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Heavy nickel isotope compositions in rivers and the oceans

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27 **ABSTRACT**

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

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

44 In stark contrast to the rivers, the dataset for seawater is very homogeneous, with 2SD of the entire
45 dataset being only twice the analytical reproducibility. The second main feature is that seawater is
46 distinctly heavier in Ni isotopes than rivers. The average $\delta^{60}\text{Ni}$ is $1.44 \pm 0.15\text{‰}$ (2SD), and only 2 of
47 the 29 seawater analyses have a Ni isotopic composition that is lighter than the heaviest river. The
48 lack of an isotopic shift associated with the drawdown of nickel concentrations in the surface ocean
49 suggests that the cycling of nickel between the surface and deep ocean is not associated with a
50 pronounced isotopic fractionation. The isotopic data also present a mass balance problem. The main

51 output of nickel from the oceans (sorption to Fe-Mn oxides) appears to be similar in isotopic
52 composition to the dissolved phase, yet the riverine input is lighter than the dissolved pool. This
53 observation either requires other inputs that are isotopically heavy, or an output that is isotopically
54 light. Further large inputs, over and above the dissolved riverine source, appear to be required by
55 what we know of the elemental budget, but the isotopic mass balance suggests that such an input
56 needs to be isotopically much heavier than both the riverine dissolved load and the lithogenic
57 isotopic composition of nickel.

58

59 1. INTRODUCTION

60 Nickel (Ni), like other transition metals, is a biologically-active element (Frausto da Silva and
61 Williams, 2001; Ragsdale, 2009). It has long been known (Sclater et al., 1976; Bruland, 1980) that
62 dissolved Ni concentrations in the modern ocean show a “nutrient-like” distribution with depth.
63 Thus Ni concentrations show depletions in the photic zone that are suggestive of biological uptake.
64 In addition, concentration increases with depth follow the regeneration of major nutrients like
65 phosphate and silica, and the slopes of Ni-phosphate and Ni-silica correlations for dissolved
66 concentrations are similar to those for the Ni-Si-PO₄ inventories of oceanic phytoplankton (e.g. Lai
67 et al., 2008; Twining et al., 2012). Nickel may have had a more fundamental role in the
68 biogeochemistry of the early Earth (e.g. Williams and Frausto da Silva, 2003; Domagal-Goldman et
69 al., 2008). Methanogens have an absolute requirement for Ni, through the Ni cofactor in methyl-
70 coenzyme reductase (MCR), which catalyses the terminal step in methanogenesis and may also be
71 involved in methane oxidation (e.g. Thauer, 1998; Kruger et al., 2003; Shima et al., 2012). Methane
72 is a favoured candidate for the dominant greenhouse gas in the anoxic Archean atmosphere (e.g.
73 Kasting, 2005), and it has recently been suggested (Konhauser et al., 2009) that a nickel famine in
74 the late Archean ocean might have precipitated the dramatic rise in atmospheric oxygen that has
75 become known as the Great Oxidation Event (GOE).

76 The isotope systems of the transition metals are increasingly being developed to investigate both the
77 modern oceanic cycling of the transition metals (e.g. Bermin et al., 2006; John et al., 2010;
78 Abouchami et al., 2011; Little et al., 2013; Zhao et al., 2013) and to understand the biogeochemistry
79 of the past Earth (e.g. review by Anbar and Rouxel, 2007). Nickel stable isotopes have been slower
80 to develop than some others. Cameron et al. (2009) presented the first data for terrestrial materials,
81 specifically loess, river sediments and basalts, which had an average $\delta^{60}\text{Ni}$ (= $[(^{60}\text{Ni}/^{58}\text{Ni})_{\text{sample}}/(^{60}\text{Ni}/^{58}\text{Ni})_{\text{NISTSRM986}} - 1] \times 1000$) = 0.15 ± 0.12 (1SD, n = 16). These authors also

83 showed that, in contrast to this homogeneity, methanogens grown in culture take up Ni that is about
84 1‰ lighter than the culture medium. More recently, Gall et al. (2013) have presented data for
85 hydrogenous Fe-Mn crusts which have $\delta^{60}\text{Ni} = 0.9\text{--}2.5\text{‰}$. Gueguen et al. (2013) reported data for
86 basalts, Mn nodules and organic-rich rocks and suggested a value for the bulk silicate Earth of
87 $+0.05\text{‰}$ while Hofmann et al. (2013) showed enrichment of light Ni isotopes in magmatic
88 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
89 theoretical and experimental approach to suggest that the Ni isotope compositions of different
90 aqueous species of Ni could be as great as 2.5‰ .

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

100

101 **2. BACKGROUND: OCEANIC BIOGEOCHEMISTRY OF NICKEL**

102 In the oceanic realm nickel exhibits many biogeochemical features that, qualitatively at least, are
103 common to other transition metals (see review in Bruland and Lohan, 2003). Beginning with the
104 pioneering studies of Sclater et al. (1976) and Bruland (1980), measurements of dissolved nickel
105 distributions have revealed “nutrient-like” profiles. Surveys of the dissolved concentrations of
106 bioactive metals in the oceans have typically found close associations between the depth

107 distributions of these metals and individual major nutrients, such as that of Zn with silicate (e.g.
108 Bruland, 1980; Lohan et al., 2002) and Cd with phosphate (e.g. Boyle et al., 1976; Bruland, 1980;
109 Norisuye et al., 2007). Ni appears to be re-mineralised in close stoichiometry with phosphate in the
110 upper water column, but with silicate (Si) in the deep ocean (Sclater et al. 1976; Bruland 1980). The
111 association with phosphate in the upper ocean implies a sizeable inventory associated with more
112 labile organic matter in phytoplankton. The association with Si in the deep ocean is common to Zn,
113 and is expressed in the longer lengthscale of remineralisation of Si, Ni and Zn relative to the labile
114 nutrients and Cd. Though this finding also suggests an association with diatom opal, the very low
115 Zn content of diatom opal itself (e.g. Ellwood and Hunter, 2000; Andersen et al., 2011) means that
116 it cannot be the dominant regenerative source of Zn. Such considerations may also be relevant to
117 Ni. Twining et al. (2012) have shown that cellular Ni in diatoms collected in the field and grown in
118 culture is split approximately equally between frustule and organic material, and that cellular Ni/Si
119 ratios are comparable to the slopes of dissolved Ni-Si relationships in the oceans. In the upper water
120 column of the Southern Ocean, Lai et al. (2008) find slopes for dissolved Ni-PO₄ and Ni-Si
121 correlations that are both close to stoichiometric ratios for individual plankton cells observed during
122 Southern Ocean fertilization experiments (Twining et al., 2004).

123 There are also some key differences between the oceanic biogeochemistry of Ni and that of other
124 bioactive trace metals. Thus, unlike Cd and Zn, concentrations of Ni are never reduced to near zero
125 in the euphotic zone, and in fact never descend beneath about 1.5-2 nM (e.g. Bruland, 1980; Boyle
126 et al., 1981; Bruland and Franks, 1983; Yeats and Campbell, 1983; Morley et al., 1993; Yeats et al.,
127 1995; Saager et al., 1997; Mackey et al., 2002; Bowie et al., 2002; Norisuye et al., 2007; Ellwood,
128 2008). Moreover, the increase in concentrations as deep water ages between the Atlantic and
129 Pacific, at factor 1.8, is smaller than for Zn and Cd, at factor 4-5 (Sclater et al., 1976; Bruland,
130 1980; Bruland and Franks, 1983). Finally, Ellwood (2008) finds little seasonal variation in surface

131 Ni concentrations in the Subantarctic Zone of the Pacific, despite large changes in Cd and Zn
132 correlated with the summer algal bloom and with phosphate depletion.

133 In terms of specific biochemical functions, the identification of nickel-containing metalloenzymes
134 has developed more slowly than for some other metals (see review by Ragsdale, 2009). There have
135 been three biochemical roles identified for Ni that are important in the marine microbial realm, and
136 to its biogeochemical cycling. The importance of Ni in enzymes involved in methane cycling, such
137 as MCR, is well established (e.g. Thauer, 1998; Kruger et al., 2003). Though likely much more
138 widespread on the early Earth (e.g. Kasting, 2005), this metabolism is only relevant to restricted
139 anoxic basins or sediments of the modern ocean, and to life associated with hydrothermal systems
140 (e.g. Kelley et al., 2002). In the modern oxic oceans the most commonly cited role of Ni is in
141 urease, by which phytoplankton hydrolyse urea to yield ammonia (Frausto da Silva and Williams,
142 2001). Thus cultures of diatoms (Price and Morel, 1991) and cyanobacteria (Dupont et al., 2008a)
143 grown on urea as the sole source of nitrogen are limited by Ni, and Ni-N co-limitation of
144 phytoplankton is deemed likely in some oceanographic regimes (Price and Morel, 1991). Culturing
145 studies have also found that cyanobacteria are limited by Ni even when grown on nitrate (Dupont et
146 al., 2008a), consistent with the suggestion that these organisms contain a Ni superoxide dismutase,
147 Ni-SOD, an enzyme which catalyses the breakdown of toxic superoxide (Dupont et al., 2008a,b).

148 Concentrations of total dissolved Ni that are never beneath about 1.5-2 nM in the euphotic zone are
149 not consistent with the suggestion, for example, that Ni-N co-limitation may occur in some
150 oceanographic regimes, unless only a small fraction of the dissolved pool is bioavailable (c.f.
151 Mackey et al., 2002). This brings up another feature of Ni's oceanic biogeochemistry that is
152 common to other transition metals. It is commonly assumed that only free metal ions are available
153 for uptake into phytoplankton cells. But for many metals a large proportion of the dissolved pool
154 (operationally-defined as the material passing through a 0.45 μm filter) is bound in complexes with
155 organic ligands. It appears that this may be the case for Ni too (van den Berg and Nimmo, 1987;

156 Donat et al., 1994; Xue et al., 2001; Turner and Martino, 2006), though estimates of the portion of
157 dissolved Ni that is organically-bound (in complexes with conditional stability constants between
158 10^{12} and 10^{17}) varies from 25 to 99.9%. There is also some debate over the extent to which these
159 results reflect the slow kinetics of exchange of these Ni-organic complexes (Xue et al., 2001), as
160 opposed to their thermodynamic stability (Gerringa, 1991; Mackey et al., 2002).

161 In terms of whole ocean mass balance, Sclater et al. (1976) suggested a residence time of Ni on the
162 order of 10 kyr, with the dissolved load of rivers as the major input. More recently, Gall et al.
163 (2013), on the basis of revised values for the output to pelagic sediments, have calculated a shorter
164 residence time of 4 kyr. It appears that dust and hydrothermal fluids are minor inputs in comparison
165 with some other metals (Sclater et al., 1976; Bruland, 1980; Bowie et al., 2002), while Danielsson
166 et al. (1985) and Bowie et al. (2002) document evidence for a source of Cu and Fe, but minimal Ni,
167 from sediment. Sclater et al. (1976) also suggested that scavenging by Fe-Mn oxides is the major
168 output. There is no impact on Ni concentrations of the intense oxygen minimum zone of the NW
169 Indian Ocean (e.g. Saager et al., 1992), and Ni concentrations in the deep sulphidic Black Sea are
170 not drawn down by reaction with H_2S , as they are for many other metals (e.g. Haraldsson and
171 Westerlund, 1988), suggesting that suboxic-anoxic or euxinic sediments may not be as important a
172 sink for Ni as they are for many other metals (e.g. Tribovillard et al., 2006). Ni is actually mildly
173 enriched in euxinic Black Sea sediments relative to upper continental crust, but is much more
174 strongly enriched in non-sulphidic open ocean settings that are characterised by intense upwelling
175 such as the Peru Margin (Boning et al., 2004). This, along with the ubiquity of lowered dissolved Ni
176 concentrations in the photic zone, might suggest that transfer in organic matter is a significant
177 sedimentary sink for Ni (c.f. Tribovillard et al., 2006).

178 The above relatively simple picture may, however, be complicated by a major apparent imbalance
179 in the oceanic Ni budget. Krishnaswami (1976) used measurements of the authigenic output of Ni
180 to pelagic Pacific sediment, as well as the little that was known about the dissolved riverine input at

181 that time, to suggest that the total output of Ni is up to six times greater than the dissolved riverine
182 input. We return to this issue in the Discussion section with the additional constraints that derive
183 from the data presented here.

184

185 **3. SAMPLES AND METHODS**

186 **3.1 River samples**

187 Details of the river samples and their collection can be found in Vance et al. (2008) and Archer and
188 Vance (2008), where data are reported for Cu and Mo isotopes, respectively, on these samples. In
189 addition, Zn isotopic data for many of them can be found in Little et al. (2013). All river samples
190 were collected from close to the bank into pre-cleaned, low density polyethylene bottles after pre-
191 rinsing with the sample 2-3 times. The Amazon, Brahmaputra, Nile and Chang Jiang samples were
192 immediately passed through a pre-cleaned cellulose nitrate 0.2 μm filter using a pre-cleaned plastic
193 filter holder and reservoirs, pre-rinsed with filtered sample before final filtrate collection, then
194 decanted into a new pre-cleaned low density polyethylene bottle. The Kalix, Missouri and
195 Tocantins samples were filtered in the same manner up to 2 weeks after collection, on return to the
196 laboratory. All samples were acidified to pH 2 after filtration with concentrated twice-distilled HCl.
197 Samples were pre-concentrated prior to column chromatography and mass spectrometry (see
198 section 3.3) by drying down, treatment with concentrated nitric acid (containing a small amount of
199 H_2O_2) to oxidise organics, and re-dissolution in a few ml HCl before chromatographic separation of
200 Ni (see section 3.3). Following Cameron et al. (2009) mass bias correction for Ni was achieved
201 using a mixed ^{61}Ni - ^{62}Ni double spike (details in section 3.3) and samples were spiked before being
202 dried. Ni concentrations of river samples were first measured by ICPMS to allow accurate spiking
203 (though all concentrations reported here are from the isotope dilution analysis via the double-spike
204 analysis).

205 3.2 Seawater samples

206 Samples from the Iceland Basin were collected in August 2010 by E.Achterberg (NOCS, UK) on
207 cruise 354 of the *RRS Discovery*. The cruise was primarily aimed at investigating high-latitude Fe
208 limitation. The single depth profile measured here for Ni and its isotopes is from Station 28.
209 Samples were collected using a trace metal clean titanium CTD frame fitted with 10 L trace metal
210 clean Teflon coated OTE (Ocean Technology Equipment) bottles, and were filtered under pressure
211 using 0.2 µm pore size cartridge filters (Sartobran P- 300, Sartorius). Samples were acidified to pH
212 1.9 upon return to the Bristol laboratory, and equilibrated with the added acid for weeks before
213 analysis for Ni isotopes. Water depth at this site was 2229m, so that the profile presented here
214 covers the entire water column.

215 The single 1000m sample from the sub-tropical North Atlantic site was collected during the June
216 2008 US-Geotraces Intercalibration cruise (IC1) aboard *R/V Knorr* to the Bermuda Atlantic Time
217 Series (BATS) site. The sample was collected with the US GEOTRACES 24-sample 12-L trace
218 element General Oceanics GO-Flo Rosette system deployed on a Kevlar cable. The sample was
219 filtered through 0.2 µm Pall Acropak capsule filters in the GEOTRACES clean van, and acidified
220 with 2 mL distilled 6N HCl per liter of sample. Further details of sampling, as well as data for other
221 trace metal systems, can be found in Boyle et al. (2012). The water depth at this site is
222 approximately 4680m so the sample reported here is from well above the bottom.

223 Samples from the Southern Ocean, including 4 surface transect samples and one depth profile
224 through the upper 1500m of the water column, were collected during *Polarstern* cruise ANT-
225 XXIV/3 (Feb-April 2008) in the Atlantic sector of the Southern Ocean as part of the International
226 GEOTRACES program and a contribution to the International Polar Year (IPY). Surface samples
227 were collected at 2-5m using an IFISH torpedo sampler with an all-Teflon pump. The depth profile
228 was sampled using the TITAN frame (de Baar et al., 2008). Samples were filtered on board in a
229 class 100 clean room environment through 0.2 µm filter capsules (Sartobran-300, Sartorius) under

230 slight nitrogen pressure and collected into acid-cleaned Nalgene high density polyethylene (HDPE)
231 bottles and canisters. Acidification was done onboard to pH=2 with 12 N HCl (Baseline, Seastar).
232 The water depth at the depth profile station PS71-104 was 4202m – thus well below the deepest
233 sample reported here for Ni isotopes. These samples have been the subject of studies for both Cd
234 (Abouchami et al., 2011) and Zn isotopes (Zhao et al., 2013).

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

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

255 samples analysed here were collected.

256 All seawater samples were pre-concentrated by co-precipitation with $\text{Al}(\text{OH})_3$, using an approach
257 identical to that used previously for zinc and described in detail in Zhao et al. (2013). Briefly, the
258 acidified sample was spiked (see section 3.3) and doped with an aluminium solution pre-cleaned of
259 nickel. Seawater concentrations were known well enough from previous work to allow appropriate
260 spiking. Following at least 24 hours equilibration, the pH was raised to 8.5-8.8 to produce an
261 $\text{Al}(\text{OH})_3$ precipitate. This precipitate was centrifuged, the supernatant poured off and a volume of
262 MQ adjusted to a similar pH, was added. The mixture was again centrifuged and the supernatant
263 removed; this washing process was repeated once more. The precipitate was finally dissolved in 7M
264 HCl and purified for Ni isotopic analysis as described in section 3.3. The nickel yield from this
265 procedure was 40-90%, as obtained by comparison of the signal size for a spike-free isotope with
266 that of a standard, versus the result for Ni abundance from isotope dilution. Because the double
267 spike is added before pre-concentration, 100% yields are not necessary for the accuracy of either Ni
268 concentrations (by isotope dilution) or isotopic composition (from the double spike reduction).
269 Total analysed amounts of Ni were 110-680 ng, while total procedural blank for the Ni procedure
270 was 11 ng, half of which comes from the aluminium solution. Thus, blank corrections to these
271 samples would be 0.02-0.16‰, given a likely $\delta^{60}\text{Ni}$ of around 0‰. As will be seen later, the dataset
272 presented here is very homogeneous in Ni isotopes, and there is no correlation at all between Ni
273 isotopic composition and the amount of Ni analysed so that these small blank corrections were not
274 applied.

275 **3.3 Chemical purification and mass spectrometric analysis of nickel**

276 Separation and purification of nickel was carried out as described in detail in Cameron et al. (2009)
277 with the exception of one additional column step. Briefly, spiked co-precipitated seawater and river
278 samples (see section 3.1) in 7M HCl+H₂O₂ were loaded onto a first ion-exchange column in which
279 the anion resin AG MP-1M (Bio-Rad) is used to remove Fe and Zn. The dried samples are then

280 taken up in 1M HCl/1M ammonium citrate, and the pH adjusted to 8-9 before loading onto columns
281 filled with Ni resin (Eichrom Technologies). This is a reversal of the column procedure outlined in
282 Cameron et al., (2009) as we discovered that the seawater samples would precipitate (most likely
283 due to the heavy solute load) when adjusted to the high pH values required for the Ni column. After
284 oxidation to remove Ni-bound DMG, the samples are finally put through a third column, which is a
285 repeat of the first anion column, to clean up any residual Fe and Zn. This last column was deemed
286 necessary as ^{56}Fe after the Ni-resin column was significant. Given the initial anion column, and
287 given the low Fe concentrations in seawater, this post-Ni-column Fe is presumably blank addition.
288 In any case, it was monitored in all samples measured for Ni isotopes, as detailed below.

289 All isotope analyses were performed at low mass resolution on a ThermoFinnigan Neptune
290 multicollector ICPMS, with samples introduced in 2% nitric acid via a CPI PFA nebuliser (50
291 $\mu\text{l}/\text{minute}$) attached to an Aridus desolvating nebuliser system (Cetac, Omaha, NE, USA). Signals
292 were monitored at masses 58, 60, 61, 62 and 64. The latter has a potential ^{64}Zn interference but is
293 not used here. For some types of samples an isobaric interference from residual sample ^{58}Fe is a
294 potential problem at mass 58. This was dealt with by manual checking of the $^{56}\text{Fe}/^{58}\text{Ni}$ ratio in high
295 resolution prior to the Ni isotopic analysis and applying a correction to the 58 signal. However, this
296 correction was insignificant, e.g. relative to the propagated internal uncertainty on $\delta^{60}\text{Ni}$, except for
297 two samples. In the case of sample Kx4 it resulted in an upward correction of 0.38‰, and the
298 corrected value is identical to that obtained for sample Kx5. In the case of sample Negro3 it resulted
299 in an upward correction of 0.17‰, and the corrected result is identical to sample Negro2. The other
300 potentially problematic interference is the $^{40}\text{Ar}^{18}\text{O}$ molecular at mass 58, given that these samples
301 were measured in low resolution. This was reduced to levels of $1\text{--}2 \times 10^{-14}\text{A}$ compared with ^{58}Ni
302 signals in the 10^{-10}A range for all samples, by the addition of a small amount of N_2 to the Aridus
303 sweep gas. The size of the ^{58}Ni molecular, and those of the background signals on all measured Ni
304 masses, was monitored by the measurement of on-peak zeros (aspirating 2% nitric) prior to each

305 sample or standard. The “blank” values obtained were subtracted from sample signals before
306 double-spike reduction.

307 A potential issue with double spike analysis was raised by Bermin et al. (2006) for Zn. The isotopic
308 composition of the double-spike used here is referenced to the following isotope ratios for
309 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
310 ratios is assumed. The other two are obtained by mass-bias correction of measured ratios for pure
311 SRM986 obtained during the session in which the spike was calibrated, using an exponential law.
312 Small deviations in the behaviour of the instrument after this session, on any subsequent day when
313 spiked samples and standards are analysed, can arise through, e.g. deviations from the exponential
314 mass bias law used in data reduction or changes in cup efficiencies. These can propagate through to
315 inaccuracies in the $\delta^{60}\text{Ni}$ of the sample. Following Bermin et al. (2006) this is dealt with here using
316 multiple measurements of pure NIST SRM986 during each analytical session to monitor variations
317 in instrument behaviour. The normalised $^{60}\text{Ni}/^{58}\text{Ni}$ and $^{62}\text{Ni}/^{58}\text{Ni}$ ratios obtained are compared to
318 those listed above, and adjustment made to raw isotope ratios of the spike-sample and spike-
319 standard mixtures to take them into account, before any double-spike reduction is done. The success
320 of this approach is demonstrated by the accuracy and reproducibility of spike-standard mixtures.
321 For the period Aug 2007 until July 2012, mixtures of NIST SRM986 (treated in this case as an
322 unknown) and double-spike with std-spike ratios of 0.1-4 and run during each analytical session
323 gave $\delta^{60}\text{Ni} = 0.06 \pm 0.08$ (n = 184). All sample/spike ratios for samples analysed here were between
324 0.5 and 2.5.

325 A further test of accuracy can be obtained by comparison of our nickel isotope data with those
326 obtained independently in other laboratories. There are very few published studies of nickel
327 isotopes, but Gall et al. (2012) recently reproduced two USGS basalt standards for which data were
328 published in Cameron et al. (2009) to ≤ 0.05 ‰. Gall et al. (2013) and Gueguen et al. (2013) also
329 report $\delta^{60}\text{Ni}$ for two Fe-Mn nodule reference materials. They obtain $+1.08 \pm 0.07$ and $+1.03 \pm 0.06$

330 respectively, for Nod A-1 versus values of +1.13 and +1.06 obtained in this laboratory. They also
331 obtain $\delta^{60}\text{Ni} = +0.40 \pm 0.10$ and $+0.36 \pm 0.07$ respectively, for Nod P-1 whereas we have obtained two
332 values at +0.41.

333

334 **4. RESULTS**

335 **4.1 The nickel concentration and isotopic composition of rivers**

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

340 There are no previous data for nickel isotopes in rivers, but the concentrations reported here can be
341 compared with published data. The lowest Ni concentrations overall are for the Negro, a tributary of
342 the Amazon that drains the lowland regions of the Amazon Basin, and the Kalix, a small river in
343 Arctic Sweden. The range of nickel concentrations found here for the Kalix of 4.1-5.6 nM is within
344 the published range of 2-6 nM (Pekka et al., 2004; Dahlqvist et al., 2007). There are no published
345 nickel data specifically for the Negro, nor for the other major tributary that joins the Negro at
346 Manaus, the Solimoes, but Boyle et al. (1982) document a concentration of 4-5 nM for the riverine
347 end-member at the mouth of the Amazon. The value reported here for the Tocantins, another major
348 river that debouches into the Atlantic alongside the Amazon at Belem, is 4.5 nM. Reported Ni
349 concentrations for the Chang Jiang at its mouth (2-3 nM; Edmonds et al., 1985) are lower than the
350 6-8 nM found here at, or upstream of, Wuhan. Measurements up to 400 km inland of the mouth,
351 however, are closer to those found here, at 4-5 nM (Koshikawa et al., 2007), so there may be a real
352 increase upstream. Nickel data have been reported for the Ottawa, and the St. Lawrence system
353 generally (Rondeau et al., 2005). The reported concentrations for the Ottawa show significant inter-

354 annual variability (6-14 nM) while those at the mouth of the St. Lawrence are temporally constant
355 at 12-13 nM. Both of these are consistent with the value of 12.3 nM reported here. Finally, our
356 concentration for the Missouri at Columbia of 35 nM is just slightly higher than the range
357 previously reported for the Missouri and the Mississippi system generally, at 30-32 nM (Shiller and
358 Boyle, 1987; Shiller, 1997).

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

369 **4.2 Nickel concentrations and isotopic composition in seawater**

370 The data for seawater samples is reported in Table 2 and displayed as depth profiles in Fig. 3-5.
371 Concentrations for these samples range from 3.1 to 11.2 nmol kg⁻¹. The first striking feature of the
372 isotopic data is its homogeneity: the average and 2 standard deviations for the entire dataset is
373 1.44±0.15‰, compared to our estimate of the reproducibility based on repeat analyses of standards
374 of 0.08‰. The second is that seawater is distinctly heavier in Ni isotopes than rivers. Only 2 of the
375 29 seawater analyses have a Ni isotopic composition that is lighter than the heaviest river.

376 As with rivers, there are no published data on nickel isotopes in seawater, but our data for
377 concentrations can be compared with literature values, though this is not always easy because

378 locations of previous work are not exactly the same and some of the older concentration datasets
379 have many outliers due to the difficulties with clean sampling and analysis at the time. Despite this,
380 our dataset as a whole for the North Pacific is clearly identical to that of Bruland (1980), with
381 agreement all the way down the depth profiles to a small fraction of a nmol kg^{-1} (Fig. 6). This is all
382 the more remarkable given that the various stations in Fig. 5 are spread across 35 degrees of latitude
383 and over more than 20 degrees of longitude. Our data for the Iceland Basin in the North Atlantic are
384 similar to those for two nearby stations analysed previously (Yeats and Campbell, 1983; Danielsson
385 et al., 1985), and the same is true for our partial depth profile in the Polar Front Zone of the
386 Southern Ocean (Löscher, 1999), though the latter two datasets are rather noisy compared with the
387 Bruland (1980) North Pacific dataset.

388 Comparison can also be made between relationships between Ni concentrations and the major
389 nutrients, for the data presented here and published previously. Fig. 7 shows this relationship for
390 phosphate, with the same datasets from the North Pacific and North Atlantic that feature in Fig. 6
391 plotted for comparison. It has long been recognised (Sclater et al., 1976; Bruland, 1980) that Ni and
392 phosphate are regenerated in a similar fashion in the upper water column so that concentrations, as
393 expected, are strongly correlated there. Beneath the mid-depth phosphate maximum, however,
394 nickel concentrations continue to increase to a maximum (if present) at much deeper levels, so that
395 deep nickel concentrations are better correlated with silica. This is clearly seen on Fig. 7 for the
396 highest Ni concentrations, which are from depths beneath 1000-1200m, and which lie increasingly
397 off the Ni-PO_4 correlation at greater depth. Nearly all the data presented here, for which we also
398 have phosphate data, are for the upper 1500m of the water column, so that the relationship with
399 phosphate (Fig. 7) holds for the entire dataset. The best-fit line yields a slope of 0.0022 (mol/mol),
400 with an R^2 of 0.93. This compares with slopes of 0.0014-0.0027 for data in the literature (Sclater et
401 al., 1976; Bruland, 1980; Bruland and Fanks, 1983; Yeats and Campbell, 1983; Danielsson et al.,
402 1985; Mackey et al., 2002; Norisuye et al., 2007; Lai et al., 2008).

403

404 **5. DISCUSSION**

405 **5.1 Controls on the dissolved nickel isotope composition of rivers**

406 As noted previously, the key feature of the riverine isotopic data is that all but two rivers are
407 distinctly heavier than silicate rocks and sediments. It has also been noted that this same feature has
408 been seen for Mo and Cu isotopes in rivers (Archer and Vance, 2008; Vance et al., 2008). In these
409 previous studies the possibility that the isotopic compositions of these different metals are
410 lithologically-controlled was discussed and dismissed. For Ni, Gueguen et al. (2013) report $\delta^{60}\text{Ni}$
411 for coal and shale at +0.5 to +0.6‰ and it is possible that variably heavy Ni isotope compositions in
412 the dissolved phase in rivers can be explained by variable contributions of Ni from these lithologies.
413 However, for Mo and Cu, this does not explain the relationship between isotopic compositions and
414 reciprocal concentration, which are much more readily explained in terms of weathering processes.
415 The similarities between the Cu and Ni systems are emphasised in Fig. 8, where the Ni isotope data
416 are plotted versus $\delta^{65}\text{Cu}$ where the two are available for the same samples. For most of the data the
417 river samples extend along a positive array to heavy Ni and Cu isotopic compositions and away
418 from a value close to the “lithogenic” isotopic composition for both systems. With the exception of
419 the Brahmaputra sample, which has an anomalously light Ni isotope composition given its $\delta^{65}\text{Cu}$,
420 the R^2 for the data in Fig. 8 is 0.75.

421 The exception already mentioned is the Brahmaputra, but there are no Cu isotope data for the Negro
422 samples which, like the Brahmaputra, have Ni isotopic compositions close to the lithogenic value.
423 For Cu there is a general tendency for the isotopic composition to get heavier as riverine Cu
424 concentrations decrease, and this is also mostly the case for Ni (Fig. 2). But the Brahmaputra is
425 clearly different, and despite the fact that the Negro has the lowest Ni concentration of any river
426 measured here its Ni isotopic composition is close to the value for silicate rocks and sediments (Fig.

427 1). There is one clear and well-established characteristic of the Negro that probably explains its
428 behaviour. The River Negro is the archetypal transport-limited river of Stallard and Edmond (1983),
429 who noted its low total cation load (c.f. Ni) and cation ratios close to those of substrate rocks (c.f.
430 Ni isotopes). Of all the Amazonian rivers, the Negro drains the most intensely-weathered terrain.
431 Thus it seems likely that the Negro represents an end-member river composition that is close to
432 isotopic equilibrium with its source rocks, in a terrain that is so intensely-weathered on a time-
433 integrated basis that the modern supply rate of many cations, including Ni, is slow. It is not clear
434 whether this explanation could apply to the other exception, the Brahmaputra, as well.

435 In this view, the remaining Cu-Ni isotope data would be explained in terms of variations in
436 weathering intensity in terrains that, unlike the Negro, have not experienced intense time-integrated
437 weathering, and thus have not lost a lot of their nickel. Thus, the data for both isotopic systems are
438 consistent with decreasing modern weathering intensity along the array, providing opportunity for
439 isotopic compositions in the dissolved phase of rivers that are increasingly out of isotopic
440 equilibrium with the rocks they drain. We note that this explanation is similar to that advanced for
441 Mo isotopes and concentrations in Archer and Vance (2008), but is different from that put forward
442 for Cu in Vance et al. (2008). In the latter study, particulate analyses were also available for one
443 river, and this particulate load contained the isotopically light counterpart of the dissolved Cu load.
444 It was suggested that the Cu isotope data could be explained by equilibrium partitioning, during
445 transport, of Cu isotopes between a heavy dissolved load that was predominantly bound to organic
446 ligands and a light particulate load. In the absence of data for the particulate load of Ni in rivers,
447 this is also a tenable explanation for the Ni data, though the explanation in terms of weathering has
448 the advantage that it has an obvious rationale for the Negro data too. On the other hand, another
449 characteristic of the Negro is its high load of dissolved organic (humic) material (Stallard and
450 Edmond, 1983), perhaps allowing the organic complexation of all of its small load of Ni and little
451 partitioning into the solid phase.

452 This discussion is of general importance to the characteristics of transition metal isotope systems in
453 rivers, but its resolution must await further, more detailed, studies of river systems.

454 **5.2 The dissolved riverine input of nickel and its isotopes to the oceans**

455 Overall, if the data presented here are close to representative of the global riverine flux, the Ni
456 concentration data combined with the water discharges suggest an annual flux of Ni to the oceans of
457 3.6×10^8 moles. This is very close to the estimate of 3.2×10^8 moles yr^{-1} made by Sclater et al. (1976),
458 though both are below the Gaillardet et al. (2003) estimate of 5.2×10^8 moles yr^{-1} . However, the
459 latter was based solely on an early measurement of the Amazon, whereas roughly half of the Ni
460 discharge we have measured is also from the Amazon, so this estimate could change with the
461 addition of further data. Boyle et al. (1992) and Edmond et al. (1985) show that the mixing of
462 freshwater and seawater in the Amazon plume and the Chang Jiang estuary are both close to
463 conservative for nickel, so that, at least based on these estuaries, this estimate is not likely to be
464 significantly modified by estuarine processes. In terms of isotopes, the discharge- and
465 concentration-weighted average $\delta^{60}\text{Ni}$ for this group of rivers is +0.80‰, about 0.6-0.7‰ heavier
466 than the “lithogenic” value.

467 An initial question that is relevant to our overall aim to use these data as an estimate of the input of
468 Ni and its isotopes to the oceans, is whether this flux and its isotopic composition is representative
469 of the long-term global flux, particularly in the light of potential anthropogenic perturbation. This
470 question is very difficult to address unequivocally. Generally speaking there does not seem to be a
471 strong correspondence between high Ni concentrations and polluted river systems. For example, the
472 Solimoes and Negro at Manaus, relatively undisturbed rivers, have Ni concentrations that bracket
473 those of the Tocantins at Belem, likely more polluted. This range for the two Amazon tributaries
474 also encompasses the measured concentrations in the Chang Jiang and Brahmaputra, and these are
475 all similar to the likely pristine Kalix (e.g. Pekka et al., 2004). The Nile and Ottawa concentrations
476 are higher at 12-13 nM, but again the Nile in Sudan, where these samples were collected, is likely to

477 be relatively undisturbed. The Missouri clearly stands out as having a high Ni concentration, but we
478 note that concentrations down the length of the Mississippi system do not vary dramatically (20-35
479 nM; Shiller and Boyle, 1987; Shiller, 1997) so that it is possible that this is also close to the river's
480 natural Ni concentration. It is also the case that Ni concentrations in rivers have not increased
481 greatly through the 20th century – unlike e.g. Pb, Zn, Cd, Hg and some others. For example,
482 concentrations in sediments from the Rhine and UK lakes increased by less than factor 2 from 1900
483 to 1980, while concentrations in reservoirs along the Neckar have actually decreased (Foster and
484 Charlesworth, 1996).

485 **5.3 The homogeneity of dissolved Ni isotopes in the oceans**

486 There are two significant aspects of the isotopic data for seawater: first its homogeneity at $\delta^{60}\text{Ni} =$
487 $+1.44 \pm 0.15\text{‰}$ (average and 2 standard deviations), and second the fact that this average is 0.6-0.7‰
488 heavier than the riverine input estimated in section 5.2. In fact, only 3 out of the 29 seawater
489 samples measured have $\delta^{60}\text{Ni}$ lighter than the heaviest river measured. This section discusses the
490 implications of the first of these first-order observations for cycling of Ni within the oceans, while
491 the next section deals with the implications of the second for whole ocean elemental and isotopic
492 mass balance of Ni

493 Given the putative roles of Ni in phytoplankton, the ubiquitous depletion of Ni in the surface ocean,
494 and the possibility that phytoplankton uptake involves a kinetic isotopic fractionation, it is perhaps
495 surprising that surface waters in this small preliminary dataset show little significant isotopic shift
496 relative to the deep ocean. There is the slightest hint of anti-correlation between Ni concentrations
497 and isotopic compositions near the surface of the depth profiles for the Iceland Basin and the
498 Southern Ocean (Fig. 3,5), and it is possible that analytical improvements in the future might turn
499 up analytically resolvable variations in near-surface dissolved Ni isotopes that would be consistent
500 with significant removal of light isotopes into particulate organic material. The maximum isotopic
501 difference between surface water and local deep water for the above sites, at the limits of the

502 uncertainties on the isotope data, is 0.2-0.3‰. Because of the modest (~20-25%) surface depletions
503 in Ni relative to the local deep ocean, this would actually allow a substantial isotope fractionation
504 associated with Ni removal, of as much as 0.8-1‰. The presence or absence of such a Ni isotopic
505 fractionation associated with phytoplankton uptake could be more easily revealed either by
506 culturing experiments or through paired measurements of filtered seawater and associated
507 particulate organic matter.

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

516 The relative lack of an obvious isotopic imprint associated with the depth cycling of Ni is further
517 emphasised in Fig. 9, where the Ni isotope data presented here are plotted versus phosphate and
518 silica concentrations. It is striking that, despite the strong correlations between phosphate and Ni
519 concentrations illustrated in Fig. 7, there is no significant relationship between phosphate and Ni
520 isotopes. In the silica plot, there are again the slightest hints of heavier isotopes associated with the
521 very lowest silica concentrations, but the isotopic values for these low silica samples are the same,
522 within uncertainty, of the deeper samples. Clearly, at least for this preliminary dataset, the
523 biogeochemical cycling of Ni between the surface and deep ocean is not associated with an isotopic
524 fractionation that is large enough to lead to significantly heavy values associated with the co-
525 removal of Ni and the major nutrients in the surface ocean. This conclusion is similar to that arrived
526 at for zinc isotopes by Zhao et al. (2013), an element for which culturing and lake studies (John et

527 al., 2007; Peel et al., 2009) point to a significant isotopic effect associated with intra-cellular
528 uptake. Zhao et al. (2013) suggest that the lack of relationships between Zn isotopes and the major
529 nutrients, despite strong correlations between the latter and Zn concentrations, indicates that Zn
530 uptake in the surface ocean, and its marine biogeochemical cycling generally, is dominated by
531 incorporation into the opal frustule of diatoms and its associated extra-cellular organic matter (c.f.
532 Twining et al., 2012). It may be that the same is true for nickel isotopes.

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

551 significantly affected by hydrothermal inputs. Clearly, this single anomaly has to be duplicated in
552 the future.

553 **5.4 The elemental and isotopic budget of Ni in the oceans: budget imbalances and heavy Ni** 554 **isotopes**

555 The lack of Ni isotope variation in the deep ocean, as opposed to the absence of variability in the
556 surface ocean associated with biological uptake, is primarily a function of the residence time of Ni
557 relative to the oceanic mixing timescale. Sclater et al. (1976) calculate a residence time of around
558 40 kyr assuming that the dissolved load of rivers is the dominant input. The residence time
559 calculated from the riverine input flux obtained here and an average oceanic concentration of 8 nM
560 (Bruland and Lohan, 2003) is around 30 kyr. Thus, given an oceanic mixing timescale of the order
561 of 1 kyr (e.g. Jenkins, 2003) the homogeneity of deep ocean dissolved Ni isotopic compositions is
562 no surprise. However, as discussed below (and c.f. Krishnaswami 1976; Sclater et al., 1976), there
563 is a problem with balance in the oceanic Ni budget that is of wider significance than just the
564 isotopic data.

565 Fe-Mn crusts are very enriched in Ni (e.g. Gall et al., 2013; up to 0.8 wt. %) and scavenging to Fe-
566 Mn oxyhydroxides in the water column, with subsequent burial of these oxides in sediments, has
567 previously been identified as the most important output from the oceans (Krishnaswami, 1976;
568 Sclater et al., 1976). Krishnaswami (1976) noted that authigenic Ni associated with these phases in
569 Pacific pelagic sediments outweighed the dissolved riverine input by up to a factor of 6. This
570 imbalance is also implicit in the fact that Sclater et al. (1976) calculate an output-based residence
571 time for Ni in the oceans of 6-9 kyr, versus the estimate of 30-40 kyr they and we obtain based on
572 the suggestion that the dissolved riverine load is the dominant input. Both Krishnaswami (1976) and
573 Sclater et al. (1976) only had measurements of two rivers available, one of which was the Amazon.
574 Though the riverine dataset here includes more rivers, it is still dominated by the Amazon. While it
575 is possible that the estimate of the riverine flux could be revised upwards, such a revision seems

576 unlikely to close the gap on the estimated outputs. It is also possible to obtain an independent
577 constraint on the Fe-Mn oxide output of Ni, by tying it to the slightly better known oceanic Mo
578 budget. The input of Mo to the oceans *is* dominated by the dissolved load of rivers, and Archer and
579 Vance (2008) estimate it at $2.3 \times 10^8 \text{ mol yr}^{-1}$ with a $\delta^{98/95}\text{Mo} = +0.7\text{‰}$. Scott et al. (2008) present an
580 analysis of the oceanic Mo budget and suggest that 35% of this input, or $8 \times 10^7 \text{ mol yr}^{-1}$, is lost to
581 the Fe-Mn oxide sink. The size of this sink for Mo is particularly well constrained by some features
582 of the marine isotopic budget. It is well known that the Mo isotopic composition of the oceans is
583 homogeneous and heavy, at $\delta^{98/95}\text{Mo} = +2.3\text{‰}$ (Nakagawa et al., 2012). This requires a light sink.
584 Fe-Mn crusts are 3‰ lighter than seawater (Barling et al., 2001; Siebert et al., 2003), and
585 experimental sorption of Mo to Mn oxides produces a sorbed phase that is 3‰ lighter than the
586 aqueous phase (Barling and Anbar, 2004; Wasylenki et al., 2011). Thus it seems certain that the
587 dominant light output is sorption to Mn oxides and the size of the fractionation, along with the
588 difference between the homogeneous dissolved oceanic pool and the input, puts a relatively tight
589 constraint on the size of the Fe-Mn oxide output for Mo. The USGS (Manheim et al., 1991) have
590 compiled data on the chemistry of over 700 Fe-Mn crusts and nodules and these have a Ni/Mo ratio
591 of 18 ± 10 (molar, 1 SD). Thus, an output of $1.5 \times 10^9 \text{ mol yr}^{-1}$ Ni to this type of sediment is implied,
592 four times the dissolved riverine input. It is possible that there is some bias in the type of Fe-Mn
593 oxide samples included in the above database so that it is, for example, not representative of
594 dispersed Fe-Mn oxides in sediment. However, the concordance between the imbalance suggested
595 here and that suggested by Krishnaswami (1976) based on the chemistry of pelagic sediments
596 suggests that the conclusion is robust.

597 The inclusion of other potential sinks for nickel from the ocean would, of course, worsen this
598 imbalance problem, but probably to an insignificant degree. Sediments beneath both euxinic water
599 columns in restricted basins (significant H_2S in bottom water, e.g. Black Sea), and upwelling open
600 ocean settings (near zero bottom-water O_2 e.g. Namibian and Peru Margin) have authigenic Ni/Mo

601 ratios close to 1 (e.g. Brumsack et al., 2006). Scott et al. (2008) estimate that these sinks represent
602 the other 65% of the total oceanic Mo output. Using the same approach as for crusts, with the above
603 authigenic Ni/Mo ratio, this implies an output of about $1.5 \times 10^8 \text{ mol yr}^{-1}$, or an order of magnitude
604 less than the Fe-Mn crust output calculated in the same way.

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

616 Of the candidates for extra inputs to the ocean, it was argued earlier that the hydrothermal source is
617 likely to be insignificant. We note that Douville et al. (2002) report high Ni concentrations in
618 hydrothermal fluids emanating from ultramafic substrate, but concentrations below detection limits
619 for fluids from basaltic substrates. There have never been any indications from depth profiles near
620 ridges that hydrothermal inputs are anything other than minor. Sclater et al. (1976) also arrive at
621 this conclusion in noting that Ni/Fe ratios in sediment near ridges are lower than open ocean Fe-Mn
622 nodules. Total dust input to the ocean has been estimated by Jickells et al. (2005) at $4.5 \times 10^{14} \text{ g yr}^{-1}$.
623 At an average Ni concentration for the continental crust of 47 ppm (Rudnick and Gao, 2003) this is
624 equivalent to a total Ni flux of $2.1 \times 10^{10} \text{ g yr}^{-1}$, or $3.6 \times 10^8 \text{ mol yr}^{-1}$, close to the riverine flux of Ni.
625 However, DesBoeufs et al. (2005) estimate the Ni solubility in dust to be on the order of 2%,

626 suggesting that the Ni flux to the dissolved phase is unimportant. This conclusion is the same as that
627 arrived at by others based on surface ocean dissolved Ni concentrations (e.g. Bruland, 1980; Bowie
628 et al., 2002). Moreover, any source of Ni from dust presumably has an isotopic composition close to
629 the lithogenic value, so that this source is unable to provide the heavy Ni seen in the oceans.
630 Another possibility is a diffusive flux out of sediments. Because of the strong association of Ni with
631 Mn oxides in sediment, Ni concentrations can be high in the pore fluids of sediments where the
632 reduction of Mn oxide is occurring (up to 600 nM, see Shaw et al., 1990). But our conclusion
633 earlier that the Mn oxide output is much greater than the dissolved riverine input is tied to Mo.
634 Since Mo will also be mobilised from reduced Mn oxide, this suggestion does not get around the
635 imbalance in the oceanic Ni budget with respect to that for Mo.

636 A final possibility is that mobilisation of the riverine suspended load of Ni occurs in estuaries, and
637 that this reservoir is isotopically heavy. It was noted earlier that Ni in the Amazon plume and the
638 Chang Jiang estuary behaves pseudo-conservatively. But it is possible that estuaries where surface
639 sediment is anoxic could reductively release Ni associated with Mn-oxide coatings. This
640 explanation of the imbalance problem is attractive for a number of reasons. Firstly, 95-97% of the
641 Ni inventory of rivers is in the suspended load rather than the dissolved load (Gibbs 1973; Martin
642 and Meybeck 1979; Gaillardet et al 2003; Viers et al. 2009). Secondly, in a study of the Amazon
643 and Yukon rivers, Gibbs (1973) showed that approximately half of this suspended load reservoir of
644 Ni is associated with oxide coatings on grains. Thirdly, the suspended load of Mo is relatively much
645 less important than for Ni. Martin and Meybeck (1979) suggest that 30% of the total riverine load
646 of Mo is in the dissolved phase. Archer and Vance (2008) found insignificant amounts of Mo in the
647 suspended load of the Kalix and Chang Jiang. Thus, a source of Ni via the reduction of Mn oxides
648 in estuarine sediments might not come with a significant source of Mo. Finally, it is perhaps
649 noteworthy that the study of Krishnaswami (1976) also found that the oceanic Mn budget was out
650 of balance. This is confirmed by a similar approach to the Mn oxide output as taken above for Ni,

651 i.e. calculating it based on the Mo output to Fe-Mn oxides and the Mn/Mo ratio of Fe-Mn crusts.
652 Such an approach yields a sink for Mn of 7×10^{10} mol yr⁻¹, which is about 3 times the global
653 dissolved riverine flux given in Gaillardet et al. (2003). Thus co-release of Ni and Mn through the
654 reduction of Mn oxides could solve the imbalances of both Ni and Mn.

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

662

663 **6. CONCLUDING REMARKS**

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

666 (1) Ni isotopes in the dissolved phase of rivers (discharge- and concentration-weighted $\delta^{60}\text{Ni} = +0.8$
667 ‰) are heavier than the average of the small dataset for silicate rocks and sediments on the
668 continent (at around 0 to +0.3‰; Cameron et al., 2009). This feature is common to other transition
669 metal isotope systems such as Mo and Cu (Archer and Vance, 2008; Vance et al., 2008), and likely
670 reflects isotope fractionation in the weathering environment or during transport in rivers.

671 (2) Ni isotopes in the dissolved phase of the ocean are significantly heavier than this dissolved
672 riverine source, at $\delta^{60}\text{Ni} = +1.44 \pm 0.15$ ‰ (2SD, n = 29 from the Atlantic, Pacific and Southern
673 Oceans), necessitating either another input that is heavier than rivers, or an isotopically light output.

674 (3) Oceanic dissolved Ni isotopes are strikingly homogeneous, with little significant difference
675 between the surface ocean where Ni concentrations drop as low as 1.5-2 nM and the deep ocean
676 where they are as high as 10-11 nM. Thus, the drawdown of Ni in the surface ocean must occur via
677 a process that does not involve a significant enough isotopic fractionation to yield residual heavy
678 isotopic compositions in the surface dissolved pool.

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

695 The homogeneity of oceanic nickel isotopes is something of a surprise, given that the drawdown of
696 Ni in the surface ocean appears to be via biological uptake (e.g. Twining et al., 2012), and the fact
697 that such uptake usually involves a preference for the light isotope via a kinetic fractionation. Ni
698 concentrations in the deep ocean are well known to be closely correlated with silica (e.g. Bruland,

699 1980), and it may be that Ni incorporation into diatom opal, or sorption onto organic matter
700 associated with diatom opal, may dominate Ni drawdown in the surface ocean and be associated
701 with only a minor isotopic fractionation. Culturing work on marine phytoplankton, as well as Ni
702 isotopic analysis of photic zone particulate material, would greatly contribute to the resolution of
703 this discussion.

704

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964 **FIGURE CAPTIONS**

965
966 **Figure 1:** Frequency distribution of Ni isotope compositions for all river and seawater samples
967 measured here, with frequency for each individual dataset (rivers, seawater) normalised to the total
968 number of measurements.

969
970 **Figure 2:** Nickel isotope data for rivers plotted against reciprocal concentration. Error bars are for
971 long-term reproducibility of standards analysed using the double spike method. The horizontal
972 black line and grey band give the average and 1SD of Ni isotope compositions of samples of
973 continental silicate rocks (Cameron et al., 2009).

974
975 **Figure 3:** Nickel isotopic and concentration data for the Iceland Basin, North Atlantic.
976 Uncertainties on isotopic data correspond to the long-term reproducibility of standards using the
977 double spike procedure.

978
979 **Figure 4:** Nickel isotopic and concentration data for the North Pacific. Filled squares are for the
980 depth profile **at 47°N, 129°W**. Open squares are for 1000m samples at 50-52°N, 133-145°W
981 Uncertainties on isotopic data correspond to the long-term reproducibility of standards using the
982 double spike procedure.

983
984 **Figure 5:** Nickel isotopic and concentration data for the Atlantic Sector of the Southern Ocean.
985 Filled squares are for the depth profile at Station PS71-104 in the Polar Front Zone (~48°S). Open
986 squares are for surface samples further south, at 52-60°S.

987
988 **Figure 6:** Nickel concentration data (filled squares) for all North Pacific data presented here, for the
989 Iceland Basin depth profile and for the Southern Ocean (partial) depth profile, compared with data
990 from the literature (open diamonds). Literature data for the North Pacific are for the three depth

991 profiles in Bruland (1980). For the Iceland Basin data are shown for two stations close to that
992 presented here (Yeats and Campbell 1983; Danielsson et al., 1985). For the Southern Ocean Polar
993 Front Zone, the literature data plotted are a composite of 6 stations in Löscher (1999).

994

995 **Figure 7:** Nickel concentration data versus phosphate where available (Southern Ocean phosphate
996 data from Abouchami et al., 2011, 2013, Iceland Basin data from E. Achterberg, pers. comm., and
997 NE Pacific 1999-2001 data from M. Lohan, pers. comm.). Symbols as in Figure 3, except that
998 literature data (open diamonds) are split into Atlantic (green) and Pacific (black). The line shown is
999 fitted to all the data presented here. Data from the greatest depths in the North Pacific (Bruland,
1000 1980) is well-known to deviate from a linear relationship due to the fact that phosphate usually
1001 presents a maximum at 1000-1500m whereas Ni continues increasing below this depth, reaching a
1002 maximum, if present, much deeper in the water column. Virtually all the data in this paper are from
1003 above 1500m.

1004

1005 **Figure 8:** Nickel isotope data for rivers versus Cu isotope data where available (Vance et al., 2008).
1006 Symbols as in Figure 1. For all samples except two, the Cu and Ni isotopic analyses were done on
1007 samples from the same bottles. The two exceptions are the Nile samples, where Cu and Ni analyses
1008 for the main Nile (dry and wet season) come from different samples collected at nearby localities.
1009 The grey box gives the range (average $\pm$ 1SD) of Cu and Ni isotope compositions of samples of
1010 continental silicate rocks (Cameron et al., 2009; Cu data compiled in Little et al., 2013). With the
1011 exception of the Brahmaputra sample, which has an anomalously light Ni isotope composition
1012 given its $\delta^{65}\text{Cu}$, the R^2 for the data is 0.75.

1013

1014 **Figure 9:** Nickel isotope data for seawater versus phosphate and silica concentrations. See caption
1015 to Figure 7 for the sources of the major nutrient data.

Table 1: Nickel concentration and isotope data for rivers.

River	Tributary or Location	Sample ID	[Ni] (nmol kg ⁻¹)	$\delta^{60}\text{Ni}$ (‰)	2 σ^1	River Averages		
						[Ni] (nmol kg ⁻¹)	$\delta^{60}\text{Ni}$ (‰)	Discharge ² (10 ¹² litre yr ⁻¹)
Amazon	Negro at Manaus	Negro 2	2.2	0.31	0.07	2.5	0.36	946
	Negro at Manaus	Negro 3	2.7	0.41	0.06			
	Solimoes at Manaus	Sol 1	9.4	0.88	0.05	9.5	0.88	3248
	Solimoes at Manaus	Sol 2	9.5	0.88	0.07			
Tocantins	Belem	TOC1	4.5	0.88	0.09	4.5	0.88	372
Chang Jiang	Upstream Wuhan	CJ-1	6.3	1.34	0.05	6.6	1.27	928
	Upstream Wuhan	CJ-2	7.7	1.19	0.04			
	Wuhan	CJ-5	6.0	1.27	0.04			
Main Nile	El Gaili, Sudan (wet)	Sample 5	13.6	0.84	0.02	13.7	0.91	83
	Sayala, Sudan (dry)	ATB01/5	13.9	0.99	0.05			
Missouri	Columbia	Mizz1	35.0	0.68	0.03	35.0	0.68	580
Brahmaputra	Tezpur, Assam	Brahm	5.1	0.29	0.07	5.1	0.29	1003
Ottawa	Chenau	Aylmer	12.3	0.82	0.07	12.3	0.82	337
Kalix	Angesa	Kx2	4.1	0.73	0.07	5.1	0.90	9
	Kalix	Kx4	5.6	1.00	0.08			
	Kalix	Kx5	5.6	0.97	0.07			

¹ Measured internal 2 sigma – see Methods for reproducibility.

² Discharges as in Gaillardet et al. (1999), Pontr 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.

Sample	Latitude	Longitude	Depth (m)	[Ni] (nmol/kg)	$\delta^{60}\text{Ni}$ (‰)	$2\sigma^1$
<i>RRS Cruise 354 Station 28, Iceland Basin, North Atlantic (Aug 2010)</i>						
CTD T027 - 13	61° 15.19'N	20°45.82'W	20	3.13	1.52	0.05
CTD T027 - 10	61° 15.19'N	20°45.82'W	50	3.54	1.53	0.05
CTD T027 - 7	61° 15.19'N	20°45.82'W	150	3.64	1.52	0.04
CTD T027 - 5	61° 15.19'N	20°45.82'W	500	3.61	1.53	0.03
CTD T027 - 4	61° 15.19'N	20°45.82'W	830	4.12	1.34	0.06
CTD T027 - 3	61° 15.19'N	20°45.82'W	1300	4.07	1.41	0.06
CTD T027 - 24	61° 15.19'N	20°45.82'W	2210	4.06	1.48	0.04
<i>US Geotraces cruise ICI, R/V Knorr, Tropical North Atlantic (June 2008)</i>						
GPrI 20	31°40'N	64°10'W	1000	4.91	1.37	0.04
<i>Geotraces-IPY cruise ANT XXIV/3, Polarstern, Atlantic Sector, Southern Ocean (Feb-Apr 2008)</i>						
PS71-109	51.67°S	0.00	2-5	6.51	1.43	0.05
PS71-111	52.17°S	0.54°W	2-5	6.35	1.45	0.07
PS71-126	57.21°S	0.00	2-5	6.36	1.47	0.04
PS71-136	60.24°S	0.00	2-5	6.27	1.44	0.05
PS71-104-2-24	47°39.36'S	4°15.7'E	15	5.77	1.45	0.05
PS71-104-2-22	47°39.36'S	4°15.7'E	50	5.87	1.58	0.05
PS71-104-2-22; repeat	47°39.36'S	4°15.7'E	50	5.71	1.54	0.04
PS71-104-2-20	47°39.36'S	4°15.7'E	101	5.56	1.51	0.06
PS71-104-2-18	47°39.36'S	4°15.7'E	202	5.67	1.47	0.05
PS71-104-2-16	47°39.36'S	4°15.7'E	301	6.13	1.47	0.05
P71-S104-2-14	47°39.36'S	4°15.7'E	399	6.24	1.46	0.06
PS71-104-2-11	47°39.36'S	4°15.7'E	998	7.02	1.40	0.03
PS71-S104-2-9	47°39.36'S	4°15.7'E	1500	6.81	1.42	0.05
<i>EAGER Cruise AT15-47, R/V Atlantis, Juan de Fuca Ridge, NE Pacific Ocean (June 2009)</i>						
E22	47°56.00'N	129°04.30'W	100	5.54	1.32	0.05
E20	47°56.00'N	129°04.30'W	300	6.63	1.42	0.03
E18	47°56.00'N	129°04.30'W	800	8.87	1.36	0.02
E16	47°56.00'N	129°04.30'W	1300	9.86	1.41	0.03
E14	47°56.00'N	129°04.30'W	1800	11.2	1.21	0.02
E12	47°56.00'N	129°04.30'W	2300	10.6	1.43	0.02
<i>NE Pacific (1999-2001)</i>						
26P1000	50°N	145°W	1000	9.48	1.45	0.04
C1000 - (Haida Eddy centre)	51.15°N	133.60°W	1000	9.47	1.42	0.03
E1000 - (Haida Eddy edge)	51.35°N	133.50°W	1000	9.36	1.47	0.03

¹ Measured internal 2 sigma – see Methods for reproducibility.

Cameron and Vance - Figure 1

Cameron and Vance - Figure 2

Cameron and Vance - Figure 3

Iceland Basin, North Atlantic

Cameron and Vance - Figure 4

North Pacific

Cameron and Vance - Figure 5

Southern Ocean, Atlantic Sector

Cameron and Vance - Figure 6

Cameron and Vance - Figure 7

Cameron and Vance - Figure 8

Cameron and Vance - Figure 9