were collected, is likely to
be relatively undisturbed. The Missouri clearly stands out as having a high Ni concentration, but we note that concentrations down the length of the Mississippi system do not vary dramatically (20-35 nM; Shiller and Boyle, 1987; Shiller, 1997) so that it is possible that this is also close to the river’s natural Ni concentration. It is also the case that Ni concentrations in rivers have not increased greatly through the 20th century – unlike e.g. Pb, Zn, Cd, Hg and some others. For example, concentrations in sediments from the Rhine and UK lakes increased by less than factor 2 from 1900 to 1980, while concentrations in reservoirs along the Neckar have actually decreased (Foster and Charlesworth, 1996).

5.3 The homogeneity of dissolved Ni isotopes in the oceans

There are two significant aspects of the isotopic data for seawater: first its homogeneity at $\delta^{60}\text{Ni} = +1.44 \pm 0.15\‰$ (average and 2 standard deviations), and second the fact that this average is 0.6-0.7‰ heavier than the riverine input estimated in section 5.2. In fact, only 3 out of the 29 seawater samples measured have $\delta^{60}\text{Ni}$ lighter than the heaviest river measured. This section discusses the implications of the first of these first-order observations for cycling of Ni within the oceans, while the next section deals with the implications of the second for whole ocean elemental and isotopic mass balance of Ni.

Given the putative roles of Ni in phytoplankton, the ubiquitous depletion of Ni in the surface ocean, and the possibility that phytoplankton uptake involves a kinetic isotopic fractionation, it is perhaps surprising that surface waters in this small preliminary dataset show little significant isotopic shift relative to the deep ocean. There is the slightest hint of anti-correlation between Ni concentrations and isotopic compositions near the surface of the depth profiles for the Iceland Basin and the Southern Ocean (Fig. 3,5), and it is possible that analytical improvements in the future might turn up analytically resolvable variations in near-surface dissolved Ni isotopes that would be consistent with significant removal of light isotopes into particulate organic material. The maximum isotopic difference between surface water and local deep water for the above sites, at the limits of the
uncertainties on the isotope data, is 0.2-0.3‰. Because of the modest (~20-25%) surface depletions in Ni relative to the local deep ocean, this would actually allow a substantial isotope fractionation associated with Ni removal, of as much as 0.8-1‰. The presence or absence of such a Ni isotopic fractionation associated with phytoplankton uptake could be more easily revealed either by culturing experiments or through paired measurements of filtered seawater and associated particulate organic matter.

On the other hand, the NE Pacific (Fig. 4) shows the biggest surface depletion in Ni isotopes relative to the local deep ocean, with no hint at all of heavy surface isotopes. However, the North Pacific is very stratified near the surface, and it is very possible that the topmost measurement here (at 100m) misses any isotopically heavy Ni associated with photic zone uptake of light Ni. For example, recent Zn isotopic data for depth profiles from the NE Pacific (Vance et al., 2012) reveal that the heavy isotopic residue in the dissolved phase as a result of biological metal uptake is restricted to the top 50m of the water column, while at 100m a light isotopic composition associated with shallow regeneration is observed.

The relative lack of an obvious isotopic imprint associated with the depth cycling of Ni is further emphasised in Fig. 9, where the Ni isotope data presented here are plotted versus phosphate and silica concentrations. It is striking that, despite the strong correlations between phosphate and Ni concentrations illustrated in Fig. 7, there is no significant relationship between phosphate and Ni isotopes. In the silica plot, there are again the slightest hints of heavier isotopes associated with the very lowest silica concentrations, but the isotopic values for these low silica samples are the same, within uncertainty, of the deeper samples. Clearly, at least for this preliminary dataset, the biogeochemical cycling of Ni between the surface and deep ocean is not associated with an isotopic fractionation that is large enough to lead to significantly heavy values associated with the co-removal of Ni and the major nutrients in the surface ocean. This conclusion is similar to that arrived at for zinc isotopes by Zhao et al. (2013), an element for which culturing and lake studies (John et
al., 2007; Peel et al., 2009) point to a significant isotopic effect associated with intra-cellular uptake. Zhao et al. (2013) suggest that the lack of relationships between Zn isotopes and the major nutrients, despite strong correlations between the latter and Zn concentrations, indicates that Zn uptake in the surface ocean, and its marine biogeochemical cycling generally, is dominated by incorporation into the opal frustule of diatoms and its associated extra-cellular organic matter (c.f. Twining et al., 2012). It may be that the same is true for nickel isotopes.

In the entire dataset, the only sample that has an analytically resolvable difference in Ni isotopes relative to samples above and below it in the water column is that from 1800m in the suite of Juan de Fuca Ridge samples of the NE Pacific profile (Table 2; Fig.4). This sample is ~0.2 ‰ lighter, and it also has around 1 nmol kg$^{-1}$ more Ni, than those on either side. Long-lived, deep scattering layers associated with a neutrally-buoyant plume, and identified by acoustic anomalies, have been documented for the Juan de Fuca Ridge, in the on-axis vicinity of the 1800m depth, off-axis sample (Lupton et al., 1985; Thomson et al., 1992; Burd & Thomson, 1994). These and other studies (e.g. Cowen et al., 2001) also report the presence of a significant concentration of planktonic and microbial biomass associated with the scattering layer that take advantage of the chemical and nutrient gradients imparted by the plume. It is not certain whether the close proximity of the plume with its attendant suite of abiotic and biotic processes can account for the lighter $\delta^{60}$Ni and increased concentration, but we note that similar data has been reported for dissolved Fe associated with hydrothermal plumes (Bennett et al., 2008; 2009; Sharma et al., 2001). Two possibilities that could account for the anomalous datum: (1) given the current lack of data for estimates of hydrothermal impact on oceanic Ni budgets in general, this single sample may represent a local feature attributable to the vent/plume (and we note that different vents may be geochemically distinct in regards to Ni); (2) alternatively, there could have been some sort of contamination during sampling or analysis. Both prospects would suggest that the seawater Ni budgets would not be
significantly affected by hydrothermal inputs. Clearly, this single anomaly has to be duplicated in the future.

5.4 The elemental and isotopic budget of Ni in the oceans: budget imbalances and heavy Ni isotopes

The lack of Ni isotope variation in the deep ocean, as opposed to the absence of variability in the surface ocean associated with biological uptake, is primarily a function of the residence time of Ni relative to the oceanic mixing timescale. Sclater et al. is (1976) calculate a residence time of around 40 kyr assuming that the dissolved load of rivers is the dominant input. The residence time calculated from the riverine input flux obtained here and an average oceanic concentration of 8 nM (Bruland and Lohan, 2003) is around 30 kyr. Thus, given an oceanic mixing timescale of the order of 1 kyr (e.g. Jenkins, 2003) the homogeneity of deep ocean dissolved Ni isotopic compositions is no surprise. However, as discussed below (and c.f. Krishnaswami 1976; Sclater et al., 1976), there is a problem with balance in the oceanic Ni budget that is of wider significance than just the isotopic data.

Fe-Mn crusts are very enriched in Ni (e.g. Gall et al., 2013; up to 0.8 wt. %) and scavenging to Fe-Mn oxyhydroxides in the water column, with subsequent burial of these oxides in sediments, has previously been identified as the most important output from the oceans (Krishnaswami, 1976; Sclater et al., 1976). Krishnaswami (1976) noted that authigenic Ni associated with these phases in Pacific pelagic sediments outweighed the dissolved riverine input by up to a factor of 6. This imbalance is also implicit in the fact that Sclater et al. (1976) calculate an output-based residence time for Ni in the oceans of 6-9 kyr, versus the estimate of 30-40 kyr they and we obtain based on the suggestion that the dissolved riverine load is the dominant input. Both Krishnaswami (1976) and Sclater et al. (1976) only had measurements of two rivers available, one of which was the Amazon. Though the riverine dataset here includes more rivers, it is still dominated by the Amazon. While it is possible that the estimate of the riverine flux could be revised upwards, such a revision seems
unlikely to close the gap on the estimated outputs. It is also possible to obtain an independent
constraint on the Fe-Mn oxide output of Ni, by tying it to the slightly better known oceanic Mo
budget. The input of Mo to the oceans is dominated by the dissolved load of rivers, and Archer and
Vance (2008) estimate it at 2.3x10^8 mol yr^{-1} with a δ^{98/95}Mo = +0.7‰. Scott et al. (2008) present an
analysis of the oceanic Mo budget and suggest that 35% of this input, or 8x10^7 mol yr^{-1}, is lost to
the Fe-Mn oxide sink. The size of this sink for Mo is particularly well constrained by some features
of the marine isotopic budget. It is well known that the Mo isotopic composition of the oceans is
homogeneous and heavy, at δ^{98/95}Mo = +2.3‰ (Nakagawa et al., 2012). This requires a light sink.
Fe-Mn crusts are 3‰ lighter than seawater (Barling et al., 2001; Siebert et al., 2003), and
experimental sorption of Mo to Mn oxides produces a sorbed phase that is 3‰ lighter than the
aqueous phase (Barling and Anbar, 2004; Wasylenki et al., 2011). Thus it seems certain that the
dominant light output is sorption to Mn oxides and the size of the fractionation, along with the
difference between the homogeneous dissolved oceanic pool and the input, puts a relatively tight
constraint on the size of the Fe-Mn oxide output for Mo. The USGS (Manheim et al., 1991) have
compiled data on the chemistry of over 700 Fe-Mn crusts and nodules and these have a Ni/Mo ratio
of 18±10 (molar, 1 SD). Thus, an output of 1.5x10^9 mol yr^{-1} Ni to this type of sediment is implied,
four times the dissolved riverine input. It is possible that there is some bias in the type of Fe-Mn
oxide samples included in the above database so that it is, for example, not representative of
dispersed Fe-Mn oxides in sediment. However, the concordance between the imbalance suggested
here and that suggested by Krishnaswami (1976) based on the chemistry of pelagic sediments
suggests that the conclusion is robust.

The inclusion of other potential sinks for nickel from the ocean would, of course, worsen this
imbalance problem, but probably to an insignificant degree. Sediments beneath both euxinic water
columns in restricted basins (significant H_2S in bottom water, e.g. Black Sea), and upwelling open
ocean settings (near zero bottom-water O_2 e.g. Namibian and Peru Margin) have authigenic Ni/Mo
ratios close to 1 (e.g. Brumsack et al., 2006). Scott et al. (2008) estimate that these sinks represent
the other 65% of the total oceanic Mo output. Using the same approach as for crusts, with the above
authigenic Ni/Mo ratio, this implies an output of about $1.5 \times 10^8$ mol yr$^{-1}$, or an order of magnitude
less than the Fe-Mn crust output calculated in the same way.

These calculations, while obviously not precise, are clearly consistent with the earlier suggestion
(e.g. Sclater et al., 1976) that scavenging to Fe-Mn oxides is the dominant sink for Ni from the
oceans. Gall et al. (2013) have recently published Ni isotope data for the surfaces of a variety of
crusts. The dataset is quite variable, at $\delta^{60}\text{Ni} = 1.60 \pm 0.4\%$ (1SD), with no clear indication of the
key control on this variability. But the average is very close to the seawater value obtained here. If
these Fe-Mn crust data are representative of the Fe-Mn oxide-associated output of Ni from the
oceans there is apparently little isotopic fractionation involved in this output. The lack of an
isotopic fractionation associated with the main output then imposes another constraint on the
missing input implied by the elemental imbalance discussed above. The missing source must be as
isotopically heavy as the dissolved pool of the oceans itself – and apparently heavier than the
dissolved load of rivers.

Of the candidates for extra inputs to the ocean, it was argued earlier that the hydrothermal source is
likely to be insignificant. We note that Douville et al. (2002) report high Ni concentrations in
hydrothermal fluids emanating from ultramafic substrate, but concentrations below detection limits
for fluids from basaltic substrates. There have never been any indications from depth profiles near
ridges that hydrothermal inputs are anything other than minor. Sclater et al. (1976) also arrive at
this conclusion in noting that Ni/Fe ratios in sediment near ridges are lower than open ocean Fe-Mn
nodules. Total dust input to the ocean has been estimated by Jickells et al. (2005) at $4.5 \times 10^{14}$ g yr$^{-1}$.
At an average Ni concentration for the continental crust of 47 ppm (Rudnick and Gao, 2003) this is
equivalent to a total Ni flux of $2.1 \times 10^{10}$ g yr$^{-1}$, or $3.6 \times 10^8$ mol yr$^{-1}$, close to the riverine flux of Ni.
However, Desboeufs et al. (2005) estimate the Ni solubility in dust to be on the order of 2%,
suggesting that the Ni flux to the dissolved phase is unimportant. This conclusion is the same as that arrived at by others based on surface ocean dissolved Ni concentrations (e.g. Bruland, 1980; Bowie et al., 2002). Moreover, any source of Ni from dust presumably has an isotopic composition close to the lithogenic value, so that this source is unable to provide the heavy Ni seen in the oceans. Another possibility is a diffusive flux out of sediments. Because of the strong association of Ni with Mn oxides in sediment, Ni concentrations can be high in the pore fluids of sediments where the reduction of Mn oxide is occurring (up to 600 nM, see Shaw et al., 1990). But our conclusion earlier that the Mn oxide output is much greater than the dissolved riverine input is tied to Mo. Since Mo will also be mobilised from reduced Mn oxide, this suggestion does not get around the imbalance in the oceanic Ni budget with respect to that for Mo.

A final possibility is that mobilisation of the riverine suspended load of Ni occurs in estuaries, and that this reservoir is isotopically heavy. It was noted earlier that Ni in the Amazon plume and the Chang Jiang estuary behaves pseudo-conservatively. But it is possible that estuaries where surface sediment is anoxic could reductively release Ni associated with Mn-oxide coatings. This explanation of the imbalance problem is attractive for a number of reasons. Firstly, 95-97% of the Ni inventory of rivers is in the suspended load rather than the dissolved load (Gibbs 1973; Martin and Meybeck 1979; Gaillardet et al 2003; Viers et al. 2009). Secondly, in a study of the Amazon and Yukon rivers, Gibbs (1973) showed that approximately half of this suspended load reservoir of Ni is associated with oxide coatings on grains. Thirdly, the suspended load of Mo is relatively much less important than for Ni. Martin and Meybeck (1979) suggest that 30% of the total riverine load of Mo is in the dissolved phase. Archer and Vance (2008) found insignificant amounts of Mo in the suspended load of the Kalix and Chang Jiang. Thus, a source of Ni via the reduction of Mn oxides in estuarine sediments might not come with a significant source of Mo. Finally, it is perhaps noteworthy that the study of Krishnaswami (1976) also found that the oceanic Mn budget was out of balance. This is confirmed by a similar approach to the Mn oxide output as taken above for Ni,
i.e. calculating it based on the Mo output to Fe-Mn oxides and the Mn/Mo ratio of Fe-Mn crusts. Such an approach yields a sink for Mn of $7 \times 10^{10}$ mol yr$^{-1}$, which is about 3 times the global dissolved riverine flux given in Gaillardet et al. (2003). Thus co-release of Ni and Mn through the reduction of Mn oxides could solve the imbalances of both Ni and Mn.

The suggestion that estuarine release of suspended load Ni might solve the imbalance problem must await further studies in these settings. A real problem with this suggestion, though, is the isotopic heaviness of oceanic dissolved Ni. Given the fact that the major output from seawater, as represented by Fe-Mn crusts, is as heavy as the dissolved pool, the isotopic mass balance requires that the overall input is also heavy. This, in turn, creates a requirement for the permanent storage of a counterpart isotopically light pool of Ni somewhere on the continents. At this stage, it is not at all obvious where this isotopically light reservoir might be.

6. CONCLUDING REMARKS

We have demonstrated three main features with this first dataset for the Ni isotopic compositions of the dissolved phase of rivers and the oceans:

(1) Ni isotopes in the dissolved phase of rivers (discharge- and concentration-weighted $\delta^{60}$Ni = +0.8‰) are heavier than the average of the small dataset for silicate rocks and sediments on the continent (at around 0 to +0.3‰; Cameron et al., 2009). This feature is common to other transition metal isotope systems such as Mo and Cu (Archer and Vance, 2008; Vance et al., 2008), and likely reflects isotope fractionation in the weathering environment or during transport in rivers.

(2) Ni isotopes in the dissolved phase of the ocean are significantly heavier than this dissolved riverine source, at $\delta^{60}$Ni = +1.44±0.15‰ (2SD, n = 29 from the Atlantic, Pacific and Southern Oceans), necessitating either another input that is heavier than rivers, or an isotopically light output.
Oceanic dissolved Ni isotopes are strikingly homogeneous, with little significant difference between the surface ocean where Ni concentrations drop as low as 1.5-2 nM and the deep ocean where they are as high as 10-11 nM. Thus, the drawdown of Ni in the surface ocean must occur via a process that does not involve a significant enough isotopic fractionation to yield residual heavy isotopic compositions in the surface dissolved pool.

The isotopic data put quite tight constraints on the nickel budget of the oceans, but at the moment the processes which close the budget are not clear. The main output of nickel from the oceans is via sorption to Fe-Mn oxides and this output is around a factor of five greater than the dissolved riverine input (Sclater et al., 1976; Krishnaswami, 1976). Thus, there appears to be a requirement for one or more extra sources from the elemental budget alone. Moreover, the fact that the Ni isotopic composition of this principal output, Fe-Mn crusts, is not very different (Gallet al., 2013) from the dissolved phase data reported here, suggests that an isotopically light sink is unlikely. The identity of the putative missing source is not obvious, however. Previous work (Gibbs, 1973; Martin and Meybeck, 1979) has suggested that the riverine load of nickel is overwhelmingly located in particulate material, and that this nickel is, in turn, overwhelmingly associated with surface Mn-oxide coatings. It is possible that release of this nickel in anoxic estuaries could constitute the missing isotopically heavy input. But if this is the case then there must be a sink for the counterpart isotopically-light nickel on the continents, perhaps associated with biological uptake in setting such as bogs and wetlands where methanogenesis is active (e.g. Cameron et al., 2009).

Characterisation of riverine particulates, as well as sedimentary processes in anoxic estuaries, may be key to the resolution of this budgetary discussion.

The homogeneity of oceanic nickel isotopes is something of a surprise, given that the drawdown of Ni in the surface ocean appears to be via biological uptake (e.g. Twining et al., 2012), and the fact that such uptake usually involves a preference for the light isotope via a kinetic fractionation. Ni concentrations in the deep ocean are well known to be closely correlated with silica (e.g. Bruland,
1980), and it may be that Ni incorporation into diatom opal, or sorption onto organic matter associated with diatom opal, may dominate Ni drawdown in the surface ocean and be associated with only a minor isotopic fractionation. Culturing work on marine phytoplankton, as well as Ni isotopic analysis of photic zone particulate material, would greatly contribute to the resolution of this discussion.

Acknowledgements

The authors thank Lian Zhou, Alan Whittington, Corey Archer, Nigel Harris, Eric Achterberg, Hein de Baar, Wafa Abouchami and Maeve Lohan for supplying some of the samples for this work, and Eric Achterberg, Maeve Lohan and M. Stinchcombe for sharing phosphate data. We thank David Butterfield and the personnel onboard the R/V Atlantis for technical assistance as well as Alden Denny and Sanjoy Som for carrying out the CTD operations. We also thank Corey Archer and Chris Coath for assistance in the Bristol laboratories. This work was supported by NERC grant NE/F019092/1 and a Leverhulme Trust Research Fellowship to D. Vance.
REFERENCES


affinity and low-affinity zinc transport by the marine diatom Thalassiosira oceanica. Limnol. Oceanogr. 52, 2710-2714.


**FIGURE CAPTIONS**

**Figure 1:** Frequency distribution of Ni isotope compositions for all river and seawater samples measured here, with frequency for each individual dataset (rivers, seawater) normalised to the total number of measurements.

**Figure 2:** Nickel isotope data for rivers plotted against reciprocal concentration. Error bars are for long-term reproducibility of standards analysed using the double spike method. The horizontal black line and grey band give the average and 1SD of Ni isotope compositions of samples of continental silicate rocks (Cameron et al., 2009).

**Figure 3:** Nickel isotopic and concentration data for the Iceland Basin, North Atlantic. Uncertainties on isotopic data correspond to the long-term reproducibility of standards using the double spike procedure.

**Figure 4:** Nickel isotopic and concentration data for the North Pacific. Filled squares are for the depth profile at 47°N, 129°W. Open squares are for 1000m samples at 50-52°N, 133-145°W. Uncertainties on isotopic data correspond to the long-term reproducibility of standards using the double spike procedure.

**Figure 5:** Nickel isotopic and concentration data for the Atlantic Sector of the Southern Ocean. Filled squares are for the depth profile at Station PS71-104 in the Polar Front Zone (~48°S). Open squares are for surface samples further south, at 52-60°S.

**Figure 6:** Nickel concentration data (filled squares) for all North Pacific data presented here, for the Iceland Basin depth profile and for the Southern Ocean (partial) depth profile, compared with data from the literature (open diamonds). Literature data for the North Pacific are for the three depth
profiles in Bruland (1980). For the Iceland Basin data are shown for two stations close to that presented here (Yeats and Campbell 1983; Danielsson et al., 1985). For the Southern Ocean Polar Front Zone, the literature data plotted are a composite of 6 stations in Löscher (1999).

**Figure 7:** Nickel concentration data versus phosphate where available (Southern Ocean phosphate data from Abouchami et al., 2011, 2013, Iceland Basin data from E. Achterberg, pers. comm., and NE Pacific 1999-2001 data from M. Lohan, pers. comm.). Symbols as in Figure 3, except that literature data (open diamonds) are split into Atlantic (green) and Pacific (black). The line shown is fitted to all the data presented here. Data from the greatest depths in the North Pacific (Bruland, 1980) is well-known to deviate from a linear relationship due to the fact that phosphate usually presents a maximum at 1000-1500m whereas Ni continues increasing below this depth, reaching a maximum, if present, much deeper in the water column. Virtually all the data in this paper are from above 1500m.

**Figure 8:** Nickel isotope data for rivers versus Cu isotope data where available (Vance et al., 2008). Symbols as in Figure 1. For all samples except two, the Cu and Ni isotopic analyses were done on samples from the same bottles. The two exceptions are the Nile samples, where Cu and Ni analyses for the main Nile (dry and wet season) come from different samples collected at nearby localities. The grey box gives the range (average ± 1SD) of Cu and Ni isotope compositions of samples of continental silicate rocks (Cameron et al., 2009; Cu data compiled in Little et al., 2013). With the exception of the Brahmaputra sample, which has an anomalously light Ni isotope composition given its δ65Cu, the $R^2$ for the data is 0.75.

**Figure 9:** Nickel isotope data for seawater versus phosphate and silica concentrations. See caption to Figure 7 for the sources of the major nutrient data.
Table 1: Nickel concentration and isotope data for rivers.

<table>
<thead>
<tr>
<th>River</th>
<th>Tributary or Location</th>
<th>Sample ID</th>
<th>[Ni]</th>
<th>δ(^{60})Ni</th>
<th>2σ (^{1})</th>
<th>River Averages</th>
<th>[Ni]</th>
<th>δ(^{60})Ni</th>
<th>Discharge (^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amazon</td>
<td>Negro at Manaus</td>
<td>Negro 2</td>
<td>2.2</td>
<td>0.31</td>
<td>0.07</td>
<td></td>
<td>2.5</td>
<td>0.36</td>
<td>946</td>
</tr>
<tr>
<td>Amazon</td>
<td>Negro at Manaus</td>
<td>Negro 3</td>
<td>2.7</td>
<td>0.41</td>
<td>0.06</td>
<td></td>
<td>9.5</td>
<td>0.88</td>
<td>3248</td>
</tr>
<tr>
<td>Amazon</td>
<td>Solimoes at Manaus</td>
<td>Sol 1</td>
<td>9.4</td>
<td>0.88</td>
<td>0.05</td>
<td></td>
<td>9.5</td>
<td>0.88</td>
<td>3248</td>
</tr>
<tr>
<td>Amazon</td>
<td>Solimoes at Manaus</td>
<td>Sol 2</td>
<td>9.5</td>
<td>0.88</td>
<td>0.07</td>
<td></td>
<td>9.5</td>
<td>0.88</td>
<td>3248</td>
</tr>
<tr>
<td>Tocantins</td>
<td>Belem</td>
<td>TOC1</td>
<td>4.5</td>
<td>0.88</td>
<td>0.09</td>
<td></td>
<td>4.5</td>
<td>0.88</td>
<td>372</td>
</tr>
<tr>
<td>Chang Jiang</td>
<td>Upstream Wuhan</td>
<td>CJ-1</td>
<td>6.3</td>
<td>1.34</td>
<td>0.05</td>
<td></td>
<td>6.6</td>
<td>1.27</td>
<td>928</td>
</tr>
<tr>
<td>Chang Jiang</td>
<td>Upstream Wuhan</td>
<td>CJ-2</td>
<td>7.7</td>
<td>1.19</td>
<td>0.04</td>
<td></td>
<td>7.7</td>
<td>1.19</td>
<td>928</td>
</tr>
<tr>
<td>Chang Jiang</td>
<td>Wuhan</td>
<td>CJ-5</td>
<td>6.0</td>
<td>1.27</td>
<td>0.04</td>
<td></td>
<td>6.6</td>
<td>1.27</td>
<td>928</td>
</tr>
<tr>
<td>Main Nile</td>
<td>El Gaili, Sudan (wet)</td>
<td>Sample 5</td>
<td>13.6</td>
<td>0.84</td>
<td>0.02</td>
<td></td>
<td>13.7</td>
<td>0.91</td>
<td>83</td>
</tr>
<tr>
<td>Main Nile</td>
<td>Sayala, Sudan (dry)</td>
<td>ATB01/5</td>
<td>13.9</td>
<td>0.99</td>
<td>0.05</td>
<td></td>
<td>13.9</td>
<td>0.99</td>
<td>83</td>
</tr>
<tr>
<td>Missouri</td>
<td>Columbia</td>
<td>Mizz1</td>
<td>35.0</td>
<td>0.68</td>
<td>0.03</td>
<td></td>
<td>35.0</td>
<td>0.68</td>
<td>580</td>
</tr>
<tr>
<td>Brahmaputra</td>
<td>Tezpur, Assam</td>
<td>Brahm</td>
<td>5.1</td>
<td>0.29</td>
<td>0.07</td>
<td></td>
<td>5.1</td>
<td>0.29</td>
<td>1003</td>
</tr>
<tr>
<td>Ottawa</td>
<td>Chenaux</td>
<td>Aylmer</td>
<td>12.3</td>
<td>0.82</td>
<td>0.07</td>
<td></td>
<td>12.3</td>
<td>0.82</td>
<td>337</td>
</tr>
<tr>
<td>Kalix</td>
<td>Angesa</td>
<td>Kx2</td>
<td>4.1</td>
<td>0.73</td>
<td>0.07</td>
<td></td>
<td>5.1</td>
<td>0.90</td>
<td>9</td>
</tr>
<tr>
<td>Kalix</td>
<td></td>
<td>Kx4</td>
<td>5.6</td>
<td>1.00</td>
<td>0.08</td>
<td></td>
<td>5.6</td>
<td>0.97</td>
<td>9</td>
</tr>
<tr>
<td>Kalix</td>
<td></td>
<td>Kx5</td>
<td>5.6</td>
<td>0.97</td>
<td>0.07</td>
<td></td>
<td>5.1</td>
<td>0.90</td>
<td>9</td>
</tr>
</tbody>
</table>

\(^{1}\) Measured internal 2 sigma – see Methods for reproducibility.
\(^{2}\) Discharges as in Gaillardet et al. (1999), Pontér et al. (1990), Meade et al. (1991) and Filizola et al. (2009). Note that discharge given for Missouri is for the entire Mississippi system, that for the Brahmaputra is for the entire Ganges-Brahmaputra system and that for the Ottawa is for the entire St. Lawrence system.
Table 2: Nickel concentration and isotope data for seawater samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth (m)</th>
<th>[Ni] (nmol/kg)</th>
<th>δ⁶⁰Ni (%)</th>
<th>2σ¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTD T027 - 13</td>
<td>61° 15.19'N</td>
<td>20°45.82'W</td>
<td>20</td>
<td>3.13</td>
<td>1.52</td>
<td>0.05</td>
</tr>
<tr>
<td>CTD T027 - 10</td>
<td>61° 15.19'N</td>
<td>20°45.82'W</td>
<td>50</td>
<td>3.54</td>
<td>1.53</td>
<td>0.05</td>
</tr>
<tr>
<td>CTD T027 - 7</td>
<td>61° 15.19'N</td>
<td>20°45.82'W</td>
<td>150</td>
<td>3.64</td>
<td>1.52</td>
<td>0.04</td>
</tr>
<tr>
<td>CTD T027 - 5</td>
<td>61° 15.19'N</td>
<td>20°45.82'W</td>
<td>500</td>
<td>3.61</td>
<td>1.53</td>
<td>0.03</td>
</tr>
<tr>
<td>CTD T027 - 4</td>
<td>61° 15.19'N</td>
<td>20°45.82'W</td>
<td>830</td>
<td>4.12</td>
<td>1.34</td>
<td>0.06</td>
</tr>
<tr>
<td>CTD T027 - 3</td>
<td>61° 15.19'N</td>
<td>20°45.82'W</td>
<td>1300</td>
<td>4.07</td>
<td>1.41</td>
<td>0.06</td>
</tr>
<tr>
<td>CTD T027 - 24</td>
<td>61° 15.19'N</td>
<td>20°45.82'W</td>
<td>2210</td>
<td>4.06</td>
<td>1.48</td>
<td>0.04</td>
</tr>
<tr>
<td><strong>US Geotraces cruise IC1, R/V Knorr, Tropical North Atlantic (June 2008)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GPrl 20</td>
<td>31°40'N</td>
<td>64°10'W</td>
<td>1000</td>
<td>4.91</td>
<td>1.37</td>
<td>0.04</td>
</tr>
<tr>
<td><strong>Geotraces-IPY cruise ANT XXIV/3, Polarstern, Atlantic Sector, Southern Ocean (Feb-Apr 2008)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS71-109</td>
<td>51.67°S</td>
<td>0.00</td>
<td>2-5</td>
<td>6.51</td>
<td>1.43</td>
<td>0.05</td>
</tr>
<tr>
<td>PS71-111</td>
<td>52.17°S</td>
<td>0.54°W</td>
<td>2-5</td>
<td>6.35</td>
<td>1.45</td>
<td>0.07</td>
</tr>
<tr>
<td>PS71-126</td>
<td>57.21°S</td>
<td>0.00</td>
<td>2-5</td>
<td>6.36</td>
<td>1.47</td>
<td>0.04</td>
</tr>
<tr>
<td>PS71-136</td>
<td>60.24°S</td>
<td>0.00</td>
<td>2-5</td>
<td>6.27</td>
<td>1.44</td>
<td>0.05</td>
</tr>
<tr>
<td>PS71-104-2-24</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>15</td>
<td>5.77</td>
<td>1.45</td>
<td>0.05</td>
</tr>
<tr>
<td>PS71-104-2-22</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>50</td>
<td>5.87</td>
<td>1.58</td>
<td>0.05</td>
</tr>
<tr>
<td>PS71-104-2-22; repeat</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>50</td>
<td>5.71</td>
<td>1.54</td>
<td>0.04</td>
</tr>
<tr>
<td>PS71-104-2-20</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>101</td>
<td>5.56</td>
<td>1.51</td>
<td>0.06</td>
</tr>
<tr>
<td>PS71-104-2-18</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>202</td>
<td>5.67</td>
<td>1.47</td>
<td>0.05</td>
</tr>
<tr>
<td>PS71-104-2-16</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>301</td>
<td>6.13</td>
<td>1.47</td>
<td>0.05</td>
</tr>
<tr>
<td>PS71-S104-2-14</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>399</td>
<td>6.24</td>
<td>1.46</td>
<td>0.06</td>
</tr>
<tr>
<td>PS71-104-2-11</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>998</td>
<td>7.02</td>
<td>1.40</td>
<td>0.03</td>
</tr>
<tr>
<td>PS71-S104-2-9</td>
<td>47°39.36'S</td>
<td>4°15.7'E</td>
<td>1500</td>
<td>6.81</td>
<td>1.42</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>EAGER Cruise AT15-47, R/V Atlantis, Juan de Fuca Ridge, NE Pacific Ocean (June 2009)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E22</td>
<td>47°56.00'N</td>
<td>129°04.30'W</td>
<td>100</td>
<td>5.54</td>
<td>1.32</td>
<td>0.05</td>
</tr>
<tr>
<td>E20</td>
<td>47°56.00'N</td>
<td>129°04.30'W</td>
<td>300</td>
<td>6.63</td>
<td>1.42</td>
<td>0.03</td>
</tr>
<tr>
<td>E18</td>
<td>47°56.00'N</td>
<td>129°04.30'W</td>
<td>800</td>
<td>8.87</td>
<td>1.36</td>
<td>0.02</td>
</tr>
<tr>
<td>E16</td>
<td>47°56.00'N</td>
<td>129°04.30'W</td>
<td>1300</td>
<td>9.86</td>
<td>1.41</td>
<td>0.03</td>
</tr>
<tr>
<td>E14</td>
<td>47°56.00'N</td>
<td>129°04.30'W</td>
<td>1800</td>
<td>11.2</td>
<td>1.21</td>
<td>0.02</td>
</tr>
<tr>
<td>E12</td>
<td>47°56.00'N</td>
<td>129°04.30'W</td>
<td>2300</td>
<td>10.6</td>
<td>1.43</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>NE Pacific (1999-2001)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26P1000</td>
<td>50°N</td>
<td>145°W</td>
<td>1000</td>
<td>9.48</td>
<td>1.45</td>
<td>0.04</td>
</tr>
<tr>
<td>C1000 - (Haida Eddy centre)</td>
<td>51.15°N</td>
<td>133.60°W</td>
<td>1000</td>
<td>9.47</td>
<td>1.42</td>
<td>0.03</td>
</tr>
<tr>
<td>E1000 - (Haida Eddy edge)</td>
<td>51.35°N</td>
<td>133.50°W</td>
<td>1000</td>
<td>9.36</td>
<td>1.47</td>
<td>0.03</td>
</tr>
</tbody>
</table>

¹ Measured internal 2 sigma – see Methods for reproducibility.
Cameron and Vance - Figure 2

The graph shows the isotopic composition of nickel (δ⁶⁰Ni) plotted against the inverse of nickel concentration ([Ni] nmol kg⁻¹). Different water sources are indicated by distinct symbols and colors:

- Orange circles: Amazon System
- Green triangles: Brahmaputra
- Green triangles with fill: Chang Jiang
- Blue diamonds: Ottawa (St. Lawrence)
- Orange squares: Missouri
- Black squares: Main Nile (Dry Season)
- Orange shaded square: Main Nile (Wet Season)
- Red diamonds: Kalix (Sweden)

A horizontal band labeled "Lithogenic Ni" is also included.
Cameron and Vance - Figure 3

Iceland Basin, North Atlantic

δ⁶⁸Ni (‰) vs Depth (m) and [Ni] nmol kg⁻¹ vs Depth (m)
Cameron and Vance - Figure 4

North Pacific

δ⁶⁰Ni (%) vs. Depth (m)

[Ni] nmol kg⁻¹ vs. Depth (m)
Cameron and Vance - Figure 5

Southern Ocean, Atlantic Sector

δ⁶⁶Ni (%) vs. [Ni] nmol kg⁻¹

Depth (m)
Cameron and Vance - Figure 7

\[
\text{Ni (nmol kg}^{-1}) = 2.22\text{PO}_4\text{ (µM)} + 2.18
\]

\[R^2 = 0.93\]
Cameron and Vance - Figure 8