Nickel isotopic composition of the mantle

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Abstract

This paper presents a detailed high-precision study of Ni isotope variations in mantle peridotites and their minerals, komatiites as well as chondritic and iron meteorites. Ultramafic rocks display a relatively large range in $\delta^{60}\text{Ni}$ (permil deviation in $^{60}\text{Ni}/^{58}\text{Ni}$ relative to the NIST SRM 986 Ni isotope standard) for this environment, from $0.15 \pm 0.07\text{‰}$ to $0.36 \pm 0.08\text{‰}$, with olivine-rich rocks such as dunite and olivine cumulates showing lighter isotope compositions than komatiite, lherzolite and pyroxenite samples. The data for the mineral separates shed light on the origin of these variations. Olivine and orthopyroxene display light $\delta^{60}\text{Ni}$ whereas clinopyroxene and garnet are isotopically heavy. This indicates that peridotite whole-rock $\delta^{60}\text{Ni}$ may be controlled by variations in modal mineralogy, with the prediction that mantle melts will display variable $\delta^{60}\text{Ni}$ values due to variations in residual mantle and cumulate mineralogy. Based on fertile peridotite xenoliths and Phanerozoic komatiite samples it is concluded that the upper mantle has a relatively homogeneous Ni isotope composition, with the best estimate of $\delta^{60}\text{Ni}_{\text{mantle}}$ being $0.23 \pm 0.06\text{‰}$ (2 s.d.). Given that $>99\%$ of the Ni in the silicate Earth is located in the mantle, this also defines the Ni isotope

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composition of the Bulk Silicate Earth (BSE). This value is nearly identical to the results obtained for a suite of chondrites and iron meteorites (mean $\delta^{60}\text{Ni}$ $0.26 \pm 0.12\text{‰}$ and $0.29 \pm 0.10\text{‰}$, respectively) showing that the BSE is chondritic with respect to its Ni isotope composition, with little to no Ni mass-dependent isotope fractionation resulting from core formation.

1. Introduction

Nickel is a first-row transition metal that, under mantle melting conditions, behaves as a strongly compatible element. The Earth's upper mantle has a mean Ni concentration of $2000 \mu\text{g/g}$, which means this reservoir contains $>99\%$ of the silicate Earth's Ni inventory (e.g. McDonough and Sun, 1995; Palme and O'Neill, 2014). In mantle-derived rocks Ni is primarily concentrated in olivine, the dominant silicate mineral in the upper mantle. In Mg-rich mantle olivine, Ni^{2+} substitutes for Mg^{2+} in octahedral coordination, leading to olivine Ni concentrations of around $3000 \mu\text{g/g}$ (e.g. Sato, 1977; Stosch, 1981; Deer et al., 1982; Witt-Eickschen and O'Neill, 2005). Spinel is the only other mantle mineral that can accommodate similar amounts of Ni, also predominantly in octahedral coordination (Stosch, 1981; Witt-Eickschen and O'Neill, 2005). However, as the modal abundance of spinel in upper mantle lithologies is $<5\%$, its impact on the mantle Ni budget is minor. Orthopyroxene is the second most common mineral in the upper mantle and

16 can hold smaller, but significant, amounts of Ni ($<1000 \mu\text{g/g}$), substituting
17 into octahedral coordination space for Mg or Fe in the orthopyroxene lattice
18 structure (Stosch, 1981; Deer et al., 1982; Witt-Eickschen and O'Neill, 2005).
19 Nickel can also be found in lower concentrations ($<500 \mu\text{g/g}$) in clinopyrox-
20 ene and garnet, also situated in octahedral coordination in both minerals
21 (Witt-Eickschen and O'Neill, 2005). Although the hosts of Ni in the lower
22 mantle are less well constrained, Ni has been observed to be concentrated
23 in ferropericlasite inclusions within diamonds, where it is present in amounts
24 of 1–2.5 wt.% (Kaminsky, 2012). Nickel has also been found in its native
25 form (Kaminsky, 2012), which is potentially due to disproportionation of
26 magnesio-wustite into bridgmanite which produces Fe-Ni metal (Frost et al.,
27 2004; Wade and Wood, 2005; Williams et al., 2012).

28 Nickel stable isotopes are a relatively new geochemical tracer that has
29 not been evaluated in detail in terrestrial high-temperature environments. A
30 number of studies have attempted to quantify the degree of $\delta^{60}\text{Ni}$ (permil de-
31 viation in $^{60}\text{Ni}/^{58}\text{Ni}$ relative to the NIST SRM 986 Ni isotope standard) vari-
32 ation in igneous rocks, including mantle derived materials (Cameron et al.,
33 2009; Steele et al., 2011; Gall et al., 2012, 2013; Gueguen et al., 2013; Cher-
34 nonozhkin et al., 2015; Ratié et al., 2015; Estrade et al., 2015). However, most

35 of these data are limited to rock standards or reference materials, and no sys-
36 tematic Ni stable isotope study of mantle rocks has been published. Other
37 work on Ni stable isotopes in high-temperature environments has focused on
38 meteorites (Cook et al., 2007; Moynier et al., 2007; Steele et al., 2011, 2012)
39 and magmatic sulphide ore bearing bodies (Hofmann et al., 2014), while a
40 number of studies have focused on the application of Ni isotopes in low tem-
41 perature geochemistry (e.g. Porter et al., 2014; Cameron and Vance, 2014;
42 Wasylenki et al., 2015; Ratié et al., 2015; Estrade et al., 2015).

43 Published Ni isotope compositions for igneous rocks range between -0.1
44 and 0.3‰ in $\delta^{60}\text{Ni}$ (e.g. Cameron et al., 2009; Gueguen et al., 2013). This
45 study investigates this surprisingly large range in isotope composition for a
46 high-temperature environment. Our aim is to better define the Ni isotope
47 composition of the mantle by presenting data from peridotites, komatiites
48 and mantle mineral separates, and to discuss these in the context of published
49 whole-rock data. Finally, we aim to compare the isotope composition of the
50 Bulk Silicate Earth (i.e. the mantle) with that of meteorites, to estimate
51 the impact of core formation on the Ni isotope system on Earth. For this
52 chondrite and iron meteorite data are presented and compared with existing
53 data on such materials.

54 2. Sample selection

55 2.1. Mantle xenoliths, peridotites and mineral separates

56 Most of the ultramafic xenoliths analysed in this study are from the Neo-
57 gene volcanic province in Northern Tanzania, a part of the eastern Rift Valley
58 of East Africa. These samples were selected for this study as they have been
59 well characterised for a range of elemental and isotopic tracers and because
60 they represent ancient sub continental lithospheric mantle. The majority of
61 these samples were collected from the Lashaine volcano, an area famous for
62 carbonatite lavas and the presence of ultramafic xenoliths similar to those
63 from kimberlites (e.g. Dawson et al., 1970; Cohen et al., 1984; Dawson, 2002).
64 The samples comprise two garnet lherzolites (BD730 and BD1355), three
65 spinel harzburgites (BD774, BD822 and BD1542) and one alkaline pyroxen-
66 ite (BD744). The garnet peridotites consist of varying proportions of red to
67 purple garnet, emerald green clinopyroxene, orthopyroxene and magnesium-
68 rich olivine (Fo₉₀ for olivine from BD730), the latter without any signs of ser-
69 pentinisation (Dawson et al., 1970). The spinel peridotites contain a much
70 higher percentage of olivine (80-90 vol.% compared to 50-65 vol.% in the
71 garnet peridotites) and lower amounts of orthopyroxene (5-12 vol.% versus
72 20-40 vol.% in the garnet peridotites), but similar amounts of clinopyrox-

ene (1-3 vol.% only in both groups) (Dawson et al., 1970; Reid et al., 1975;
Rhodes and Dawson, 1975). The pyroxenite sample consists of rounded iron-
rich olivine (Fo_{84}), opaque phases (mainly chromite and magnetite), and
clinopyroxene, surrounded by mica (Dawson and Smith, 1972). Other man-
tle rocks samples analysed were a kimberlite hosted garnet lherzolite xenolith
from the Balfontain Mine in South Africa (e.g. Carswell and Dawson, 1970)
and a dunite from the Appalachian peridotite massif in Jackson County, N.
Carolina, USA (e.g. Kulp and Brobst, 1954; Stueber, 1969). These samples
were both provided by the Natural History Museum in London. For inter-
laboratory comparison we have also analysed the USGS reference materials
DTS-1 and PCC-1 for their Ni isotope compositions. The reference sample
PCC-1 is a partially serpentinised harzburgite from the Cazadero ultramafic
massif, California, USA (Flanagan, 1967, 1969; Barnes and O’Neil, 1969) and
DTS-1 is a dunite sample from the Twin Sisters Mountain, Washington, USA
(Flanagan, 1967, 1969; Ragan, 1963).

In addition to whole rock mantle xenoliths we have analysed mineral
separates from mantle xenoliths from of the Cameroon Line, which have
previously been studied for Fe isotopes (Williams et al., 2004, 2005). The
goal of these analyses was to determine the magnitude of inter-mineral Ni

92 isotope fractionation and to compare the behaviour of Ni and Fe isotopes.
93 The analysed samples comprise three spinel lherzolites from different vol-
94 canic centres in Cameroon: (1) olivine from C235A, Lake Baronbi Mbo
95 near Mount Cameroon; (2) orthopyroxene from C273Q, Lake Enep near
96 Oku in Cameroon; (3) olivine, orthopyroxene and clinopyroxene from P13,
97 Ngaoundere Plateau, Cameroon (Lee et al., 1996). Two mineral megacrysts,
98 garnet and clinopyroxene, were also analysed from sample N12, a harzburgite
99 from the Biu Plateau in Nigeria. The three analysed spinel lherzolites
100 contain 45-65 vol.% olivine, 25-35 vol.% orthopyroxene, 10-15 vol.% clinopy-
101 roxene and <5 vol.% spinel, while the Biu Plateau harzburgite contains 55-60
102 vol.% olivine and 40-45 vol.% orthopyroxene as well as small amounts ($<5\%$)
103 of clinopyroxene and garnet (Lee et al., 1996). In a previous study of the same
104 samples, Williams et al. (2005) concluded that the minerals were largely in
105 inter-mineral Fe isotopic equilibrium, based on the constant offsets between
106 the different phases from mantle xenoliths and massif samples.

107 2.2. Komatiites

108 Komatiites are generated by extremely high-degree (35 to 50%) partial
109 melting of the mantle. The occurrence of komatiites is largely restricted to
110 Archean and early Proterozoic terranes, which is considered to reflect the

111 higher ambient mantle temperatures at these times (e.g. Nisbet et al., 1993;
112 Arndt et al., 2008). As large-degree partial melts komatiites approximate the
113 chemical composition of their source, and have thus been used to constrain
114 the composition of the mantle for Fe isotopes (e.g. Dauphas et al., 2010;
115 Hibbert et al., 2012), Mo isotopes (Greber et al., 2015) and Cu isotopes
116 (Savage et al., 2015).

117 The komatiites of Gorgona Island, Colombia, are the only documented
118 occurrence of Phanerozoic komatiite (dated at ~ 90 Ma; Walker et al., 1999;
119 Sinton et al., 1998). Being the youngest known example of komatiite these
120 are also the texturally least altered specimens of this rock type available and
121 have been well characterised in previous publications (e.g. Aitken and Echev-
122 erría, 1984; Arndt et al., 1997; Kerr et al., 1996; Kerr, 2005). The mineralogy
123 of the Gorgona cumulates and komatiites consists of olivine, plagioclase, py-
124 roxene, Cr-spinel and altered, devitrified glass, with the metamorphic grade
125 not exceeding greenschist facies (Aitken and Echeverría, 1984). Some of the
126 samples analysed in this study have previously been analysed for Fe isotopes
127 by Hibbert et al. (2012).

128 2.3. Meteorites

129 For this study nine magmatic iron meteorites from six different mete-
130 orite classes were analysed (Negrillos and North Chile, IIA; Sikhote-Alin,
131 IIB; Arispe, IC; Charcas and Henbury, IIIA; Clark County, IIIF; Gibeon and
132 Duel Hill, IVA). Twelve chondrite meteorites from different classes were anal-
133 ysed, of which four were carbonaceous chondrites (Allende, CV3; Murchison,
134 CM2; Orgueil, CI1; Ornans, CO3), two enstatite chondrites (Indarch, EH4;
135 Khaipur, EL6) and six ordinary chondrites (Kernouve, H6; Baratta, L3; Bre-
136 mervorde, L4; Buderheim, L6; Parnallee, LL3; St. Severin, LL6). All but
137 three meteorites analysed were provided by the Natural History Museum,
138 London; the three remaining meteorites were supplied by the Smithsonian
139 National Museum, Washington D.C.

140 3. Methods

141 A comprehensive description of our procedures for Ni separation and iso-
142 tope analysis can be found in Gall et al. (2012) with only a summary of the
143 most important aspects given here.

144 All peridotite, komatiite and chondrite whole-rock samples for this study
145 were dissolved in high-pressure Teflon bombs to assure complete dissolution

146 of all mineral phases. These samples were weighed into pre-cleaned Savillex
147 high-pressure hexagon-cap vials and a mixture of concentrated HNO_3 and HF
148 ($\sim 1:5$) was added. The samples were then put in an oven (at 140°C) for two
149 days after which the dissolutions were complete without residue. The mineral
150 separates were weighed into pre-cleaned Savillex beakers and dissolved in a
151 $1:5$ mixture of concentrated HNO_3 and HF on a hotplate (130°C) overnight.
152 Following digestion, the all silicate samples were dried and treated first with
153 concentrated HNO_3 and then 6 M HCl to remove any remaining fluorides. To
154 remove any contamination on the outer layers of the iron meteorites the solid
155 samples were first polished with SiC paper and cleaned in MQ water, and then
156 leached in cold 6 M HCl for 30 min. This last step was repeated 3 times, after
157 which $>90\%$ of the samples still remained. The cleaned iron meteorites were
158 dissolved in 6 M HCl on a hotplate (120°C) overnight. Following complete
159 dissolution, all samples were evaporated until dry and taken up in 6 M HCl
160 before chromatography. A three stage column chromatographic technique
161 was used to separate Ni from sample matrices, exploiting the ability of Ni to
162 form strong complexes with firstly ammonia and secondly dimethylglyoxime.
163 A final anion exchange cleanup column ensured removal of any remaining
164 Fe. The full procedural blank from this separation technique was less than 3

165 ng, which is negligible compared to the amounts of Ni processed per sample
166 (1000-3000 ng). The yield for mantle rocks and meteorites was close to 100%.
167 We used the double-spike technique to ensure that any potential fractionation
168 induced during the separation procedure was corrected for by spiking of all
169 samples prior to chemical separation.

170 Nickel has five stable isotopes: ^{58}Ni , ^{60}Ni , ^{61}Ni , ^{62}Ni and ^{64}Ni , with the
171 respective abundances of 68.08%, 26.22%, 1.14%, 3.63% and 0.93% (Gram-
172 lich et al., 1989). A double-spike approach was used here for correction of
173 instrumental mass bias, and, as mentioned above, isotopic fractionation dur-
174 ing sample processing. The double spike consisted of 25:75 ^{61}Ni : ^{62}Ni and was
175 added to each sample at a sample:spike Ni ratio of 0.4. The purified Ni solu-
176 tions were analysed using a Nu Plasma II (Nu Instruments) high-resolution
177 multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS)
178 at Oxford University. Sample solutions of 100 ng/g Ni were introduced into
179 the plasma in 0.3 M (2%) HNO_3 using a Nu Instruments DSN desolvator and
180 a PFA concentric nebulizer (Elemental Scientific). Measurements consisted
181 of 40 10-second integrations and baselines were measured by ESA deflection.
182 The possible interference of ^{58}Fe on ^{58}Ni was corrected online through simul-
183 taneous measurement of ^{57}Fe . All analyses were performed at medium mass

184 resolution mode (resolving power, $m/\Delta m \approx 3000$) to ensure that any poly-
 185 atomic interferences were resolved. The mean beam intensity obtained under
 186 these conditions were ~ 3 V on mass 58, or around 40 V per ppm Ni. The
 187 data reduction procedure of measured isotope ratios followed Siebert et al.
 188 (2001).

189 Most samples analysed during this study were digested twice and all pro-
 190 cessed solutions were analysed on at least 2 different occasions. Multiple full
 191 repeats and analyses of the USGS reference materials PCC-1 (15 individual
 192 analyses), BHVO-2 (35 analyses) and SCo-1 (16 analyses) gave a long term
 193 external reproducibility of $\pm 0.07\%$ (2 s.d.) for silicate samples (Gall et al.,
 194 2012). All Ni isotope ratios reported here are presented as the $^{60}\text{Ni}/^{58}\text{Ni}$
 195 ratio relative to the Ni isotope standard SRM 986 (NIST).

$$\delta^{60}\text{Ni} = \left[\frac{(^{60}\text{Ni}/^{58}\text{Ni})_{\text{sample}}}{(^{60}\text{Ni}/^{58}\text{Ni})_{\text{SRM 986}}} - 1 \right] \times 1000$$

196 4. Results

197 All results are given in Tables 1-3. The number of replicate analyses (n)
 198 for each sample is given in these tables and all uncertainties are reported as
 199 2 standard deviations (2 s.d.) unless noted otherwise.

200 Results of peridotite and komatiite analyses can be found in Table 1.
 201 The Ni isotope composition of the two USGS peridotite reference materials
 202 DTS-1 and PCC-1 were determined to be $-0.08 \pm 0.07\text{‰}$ and $0.14 \pm 0.06\text{‰}$
 203 respectively. Our values for these rock standards are in excellent agreement
 204 with previously published data reported by Gueguen et al. (2013) (DTS-1:
 205 $-0.07 \pm 0.05\text{‰}$ and PCC-1: $0.12 \pm 0.05\text{‰}$) and Chernonozhkin et al. (2015)
 206 (DTS-1: $-0.07 \pm 0.01\text{‰}$ and PCC-1: $0.17 \pm 0.05\text{‰}$). There is a discrepancy
 207 with the $\delta^{60}\text{Ni}$ for PCC-1 reported by Cameron et al. (2009), who obtain a
 208 value nearly 0.20‰ heavier ($0.34 \pm 0.08\text{‰}$). As this heavy value has not been
 209 replicated by either this study, Gueguen et al. (2013) or Chernonozhkin et al.
 210 (2015) it is not included in the discussion nor in the comparison of new and
 211 published data in Fig. 1. To examine the effect of low- vs. high-pressure
 212 dissolution on the Ni isotope composition separate samples of the DTS-1
 213 dunite were dissolved using the different digestion techniques. No difference
 214 in $\delta^{60}\text{Ni}$ (within error) were seen between the different types of digestions
 215 of this sample, even though the spinels were clearly still undissolved in the
 216 low-pressure experiments.

217 The eight ultramafic samples display $\delta^{60}\text{Ni}$ ranging from 0.15 to 0.36‰ .
 218 The dunite (NHM-1) exhibit the lowest $\delta^{60}\text{Ni}$ of $0.15 \pm 0.07\text{‰}$. Two of the

219 three harzburgite samples also display low values of $0.18 \pm 0.07\text{‰}$ (BD1542)
 220 and $0.20 \pm 0.03\text{‰}$ (BD822), while the last harzburgite (BD774) has a higher
 221 $\delta^{60}\text{Ni}$ of $0.28 \pm 0.06\text{‰}$. The two volcanic lherzolite xenoliths possess slightly
 222 higher $\delta^{60}\text{Ni}$ than dunite, of $0.23 \pm 0.06\text{‰}$ (BD730) and $0.25 \pm 0.06\text{‰}$ (BD1355),
 223 and the kimberlite lherzolite xenolith (NHM-2) having a very similar $\delta^{60}\text{Ni}$
 224 of $0.22 \pm 0.06\text{‰}$. The single analysed pyroxenite xenolith (BD744) have a sig-
 225 nificantly higher $\delta^{60}\text{Ni}$ than all other samples: $0.36 \pm 0.08\text{‰}$. The mean $\delta^{60}\text{Ni}$
 226 value of all peridotite xenolith samples is $0.22 \pm 0.08\text{‰}$ (i.e. excluding the
 227 pyroxenite and dunite samples).

228 The Gorgona samples show a similar range in $\delta^{60}\text{Ni}$ to the peridotite
 229 xenoliths, with $\delta^{60}\text{Ni}$ values ranging from 0.15 to 0.26‰ . The three olivine
 230 cumulate samples display lower $\delta^{60}\text{Ni}$ values of $0.15 \pm 0.05\text{‰}$, $0.19 \pm 0.04\text{‰}$
 231 and $0.22 \pm 0.04\text{‰}$ respectively, while the two komatiite samples show slightly
 232 higher $\delta^{60}\text{Ni}$ of $0.24 \pm 0.06\text{‰}$ and $0.26 \pm 0.07\text{‰}$.

233 The $\delta^{60}\text{Ni}$ for each mineral separate is given in Table 2 and reveals min-
 234 eralogical differences. Olivine ranges from $0.14 \pm 0.05\text{‰}$ for sample C273Q
 235 to $0.17 \pm 0.05\text{‰}$ for P13, whereas orthopyroxenes show much lower values
 236 of $-0.04 \pm 0.04\text{‰}$ (C235A) and $-0.02 \pm 0.06\text{‰}$ (P13). The single lherzolite
 237 clinopyroxene separate analysed displays an extremely high $\delta^{60}\text{Ni}$ value of

238 $2.83 \pm 0.11\%$, while the harzburgite clinopyroxene sample also displays a
 239 heavy, though less extreme, value of $0.42 \pm 0.08\%$. The sole garnet analysed
 240 shows an intermediate $\delta^{60}\text{Ni}$ of $0.30 \pm 0.06\%$.

241 Results of meteorite analyses are given in Table 3. The Ni isotope com-
 242 position of eight of the nine iron meteorites analysed show a range in $\delta^{60}\text{Ni}$
 243 from 0.20% to 0.36% , with no systematic differences between sample groups.
 244 The last iron meteorite, Duel Hill (IVA), displays a significantly lighter iso-
 245 tope composition of $-0.06 \pm 0.06\%$. Chondrite meteorites display a range in
 246 $\delta^{60}\text{Ni}$ similar to that of iron meteorites. Of the carbonaceous chondrites
 247 the CI1 chondrite Orgueil show the lowest value of $0.18 \pm 0.04\%$, Allende
 248 and Murchison (CV3 and CM2, respectively) possess very similar values of
 249 $0.24 \pm 0.07\%$ and $0.23 \pm 0.07\%$, respectively, whereas Ornans (CO3) show
 250 a slightly higher value of $0.29 \pm 0.08\%$. The two enstatite chondrites In-
 251 darch (EH4) and Khaipur (EL6) have very similar values of $0.28 \pm 0.09\%$
 252 and $0.29 \pm 0.08\%$. The most variation in $\delta^{60}\text{Ni}$ within chondrite meteorites is
 253 found amongst ordinary chondrites. This group of six samples (two each from
 254 the H, L and LL classes) display $\delta^{60}\text{Ni}$ values varying between $0.16 \pm 0.05\%$
 255 and $0.51 \pm 0.07\%$.

256 5. Discussion

257 5.1. Evidence for mineralogical control on $\delta^{60}\text{Ni}$ variations in mantle rocks

258 The data from mineral separates demonstrate a significant degree of high
259 temperature Ni isotope fractionation in mantle rocks. The two orthopyrox-
260 ene separates are isotopically light relative to the two olivine separates and
261 both olivine and orthopyroxene separates are significantly lighter than both
262 clinopyroxene and garnet (Fig. 1). Nickel is situated in the same lattice po-
263 sition (replacing Mg in octahedral coordination) in all the analysed minerals,
264 so the different isotope compositions of minerals is unlikely to be due to crys-
265 tallographic differences. To investigate inter-sample mineral relationships all
266 main three silicate phases (olivine, orthopyroxene and clinopyroxene) of the
267 spinel lherzolite sample P13 were analysed. Analyses of dunite DTS-1 di-
268 gested in low-pressure beakers, with the spinels remaining undissolved, show
269 no difference in $\delta^{60}\text{Ni}$ from samples digested in high-pressure vessels. This
270 indicates that spinel may not have a large impact on the sample Ni isotope
271 composition. So although the co-existing spinel ($\sim 5\%$ modal mineralogy
272 of sample, Lee et al. (1996); Table 2) was not analysed for sample P13 an
273 approximative Ni isotope composition of the bulk sample was calculated as
274 $\delta^{60}\text{Ni} = 0.25 \pm 0.13\text{‰}$ (the comparatively large error on this value reflects the

275 propagation of errors on individual mineral separate analyses). This value is
276 consistent with data from other peridotites. The same mineral separates from
277 sample P13 were also analysed for their Fe isotope composition by Williams
278 et al. (2005) (see supplementary material for $\delta^{57}\text{Fe}$ values), who determined
279 them to be in inter-mineral isotope equilibrium in terms of Fe isotopes. The
280 bulk $\delta^{57}\text{Fe}$ for this sample, calculated from the mineral separate data, was
281 determined to be $\delta^{57}\text{Fe}_{P13} = 0.15 \pm 0.18\text{‰}$, which also overlaps with man-
282 tle $\delta^{57}\text{Fe}$ values (e.g. Dauphas et al., 2009). Furthermore, the trace-element
283 abundances of P13 demonstrate this sample's primitive, unmetasomatised
284 nature (Lee et al., 1996). Therefore, there is no indication that this sample
285 or its calculated bulk isotope composition is anomalous.

286 It is possible that the extremely heavy isotope composition of the P13
287 clinopyroxene represents kinetic isotope fractionation rather than equilibrium
288 fractionation. While Fe isotopes do appear to record inter-mineral isotope
289 equilibrium (within error), the mass balance of Fe and Ni is very different in
290 mantle rocks, making it possible for kinetic isotope effects to be preserved for
291 Ni isotopes alone. However, considering that the equilibration temperature
292 for sample P13 has been calculated to $>800^\circ\text{C}$ (Lee et al., 1996) it is unlikely
293 that kinetic isotope effects would be preserved in individual minerals. The

294 very heavy isotope composition of clinopyroxene from P13 could also have
 295 been skewed by undiscovered mineral inclusions present in the sample. Such
 296 inclusions would need to be both very Ni-rich and to possess an extreme
 297 isotope composition to have an effect on the sample. As the dissolution of
 298 this sample was not performed in a high-pressure vial it is unlikely that any
 299 spinel inclusion was accidentally dissolved. Similarly, published data have
 300 shown that sulphides are isotopically very light (as low as -1.03‰ ; Gueguen
 301 et al., 2013; Hofmann et al., 2014). One possibility is a base metal grain,
 302 as these are the only phases with significant Ni that are also predicted to
 303 be isotopically heavy with respect to silicate (Lazar et al., 2012). However,
 304 in this case, the sample would have displayed anomalously high Ni concen-
 305 trations, which was not observed. Moreover, these are extensively studied
 306 samples and the presence of metal grains would have been apparent in trace
 307 element analyses (Lee et al., 1996) or the Fe isotope study by Williams et al.
 308 (2005). Additionally, as the other clinopyroxene analysis (from harzburgite
 309 N12; $0.42 \pm 0.08\text{‰}$) and the analysis of the pyroxenite xenolith (BD744;
 310 $0.36 \pm 0.08\text{‰}$) both show significantly heavier values than all other miner-
 311 als and bulk rocks, it seems likely that an isotopically heavy composition for
 312 clinopyroxene in mantle rocks is normal. The limited data and variable degree

313 of Ni isotope fractionation between clinopyroxene and other silicate minerals
314 make it premature to determine the causes of the P13 clinopyroxene isotope
315 composition. Nonetheless, its heavy composition effectively demonstrates the
316 potential impact of the modal mineralogy of the fractionating assemblages on
317 the bulk Ni isotope compositions of mantle rocks. This suggests significant
318 implications for the Ni isotope compositions of mantle partial melts derived
319 from depleted (olivine-dominated) versus enriched (pyroxene-dominated, po-
320 tentially as a consequence of surface recycling) lithologies. The nickel stable
321 isotope compositions of primitive melts may therefore, in combination with
322 other tracers, be a useful tracer of mantle source lithology.

323 Figure 2 shows the modal mineral abundances of olivine, orthopyroxene
324 and clinopyroxene in the Tanzanian xenolith samples plotted against their
325 whole-rock $\delta^{60}\text{Ni}$. There is a striking positive correlation between whole-
326 rock $\delta^{60}\text{Ni}$ and the modal abundance of clinopyroxene, with the isotopically
327 heaviest sample containing the most clinopyroxene. The figure shows that
328 the heavy harzburgite (BD774) contains 2-3 times as much clinopyroxene as
329 the other two harzburgite samples. This suggests that, although the majority
330 of Ni in mantle rocks is located in olivine, whole-rock Ni isotope compositions
331 are strongly dependent on the proportion of clinopyroxene. From the very

332 strong preference of clinopyroxene for isotopically heavy Ni (Fig. 1, Table 2)
333 this is entirely understandable.

334 A compilation of all the available $\delta^{60}\text{Ni}$ data of ultramafic rocks divided
335 according to sample type is also shown in Fig. 1 (smaller triangles). Pre-
336 viously published data for unaltered peridotite samples are all analyses of
337 the rock reference material PCC-1, DTS-1, DTS-2 (USGS) and JP-1 (GJS)
338 (Steele et al., 2011; Gueguen et al., 2013; Chernonozhkin et al., 2015). The
339 USGS reference sample PCC-1 is a harzburgite (Cazadero ultramafic massif,
340 California) and DTS-1, -2 (Twin Sisters Mountain, Washington) and JP-1
341 (Horoman dunite, Japan; Imai et al., 1995) are dunites. All these reference
342 materials are from Alpine-type ultramafic massifs, similar to the Appalachian
343 dunite NHM-1 analysed during this study. All the analyses of dunites and
344 most of the harzburgites show these depleted olivine-rich rock types have
345 light Ni isotope compositions relative to lherzolites (Fig. 1). This is entirely
346 consistent with our mineral Ni isotope data, and, as discussed above, high-
347 lights the potential of Ni isotopes as a tracer of mantle mineral heterogeneity.
348 However, an alternative possibility that must be considered is that the low
349 $\delta^{60}\text{Ni}$ signatures of the peridotite massif samples (PCC-1, DTS-1 and -2, JP-1
350 and NHM-1) reflect secondary alteration processes, such as serpentinisation.

351 To evaluate this possibility we have also plotted published data for serpen-
352 tinised peridotites in Fig. 1 (smaller circles). These samples come from four
353 different locations: the Logatchev hydrothermal field on the mid-Atlantic
354 ridge (Gueguen et al., 2013), the Cerro Matoso laterite deposit, Colombia
355 (Gall et al., 2013), the Barro Alto ultramafic massif, Brazil (Ratié et al.,
356 2015), and the ophiolitic belt in Albania (Estrade et al., 2015). All but one
357 of these samples display $\delta^{60}\text{Ni}$ similar to fresh peridotite xenoliths, varying
358 between 0.09‰ and 0.32‰. These data suggest that $\delta^{60}\text{Ni}$ in peridotites is
359 not significantly affected by serpentinization and that such processes can-
360 not be responsible for the large range in $\delta^{60}\text{Ni}$ found in mantle rocks. It
361 is furthermore possible for other processes, such as refertilisation and recy-
362 cling, to have influenced the Ni isotope composition of peridotites. However,
363 metasomatic processes would enrich peridotites in mainly incompatible ele-
364 ments. As Ni is a very compatible element in mantle rocks it is unlikely that
365 peridotite Ni isotope composition should be affected by metasomatism.

366 Our data demonstrate that whole-rock $\delta^{60}\text{Ni}$ variations most likely reflect
367 mineral isotope fractionation effects and also provide an indication of how
368 this affects the isotope composition of bulk rocks and melt depleted residues.
369 Due to the non-modal nature of partial melting processes and the preferential

370 contribution of clinopyroxene to the melting assemblage, isotopically heavy
 371 clinopyroxene could contribute to melt extraction generating depleted mantle
 372 residues with light Ni isotope composition relative to fertile mantle material.
 373 This could be the reason for olivine-rich cumulate komatiites from Gorg-
 374 ona displaying lower $\delta^{60}\text{Ni}$ relative to the primitive komatiite samples from
 375 the same suite, and that dunites and harzburgites appear to be isotopically
 376 lighter than lherzolites (Fig. 1). Therefore, a best estimate of the primitive
 377 mantle $\delta^{60}\text{Ni}$ may be defined by the composition of the three lherzolites (two
 378 from Lashaine volcano and one from a South African kimberlite) and the
 379 two Gorgona komatiite samples. The suitability of these samples as a base
 380 for estimating the Ni isotope composition of the BSE is further supported
 381 by their overlap with the komatiite samples analysed. That these two sets
 382 of rock types are completely within error of each other broadly supports ho-
 383 mogenous distribution of Ni isotopes in the mantle. This yields a $\delta^{60}\text{Ni}_{\text{mantle}}$
 384 value of $0.23 \pm 0.06\text{‰}$ (mean and 2 s.d. of all measurements of these sam-
 385 ples; $n = 25$). The calculated bulk rock $\delta^{60}\text{Ni}$ for the fertile lherzolite sample
 386 P13 ($0.25 \pm 0.13\text{‰}$) is also in excellent agreement with this narrower $\delta^{60}\text{Ni}$
 387 estimate for the mantle.

388 Published Fe isotope data exist for the Gorgona komatiites (data from

389 Hibbert et al., 2012) the ultramafic reference materials PCC-1, DTS-2 (from
390 Dauphas et al., 2009), DTS-1 and JP-1 (from Poitrasson et al., 2004) and for
391 the mineral separates from spinel lherzolite P13 (from Williams et al., 2005).
392 When these data are plotted against $\delta^{60}\text{Ni}$ a clear positive relationship is
393 observed for all but one of the whole-rock samples ($R^2 = 0.936$; Fig. 3). The
394 isotopically heaviest samples for both Ni and Fe are the komatiites, while
395 olivine-rich cumulates and rocks have lower $\delta^{60}\text{Ni}$ and $\delta^{57}\text{Fe}$ values.

396 The heavy Fe isotope compositions of mantle partial melts relative to
397 peridotites has previously been interpreted in terms of partial melting and
398 the preferential partitioning of isotopically heavy Fe into the melt phase (e.g.
399 Williams et al., 2005; Dauphas et al., 2010, 2014). Interestingly, while Fe and
400 Ni isotopes appear to show similar behaviour, the partitioning of Fe isotopes
401 between melt and residue has been interpreted to be at least in part a function
402 of the more incompatible nature of isotopically heavy Fe^{3+} (Williams et al.,
403 2005; Dauphas et al., 2010, 2014). As Ni is not a redox-sensitive element
404 under the conditions of mantle partial melting the strong correlation between
405 Fe and Ni isotopes must therefore reflect other processes that do not relate to
406 variations in oxidation state but which affect both isotope systems, such as
407 variations in mantle melting lithology (e.g. Williams and Bizmis, 2014). The

408 mineral separates (olivine and orthopyroxene) as well as the reconstructed
 409 composition of P13 are also plotted in Fig. 3. The calculated composition
 410 for this sample ($\delta^{60}\text{Ni}_{P13} = 0.25 \pm 0.13\text{‰}$ and $\delta^{57}\text{Fe}_{P13} = 0.15 \pm 0.18\text{‰}$) plots
 411 together with the komatiites at the heavier end of the spectrum, another
 412 indication of this sample's fertility. The olivine separate from sample P13
 413 plots along the trend next to the Gorgona olivine cumulates. However, the
 414 P13 orthopyroxene separate has a very low $\delta^{60}\text{Ni}$ given its relatively high
 415 $\delta^{57}\text{Fe}$ and thus does not plot on the main trend. On the other hand, the P13
 416 orthopyroxene overlaps with the only whole-rock sample (DTS-1) that does
 417 not follow the general trend (Fig. 3), possibly indicating a higher prevalence
 418 of orthopyroxene in this sample. The $\delta^{57}\text{Fe}$ of the P13 clinopyroxene separate
 419 is heavier than the values for olivine and orthopyroxene (see insert on Fig.
 420 3), although due to its extremely high $\delta^{60}\text{Ni}$ this mineral plots far from
 421 the general $\delta^{60}\text{Ni}$ – $\delta^{57}\text{Fe}$ trend seen in Fig. 3. This may be indicative of
 422 isotopic disequilibrium between these phases, and future studies are required
 423 to confirm this.

424 *5.2. Isotope composition of the BSE, meteorites and Ni isotope fractionation*
425 *during core formation*

426 Given that $>99\%$ of the Ni in the silicate Earth is located in the mantle,
427 our value of $\delta^{60}\text{Ni}_{\text{mantle}}$ of $0.23 \pm 0.06\text{‰}$ is also the best estimate for the
428 BSE. This is in good agreement with the previously suggested the value
429 of $0.18 \pm 0.04\text{‰}$ by Steele et al. (2011) and overlaps with the $0.15 \pm 0.24\text{‰}$
430 proposed by Cameron et al. (2009), while a third estimate of $0.05 \pm 0.05\text{‰}$
431 by Gueguen et al. (2013) is significantly lighter than all of these. All these
432 studies however incorporate data for altered mantle and fractionated crustal
433 rocks in their estimates. In contrast, the BSE estimate presented in this
434 study is entirely based on fertile lherzolites and komatiites. Considering the
435 evidence given here for a mineralogical control on the Ni isotope composition,
436 this new estimate should represent a more accurate evaluation of the mean
437 Ni isotope composition of the Bulk Silicate Earth.

438 Chondritic meteorites have previously been found to vary between be-
439 tween 0.18‰ and 0.33‰ (Fig. 5 – Cameron et al., 2009; Steele et al., 2012).
440 The mass-dependent Ni isotope data of chondrites from Moynier et al. (2007)
441 and Cook et al. (2007) are not included here, as almost all data from these
442 studies are from measurements of chondrite metal separates and not whole-

443 rock samples. The only exception to this are two measurements of bulk
 444 silicate samples in Moynier et al. (2007), one of Allende (CV3 chondrite) and
 445 one of Murchison (CM2 chondrite). These data are however significantly
 446 lighter (approximately -0.2‰, Fig. 5) than both our and the Cameron et al.
 447 (2009) analyses of the same chondrite samples. This is probably due to the
 448 chemical separation technique used by Moynier et al. (2007), from which the
 449 Ni yield was only about 80% for silicates. As neither Moynier et al. (2007)
 450 nor Cook et al. (2007) used the double-spike technique, any stable isotope
 451 fractionation relating to chemical processing may not have been adequately
 452 corrected for. Additionally, errors on measurements performed in these two
 453 studies are significantly larger (estimated $\pm 0.14\text{‰}$ on $\delta^{60}\text{Ni}$ from Moynier
 454 et al. (2007); up to $\pm 0.80\text{‰}$ on $\delta^{60}\text{Ni}$ from Cook et al. (2007); Fig. 5)
 455 than errors for values presented here or other more recently published data,
 456 making direct comparisons difficult.

457 Our data for chondrite meteorites suggest that ordinary chondrites span
 458 a larger range of $\delta^{60}\text{Ni}$ than carbonaceous or enstatite chondrites (Fig. 6).
 459 The isotopically heaviest of these sample is Bruderheim (L5), an ordinary
 460 chondrite that has been noted to have large mineralogical variations between
 461 the metallic and the silicate phase and a lower average olivine:pyroxene ratio

462 than normal for chondrites (Duke et al., 1961). This makes it difficult to be
 463 certain that the $\delta^{60}\text{Ni}$ measured here is representative of its bulk isotope com-
 464 position, especially considering the above evidence of a mineralogical control
 465 on a sample's Ni isotope composition. Excluding this one heavy sample our
 466 mean $\delta^{60}\text{Ni}$ value for chondrites becomes $0.26 \pm 0.12\text{‰}$ (mean and 2 s.d. of
 467 all measurements of these samples; $n = 71$), which in excellent agreement
 468 with published values for similar samples (Cameron et al., 2009; Steele et al.,
 469 2012). Even excluding Bruderheim, ordinary chondrites still show a large
 470 variation in $\delta^{60}\text{Ni}$. One possible explanation is an isotopically heavy metal
 471 component, as there appears to be a relationship between the metal content
 472 (LL, L, or H class) and the Ni isotope composition in ordinary chondrites
 473 (Fig. 6). This correlates well with high T metal-talc experiments by Lazar
 474 et al. (2012) that found indications for the metal phase being isotopically
 475 heavy relative to silicate.

476 Figure 6 also shows the Ni isotope composition of iron meteorites dis-
 477 played according to their meteorite class. Apart from the one very light sam-
 478 ple (Duel Hill, IVA, $-0.06 \pm 0.06\text{‰}$) the data for iron meteorites are all within
 479 error and do not show any indications of their Ni isotope composition being
 480 dependent on class. This light outlier sample Duel Hill is likely anomalous,

481 especially considering its low concentration of Ir and W, combined with very
 482 high concentrations of Au, As, Cu and Ni (Wasson and Richardson, 2001).
 483 This points towards this meteorite being a sample of core material that has
 484 undergone extreme degrees of fractional crystallisation, possibly crystallising
 485 very late from the parental magma (Wasson and Richardson, 2001). It is
 486 also possible that this sample does not at all belong to the main crystallisa-
 487 tion sequence of the IVA parent body (Smoliar et al., 1996, based on Re-Os
 488 dating). Omitting the Duel Hill sample, our analyses of iron meteorites give
 489 a mean $\delta^{60}\text{Ni}$ of $0.29 \pm 0.10\text{‰}$ (mean and 2 s.d. of all measurements of these
 490 samples; $n = 47$). The range in $\delta^{60}\text{Ni}$ we observe for iron meteorites is in
 491 very good agreement with published data from Cameron et al. (2009); Steele
 492 et al. (2011); Gueguen et al. (2013) and Chernonozhkin et al. (2015). The
 493 Ni isotope data from Moynier et al. (2007) and Cook et al. (2007) are, again,
 494 spread over a much wider range than any other published data (Fig. 5),
 495 although this may in part be due to the wider range of samples, such as
 496 non-magmatic iron meteorites, included in these studies.

497 It has recently been shown that the BSE has a chondritic stable isotope
 498 composition for Mo (Greber et al., 2015) and Cr (Bonnand et al., 2015)
 499 (contrary to earlier suggestions by Hin et al., 2013; Burkhardt et al., 2014;

500 Moynier et al., 2011). On the other hand the BSE is non-chondritic for Si
 501 stable isotopes (ascribed to core formation by Armytage et al., 2011), and
 502 also for V isotopes (Prytulak et al., 2013; Nielsen et al., 2014, reasons re-
 503 main unclear). The similarity in mean $\delta^{60}\text{Ni}$ between chondrites, iron mete-
 504 orites and the BSE indicates that, in the case of Ni isotopes, core formation
 505 was not accompanied by any measurable isotope fractionation. This con-
 506 clusion is consistent with the study by Lazar et al. (2012), based on solid
 507 metal-talc Ni isotope fractionation experiments. These authors found that
 508 even though the metal appears to be consistently slightly isotopically heav-
 509 ier than the silicate phase, the fractionation factor is minor at core-mantle
 510 boundary conditions ($\Delta^{60}\text{Ni}_{\text{metal-talc}} = 0.02\text{‰}$ at 2500 K). The authors also
 511 noted that metal-silicate isotope fractionation appear to be temperature de-
 512 pendent. When using their expression for this ($\Delta^{62}\text{Ni}_{\text{metal-talc}} = 0.25(\pm 0.02)$
 513 $\times 10^6/\text{T}^2$ (± 2 s.e.)) to calculate the fractionation factor at mantle tem-
 514 peratures, $\Delta^{60}\text{Ni}_{\text{metal-talc}}$ varies between 0.04 and 0.09‰ for temperatures
 515 from 1400 down to 900°C (Fig. 7). If the fractionation factor is based on
 516 our $\delta^{60}\text{Ni}$ data for the BSE and iron meteorites (IM), $\Delta^{60}\text{Ni}_{\text{IM-BSE}}$ becomes
 517 0.056‰ (± 0.06 ; s.d.), which would correspond to a temperature of at least
 518 1200°C (Fig. 7). The similarity in isotope composition for chondrites and

519 iron meteorites furthermore implies that iron meteorites were all formed in
 520 equilibrium with silicate mantles at high temperatures, with no Rayleigh ef-
 521 fects preserved. This supports the concept of magmatic iron meteorites being
 522 relict planetary cores and not impact melts.

523 6. Conclusions

- 524 1. Our data show that the upper mantle is variable in its Ni isotope com-
 525 position, with a mean value of 0.23‰ . ($\pm 0.13\text{‰}$, 2 s.d.; $n = 66$)
- 526 2. There are systematic variations in $\delta^{60}\text{Ni}$ between different mantle min-
 527 erals, with olivine and orthopyroxene being significantly lighter than
 528 clinopyroxene, providing evidence that mantle Ni isotope compositions
 529 are controlled by differences in mineralogy caused by melt extraction
 530 and fractional crystallisation.
- 531 3. There is a relationship between $\delta^{57}\text{Fe}$ and $\delta^{60}\text{Ni}$ in ultramafic rocks re-
 532 lated to mineralogy, with lower values of both isotope systems recorded
 533 in olivine-rich dunite and harzburgite and higher values shown in more
 534 fertile material.
- 535 4. Our best estimate for the $\delta^{60}\text{Ni}_{BSE}$ is $0.23 \pm 0.06\text{‰}$ based solely on lher-
 536 zolite xenoliths and Phanerozoic komatiites. This is in good agreement

537 with previously suggested values of Cameron et al. (2009) and Steele
538 et al. (2011) but heavier than the value proposed by Gueguen et al.
539 (2013).

540 5. Comparison between our BSE value and Ni isotope data for chondrite
541 meteorites indicates that the BSE is chondritic and that core formation
542 did not generate any measurable Ni isotope fractionation.

543 6. Iron meteorites generally display chondritic $\delta^{60}\text{Ni}$, with a mean of
544 $0.29 \pm 0.10\text{‰}$. However, Duel Hill is very light ($-0.06 \pm 0.06\text{‰}$), which
545 is likely related to extreme fractional crystallisation associated with
546 this sample.

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562 **Figure and Table captions:**

563 **Figure 1:** The figure shows Ni isotope data for whole-rocks and min-
564 eral separates together with previously published data of peridotite reference
565 materials and serpentinites. The smaller data points represent published
566 Ni isotope data from Gueguen et al. (2013)^(1,2,8) and Chernonozhkin et al.
567 (2015)^(1,2,4), Steele et al. (2011)^(3,4), Ratié et al. (2015)⁽⁵⁾, Estrade et al.
568 (2015)⁽⁶⁾, Gall et al. (2013)⁽⁷⁾. The anomalous measurement of PCC-1 by
569 Cameron et al. (2009), is not included in this comparison. A best estimate of
570 the Ni isotope composition of the mantle, $\delta^{60}\text{Ni} = 0.23 \pm 0.06\text{‰}$, is highlighted
571 as the shaded area.

572 **Figure 2:** The figure shows the modal mineral abundances of olivine,
573 orthopyroxene and clinopyroxene in the Tanzanian lherzolite and harzburgite
574 xenoliths plotted against their whole-rock $\delta^{60}\text{Ni}$ values. Clinopyroxene
575 is highlighted separately on the right to demonstrate that a heavy isotope
576 composition for whole rocks is likely due to a larger amount of isotopically
577 heavy clinopyroxene.

578 **Figure 3:** $\delta^{60}\text{Ni}$ plotted against $\delta^{57}\text{Fe}$ for the Gorgona samples, the peri-
579 dotite reference materials PCC-1, DTS-1, DTS-2, JP-1 and the spinel lher-
580 zolite P13 mineral separates. Nickel isotope data for DTS-2 and JP-1 are

581 from Steele et al. (2011). Iron isotope data for PCC-1 and DTS-2 are from
582 Dauphas et al. (2009), DTS-1 and JP-1 from Poitrasson et al. (2004), P13
583 and its mineral separates from Williams et al. (2009), and the komatiites and
584 olivine cumulates from Hibbert et al. (2012). These data suggest a relation-
585 ship between the two isotope systems in mantle rocks. All Fe isotope data
586 can be found in a supplemental data table.

587 **Figure 4:** A summary of our Ni isotope data from mantle xenoliths,
588 komatiites, cumulates and meteorites. The Ni isotope composition of the
589 BSE, $\delta^{60}\text{Ni} = 0.23 \pm 0.06\text{‰}$, is highlighted as the shaded area.

590 **Figure 5:** Comparison between meteorite data from this study and pub-
591 lished data from Cameron et al. (2009); Steele et al. (2011, 2012); Gueguen
592 et al. (2013); Chernonozhkin et al. (2015); Moynier et al. (2007); Cook et al.
593 (2007). The chondrite data from Moynier et al. (2007) and Cook et al. (2007)
594 are from metal separates, not whole-rock samples.

595 **Figure 6:** Nickel isotope composition of meteorites plotted against the Ni
596 content and divided into meteorite class. Based on these data there appear
597 to be a relationship between a ordinary chondrite metal content (class LL,
598 L, H) and Ni isotope composition, apart from in sample Bruderheim.. Iron
599 meteorites do not show a similar relationship between $\delta^{60}\text{Ni}$ and class. The

one very light iron meteorite sample (Duel Hill, $-0.06 \pm 0.06\text{‰}$) contains up to twice the amount of Ni compared to the other iron meteorites.

Figure 7: Nickel isotope data from metal-talc experiments by Lazar et al. (2012) suggest that Ni isotope fractionation between metal and silicate is temperature dependant, with $\Delta^{60}\text{Ni}_{\text{metal-talc}}$ being very small at normal mantle temperatures. Our data from iron meteorites (IM) and mantle rocks (BSE) give an average Ni isotope fractionation ($\Delta^{60}\text{Ni}_{\text{IM-BSE}}$) between these phases of 0.056‰ ($\pm 0.12\text{‰}$, 2 s.d.; the large error on this value is due to the propagation of errors on individual sample analyses), which would put the minimum exposure temperature for these samples to $\sim 1200^\circ\text{C}$.

Table 1: Sample information and results for peridotite and komatiites analysed for their Ni isotope composition. Chemical as well as mineral compositions are taken from Dawson et al. (1970); Dawson and Smith (1972); Reid et al. (1975) for the mantle xenoliths and from Kerr et al. (1996) for the komatiites.

Table 2: Sample information and results for mineral separates from three lherzolite xenoliths from the Cameroon Line analysed for their Ni isotope composition. Modal mineral compositions are from Lee et al. (1996) and geochemical data from Williams et al. (2005).

619 **Table 3:** Sample information and results for meteorites analysed for their
620 Ni isotope composition. All samples analysed were from the Natural History
621 Museum, London (BM) apart from three iron meteorites from the Smithso-
622 nian National Museum of Natural History, Washington D.C. (USNM). The
623 Ni concentrations are published values for each meteorite: a = Kallemeyn
624 et al. (1989); b = Morgan et al. (1985); c = McSween (1977); d = Hertogen
625 et al. (1983); e = Duke et al. (1961); f = Jarosewich (1990); g = Wasson
626 (1969); h = Buchwald (1975); i = Goldberg et al. (1951); j = Wasson and
627 Richardson (2001); k = Scott et al. (1973).

628 **Supplementary material - Table 1:** Iron isotope data ($\delta^{57}\text{Fe}$) of
629 whole-rock and mineral samples used in Figure 3.

- 630 W. F. McDonough, S. S. Sun, The composition of the Earth, *Chemical Geology* 120 (3-4)
631 (1995) 223–253.
- 632 H. Palme, H. S. C. O'Neill, Cosmochemical estimates of mantle composition, in: R. W.
633 Carlson (Ed.), *Treatise on Geochemistry: The Mantle and Core*, chap. 3.1, Elsevier
634 Ltd., 2 edn., 1–38, 2014.
- 635 H. Sato, Nickel content of basaltic magmas: identification of primary magmas and a
636 measure of the degree of olivine fractionation, *Lithos* 10 (1977) 113–120.
- 637 H. G. Stosch, Sc, Cr, Co and Ni partitioning between minerals from spinel peridotite
638 xenoliths, *Contributions to Mineralogy and Petrology* 78 (2) (1981) 166–174.
- 639 W. A. Deer, R. A. Howie, J. Zussman, *Rock Forming Minerals*, vol. Vol. 1A and 2A,
640 Longman, 2nd edn., 1982.
- 641 G. Witt-Eickschen, H. S. O'Neill, The effect of temperature on the equilibrium distribution
642 of trace elements between clinopyroxene, orthopyroxene, olivine and spinel in upper
643 mantle peridotite, *Chemical Geology* 221 (1-2) (2005) 65–101.
- 644 F. Kaminsky, Mineralogy of the lower mantle: a review of ‘super-deep’ mineral inclusion
645 in diamond, *Earth Science Reviews* 110 (2012) 127–147.
- 646 D. J. Frost, C. Liebske, F. Langenhorst, M. C. A., Experimental evidence for the existence
647 of iron-rich metal in the Earth’s lower mantle, *Nature* 428 (2004) 409–412.
- 648 J. Wade, B. J. Wood, Core formation and the oxidation state of the Earth, *Earth and*
649 *Planetary Science Letters* 236 (2005) 78–95.

650 H. M. Williams, B. J. Wood, J. Wade, D. J. Frost, J. Tuff, Isotopic evidence for internal
 651 oxidation of the Earth's mantle during accretion, *Earth and Planetary Science Letters*
 652 321–322 (2012) 54–63.

653 V. Cameron, D. Vance, C. Archer, C. H. House, A biomarker based on the stable isotopes
 654 of nickel, *Proceedings of the National Academy of Sciences* 106 (27) (2009) 10944–10948.

655 R. C. J. Steele, T. Elliott, C. D. Coath, M. Regelous, Confirmation of mass-independent
 656 Ni isotopic variability in iron meteorites, *Geochimica et Cosmochimica Acta* 75 (24)
 657 (2011) 7906–7925.

658 L. Gall, H. Williams, C. Siebert, A. Halliday, Determination of mass-dependent varia-
 659 tions in nickel isotope compositions using double spiking and MC-ICPMS, *Journal of*
 660 *Analytical Atomic Spectrometry* 27 (2012) 137.

661 L. Gall, H. M. Williams, C. Siebert, A. N. Halliday, R. J. Herrington, J. R. Hein, Nickel
 662 isotopic compositions of ferromanganese crusts and the constancy of deep ocean inputs
 663 and continental weathering effects over the Cenozoic, *Earth and Planetary Science*
 664 *Letters* 375 (2013) 148–155.

665 B. Gueguen, O. Rouxel, E. Ponzevera, Nickel Isotope Variations in Terrestrial Silicate
 666 Rocks and Geological Reference Materials Measured by MC-ICP-MS, *Geostandards*
 667 *and Geoanalytical Research* (2013) doi: 10.1111/j.1751–908X.2013.00209.x.

668 S. M. Chernozhkin, S. Goderis, L. Lobo, P. Claeys, F. Vanhaecke, Development of
 669 an isolation procedure and MC-ICP-MS measurement protocol for the study of stable

670 isotope ratio variations of nickel, *Journal of Analytical Atomic Spectrometry* 30 (2015)
671 1518–1530.

672 G. Ratié, D. Jouvin, J. Garnier, O. Rouxel, S. Miska, E. Guimarães, L. C. Vieira, Y. Sivry,
673 I. Zelano, E. M. Pelletier, F. Thil, C. Quantin, Nickel isotope fractionation during
674 tropical weathering of ultramafic rocks, *Chemical Geology* 402 (C) (2015) 68–76.

675 N. Estrade, C. Cloquet, G. Echevarria, T. Sterckeman, T. Deng, Y. Tang, J.-L. Morel,
676 Weathering and vegetation controls on nickel isotope fractionation in surface ultramafic
677 environments (Albania), *Earth and Planetary Science Letters* 423 (C) (2015) 24–35.

678 D. L. Cook, M. Wadhwa, R. N. Clayton, N. Dauphas, P. E. Janney, A. M. Davis, Mass-
679 dependent fractionation of nickel isotopes in meteoritic metal, *Meteoritics & Planetary*
680 *Science* 42 (12) (2007) 2067–2077.

681 F. Moynier, J. Blichert-Toft, P. Télouk, J. M. Luck, Comparative stable isotope geo-
682 chemistry of Ni, Cu, Zn, and Fe in chondrites and iron meteorites, *Geochimica et*
683 *Cosmochimica Acta* 71 (2007) 4365–4379.

684 R. C. J. Steele, C. D. Coath, M. Regelous, S. Russell, T. Elliott, Neutron-poor Nickel
685 Isotope Anomalies in Meteorites, *The Astrophysical Journal* 758 (1) (2012) 59.

686 A. Hofmann, A. Bekker, P. Dirks, B. Gueguen, Comparing orthomagmatic and hydrother-
687 mal mineralization models for komatiite-hosted nickel deposits in Zimbabwe using
688 multiple-sulfur, iron, and nickel isotope data, *Mineralium Deposita* .

689 S. J. Porter, D. Selby, V. Cameron, Characterising the nickel isotopic composition of
690 organic-rich marine sediments, *Chemical Geology* 387 (2014) 12–21.

691 V. Cameron, D. Vance, Heavy nickel isotope compositions in rivers and the oceans,
692 *Geochimica et Cosmochimica Acta* 128 (2014) 195–211.

693 L. E. Wasylenki, H. D. Howe, L. J. Spivak-Birndorf, D. L. Bish, Ni isotope fractionation
694 during sorption to ferrihydrite: Implications for Ni in banded iron formations, *Chemical*
695 *Geology* 400 (C) (2015) 56–64.

696 J. B. Dawson, D. G. Powell, A. M. Reid, Ultrabasic Xenoliths and Lava from the Lashaine
697 Volcano, Northern Tanzania, *Journal of Petrology* 11 (3) (1970) 519–548.

698 R. S. Cohen, R. K. O’Nions, J. B. Dawson, Isotope geochemistry of xenoliths from East
699 Africa: implications for development of mantle reservoirs and their interaction, *Earth*
700 *and Planetary Science Letters* 68 (1984) 209–220.

701 J. B. Dawson, Metasomatism and partial melting in upper-mantle peridotite xenoliths from
702 the Lashaine volcano, northern Tanzania, *Journal of Petrology* 43 (2002) 1749–1777.

703 A. M. Reid, C. H. Donaldson, R. W. Brown, W. I. Ridley, J. B. Dawson, Mineral chemistry
704 of peridotite xenoliths from the Lashaine volcano, Tanzania, *Physics and Chemistry of*
705 *the Earth* 9 (1975) 525–543.

706 J. M. Rhodes, J. B. Dawson, Major and trace element chemistry of peridotite inclusions
707 from the Lashaine volcano, Tanzania, *Physics and Chemistry of the Earth* 9 (1975)
708 545–557.

709 J. B. Dawson, J. V. Smith, Alkalic Pyroxenite Xenoliths from the Lashaine Volcano,
710 Northern Tanzania, *Journal of Petrology* 14 (1) (1972) 113–131.

711 D. A. Carswell, J. B. Dawson, Garnet peridotite xenoliths in South African kimberlite
712 pipes and their petrogenesis, *Contributions to Mineralogy and Petrology* 25 (1970)
713 163–184.

714 J. L. Kulp, D. A. Brobst, Notes on the dunite and the geochemistry of vermiculite at the
715 Day Book dunite deposit, Yancey County, North Carolina, *Economic Geology* 49 (3)
716 (1954) 211–220.

717 A. M. Stueber, Abundances of K, Rb, Sr and Sr isotopes in ultramafic rocks and minerals
718 from western North Carolina, *Geochimica et Cosmochimica Acta* 33 (1969) 543–553.

719 F. J. Flanagan, US Geological Survey silicate rock standards, *Geochimica et Cosmochimica*
720 *Acta* 31 (1967) 289–308.

721 F. J. Flanagan, US Geological Survey standards II. First compilation of data for the new
722 USGS rocks, *Geochimica et Cosmochimica Acta* 33 (1969) 81–120.

723 I. Barnes, J. R. O’Neil, The relationship between fluids in some fresh Alpine-Type ultra-
724 mafics and possible modern serpentinization, Western United States. *Geol. Soc. America*
725 *Bulletin* 80 (1969) 1947–1960.

726 D. M. Ragan, Emplacement of the Twin Sisters dunite, Washington, *American Journal of*
727 *Science* 261 (1963) 549–565.

728 H. Williams, C. McCammon, A. H. Peslier, A. N. Halliday, N. Teutsch, S. Levasseur, J.-P.
729 Burg, Iron Isotope Fractionation and the Oxygen Fugacity of the Mantle, *Science* 304
730 (2004) 1656–1659.

731 H. Williams, A. Peslier, C. McCammon, A. Halliday, S. Levasseur, N. Teutsch, J. Burg,
732 Systematic iron isotope variations in mantle rocks and minerals: The effects of partial
733 melting and oxygen fugacity, *Earth and Planetary Science Letters* 235 (1-2) (2005)
734 435–452.

735 D. C. Lee, A. N. Halliday, G. R. Davies, E. J. Essene, J. G. Fitton, R. Temdjim, Melt
736 Enrichment of Shallow Depleted Mantle: a Detailed Petrological, Trace Element and
737 Isotopic Study of Mantle-Derived Xenoliths and Megacrysts from the Cameroon Line,
738 *Journal of Petrology* 37 (2) (1996) 415–441.

739 E. G. Nisbet, M. J. Cheadle, N. T. Arndt, M. J. Bickle, Constraining the potential tem-
740 perature of the Archaean mantle: A review of the evidence from komatiites, *Lithos*
741 30 (3-4) (1993) 291–307.

742 N. Arndt, C. M. Lesher, S. J. Barnes, *Komatiite*, Cambridge University Press, 2008.

743 N. Dauphas, F.-Z. Teng, N. T. Arndt, Magnesium and iron isotopes in 2.7 Ga Alexo
744 komatiites: Mantle signatures, no evidence for Soret diffusion, and identification of
745 diffusive transport in zoned olivine, *Geochimica et Cosmochimica Acta* 74 (11) (2010)
746 3274–3291.

747 K. E. J. Hibbert, H. M. Williams, A. C. Kerr, I. S. Puchtel, Iron isotopes in ancient and
748 modern komatiites: Evidence in support of an oxidised mantle from Archean to present,
749 *Earth and Planetary Science Letters* 321-322 (2012) 198–207.

750 N. D. Greber, I. S. Puchtel, T. F. Nägler, K. Mezger, Komatiites constrain molybdenum

751 isotope composition of the Earth's mantle, *Earth and Planetary Science Letters* 421 (C)
 752 (2015) 129–138.

753 P. S. Savage, F. Moynier, H. Chen, G. Shofner, J. Siebert, J. Badro, I. S. Puchtel, Copper
 754 isotope evidence for large-scale sulphide fractionation during Earth's differentiation,
 755 *Geochemical Perspectives Letters*, 1 (2015) 53–64.

756 R. J. Walker, M. Storey, A. C. Kerr, J. Tarney, N. T. Arndt, Implications of ^{187}Os iso-
 757 topic heterogeneities in a mantle plume: evidence from Gorgona Island and Curaçao,
 758 *Geochimica et Cosmochimica Acta* 63 (5) (1999) 713–728.

759 C. W. Sinton, R. A. Duncan, M. Storey, J. Lewis, J. J. Estrada, An oceanic flood basalt
 760 province within the Caribbean plate, *Earth and Planetary Science Letters* 155 (3-4)
 761 (1998) 221–235.

762 B. G. Aitken, L. M. Echeverría, Petrology and geochemistry of komatiites and tholeiites
 763 from Gorgona Island, Colombia, *Contributions to Mineralogy and Petrology* 86 (1)
 764 (1984) 94–105.

765 N. T. Arndt, A. C. Kerr, J. Tarney, Dynamic melting in plume heads: the formation of
 766 Gorgona komatiites and basalts, *Earth and Planetary Science Letters* 146 (1-2) (1997)
 767 289–301.

768 A. C. Kerr, G. F. Marriner, N. T. Arndt, J. Tarney, A. Nivia, A. D. Saunders, R. A.
 769 Duncan, The petrogenesis of Gorgona komatiites, picrites and basalts: new field, pet-
 770 rographic and geochemical constraints, *Lithos* 37 (2-3) (1996) 245–260.

- 771 A. C. Kerr, La Isla de Gorgona, Colombia: A petrological enigma?, *Lithos* 84 (1-2) (2005)
772 77–101.
- 773 J. W. Gramlich, E. S. Beary, L. A. Machlan, I. L. Barnes, The absolute isotopic com-
774 position and atomic weight of terrestrial nickel, *Journal of Research of the National*
775 *Institute of Standards and Technology* 94 (6) (1989) 357.
- 776 C. Siebert, T. F. Nägler, J. D. Kramers, Determination of molybdenum isotope fraction-
777 ation by double-spike multicollector inductively coupled plasma mass spectrometry,
778 *Geochemistry Geophysics Geosystems* 2 (7) (2001) doi: 10.1029/2000GC000124.
- 779 N. Dauphas, P. R. Craddock, P. D. Asimow, V. C. Bennett, A. P. Nutman, D. Ohnenstet-
780 ter, Iron isotopes may reveal the redox conditions of mantle melting from Archean to
781 Present, *Earth and Planetary Science Letters* 288 (1-2) (2009) 255–267.
- 782 C. Lazar, E. D. Young, C. E. Manning, Experimental determination of equilibrium nickel
783 isotope fractionation between metal and silicate from 500°C to 950°C, *Geochimica et*
784 *Cosmochimica Acta* 86 (C) (2012) 276–295.
- 785 N. Imai, S. Terashima, S. Itoh, A. Ando, 1994 compilation values for GSJ reference sam-
786 ples, "Igneous rock series"., *Geochemical Journal* 29 (1) (1995) 91–95.
- 787 F. Poitrasson, A. N. Halliday, D. C. Lee, S. Levasseur, N. Teutsch, Iron isotope differ-
788 ences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion
789 mechanisms, *Earth and Planetary Science Letters* 223 (3-4) (2004) 253–266.
- 790 N. Dauphas, M. Roskosz, E. E. Alp, D. R. Neuville, M. Y. Hu, C. K. Sio, F. L. H. Tissot,
791 J. Zhao, L. Tissandier, E. Medard, C. Cordier, Magma redox and structural controls

792 on iron isotope variations in Earth's mantle and crust, *Earth and Planetary Science*
 793 *Letters* 398 (2014) 127–140.

794 H. M. Williams, M. Bizmis, Iron isotope tracing of mantle heterogeneity within the source
 795 regions of oceanic basalts, *Earth and Planetary Science Letters* 404 (2014) 396–407.

796 M. Duke, D. Maynes, H. Brown, The petrography and chemical composition of the Bruder-
 797 heim meteorite, *Journal of Geophysical Research* 66 (10) (1961) 3557–3563.

798 J. T. Wasson, J. W. Richardson, Fractionation trends among IVA iron meteorites: Con-
 799 trasts with IIIAB trends, *Geochimica et Cosmochimica Acta* 65 (6) (2001) 951–970.

800 M. I. Smoliar, R. J. Walker, M. J. W, Re-Os ages of group IIA, IIIA, IVA and IVB iron
 801 meteorites, *Science* 271 (1996) 1099–1102.

802 P. Bonnand, H. M. Williams, I. J. Parkinson, W. B. J, A. N. Halliday, Stable chromium
 803 isotopic composition of meteorites and metal-silicate experiments: implications for frac-
 804 tionation during core formation, *Earth and Planetary Science Letters* 435 (2015) 14–21.

805 R. C. Hin, C. Burkhardt, M. W. Schmidt, B. Bourdon, T. Kleine, Experimental evidence
 806 for Mo isotope fractionation between metal and silicate liquids, *Earth and Planetary*
 807 *Science Letters* 379 (2013) 38–48.

808 C. Burkhardt, R. C. Hin, T. Kleine, B. Bourdon, Evidence for Mo isotope fractionation
 809 in the solar nebula and during planetary differentiation, *Earth and Planetary Science*
 810 *Letters* 391 (2014) 201–211.

811 F. Moynier, Q.-Z. Yin, E. Schauble, Isotopic Evidence of Cr Partitioning into Earth's
812 Core, *Science* 331 (6023) (2011) 1417–1420.

813 R. M. G. Armytage, R. B. Georg, P. S. Savage, H. M. Williams, A. N. Halliday, Silicon
814 isotopes in meteorites and planetary core formation, *Geochimica et Cosmochimica Acta*
815 75 (13) (2011) 3662–3676.

816 J. Prytulak, S. G. Nielsen, D. A. Ionov, A. N. Halliday, J. Harvey, K. A. Kelley, Y. L. Niu,
817 D. W. Peate, K. Shimizu, K. W. W. Sims, The stable vanadium isotope composition
818 of the mantle and mafic lavas, *Earth and Planetary Science Letters* 365 (C) (2013)
819 177–189.

820 S. G. Nielsen, J. Prytulak, B. J. Wood, A. N. Halliday, Vanadium isotopic difference
821 between the silicate Earth and meteorites, *Earth and Planetary Science Letters* 389
822 (2014) 167–175.

823 H. M. Williams, S. G. Nielsen, C. Renac, W. L. Griffin, S. Y. O'Reilly, C. A. McCam-
824 mon, N. Pearson, F. Viljoen, J. C. Alt, A. N. Halliday, Fractionation of oxygen and
825 iron isotopes by partial melting processes: Implications for the interpretation of stable
826 isotope signatures in mafic rocks, *Earth and Planetary Science Letters* 283 (1-4) (2009)
827 156–166.

828 G. W. Kallemeyn, A. E. Rubin, D. Wang, Ordinary chondrites: Bulk compositions, classi-
829 fication, lithophile-element fractionations and composition-petrographic type relation-
830 ships, *Geochimica et Cosmochimica Acta* 53 (10) (1989) 2747–2767.

- 831 J. W. Morgan, M. J. Janssens, H. Takahashi, H-chondrites: Trace element clues to their
832 origin, *Geochimica et Cosmochimica Acta* 49 (1) (1985) 247–259.
- 833 H. Y. McSween, Carbonaceous chondrites of the Ornans type: a metamorphic sequence,
834 *Geochimica et Cosmochimica Acta* 41 (4) (1977) 477–491.
- 835 J. Hertogen, M. J. Janssens, H. Takahashi, Enstatite chondrites: trace element clues to
836 their origin, *Geochimica et Cosmochimica Acta* 47 (12) (1983) 2241–2255.
- 837 E. Jarosewich, Chemical analyses of meteorites: A compilation of stony and iron meteorite
838 analyses, *Meteoritics & Planetary Science* 25 (4) (1990) 323–337.
- 839 J. T. Wasson, The chemical classification of iron meteorites—III. Hexahedrites and other
840 irons with germanium concentrations between 80 and 200 ppm, *Geochimica et Cos-*
841 *mochimica Acta* 33 (1969) 859–876.
- 842 V. F. Buchwald, Handbook of iron meteorites, their history, distribution, composition,
843 and structure, Center for Meteorite Studies, Arizona State University, 1975.
- 844 E. Goldberg, A. Uchiyama, H. Brown, The distribution of nickel, cobalt, gallium, pal-
845 ladium and gold in iron meteorites, *Geochimica et Cosmochimica Acta* 2 (1) (1951)
846 1–25.
- 847 E. R. D. Scott, J. T. Wasson, V. F. Buchwald, The chemical classification of iron mete-
848 orites—VII. A reinvestigation of irons with Ge concentrations between 25 and 80 ppm,
849 *Geochimica et Cosmochimica Acta* 37 (8) (1973) 1957–1983.

Table 1

Sample	Origin	Rock type	Mineralogy (modal %)	$\delta^{60}\text{Ni}$ (‰)	$\pm$ 2 s.d.	<i>n</i>	Ni ($\mu\text{g/g}$)	Mg#
<i>Peridotites</i>								
DTS-1	Washington, USA	orogenic, dunite	ol, sp	-0.077	0.073	32	2360	0.92
PCC-1	California, USA	orogenic, harzburgite	ol, opx, cpx, sp	0.141	0.056	17	2325	0.91
NHM-1	North Carolina, USA	orogenic, dunite	ol, sp	0.152	0.069	9	2830	
<i>Ultramafic xenoliths</i>								
NHM-2	South Africa	kimberlite xenolith, lherzolite	ol, opx, cpx, gt	0.224	0.058	6	1740	
BD744	Lashaine, Tanzania	volcanic xenolith, pyroxenite	ol, cpx, mica, sp	0.359	0.082	3	2700	0.92
BD822	Lashaine, Tanzania	volcanic xenolith, harzburgite	ol (84.2), opx (11.8), cpx (1.2), sp (0.4)	0.177	0.069	6	2345	0.93
BD1542	Lashaine, Tanzania	volcanic xenolith, harzburgite	ol (87.5), opx (7.7), cpx (2.0), sp (0.8)	0.200	0.027	3	2500	0.92
BD774	Lashaine, Tanzania	volcanic xenolith, harzburgite	ol (89.3), opx (4.6), cpx (3.2), sp (0.2)	0.283	0.063	6	2165	0.92
BD730	Lashaine, Tanzania	volcanic xenolith, lherzolite	ol (65.2), opx (19.9), cpx (2.0), gt (12.9)	0.226	0.057	6	1880	0.92
BD1355	Matsoka, Tanzania	volcanic xenolith, lherzolite	ol (49.4), opx (43.4), cpx, (2.2), gt (3.6)	0.245	0.055	3	2100	0.93
<i>Phanerozoic komatiites</i>								
GOR 94-3	Gorgona, Colombia	olivine cumulate	ol, plag, cpx, sp, glass	0.219	0.042	3	1575	0.84
GOR 94-17	Gorgona, Colombia	olivine cumulate	ol, plag, cpx, sp, glass	0.151	0.046	3	1110	0.81
GOR 94-44	Gorgona, Colombia	olivine cumulate	ol, plag, cpx, sp, glass	0.190	0.040	4	1325	0.82
GOR 94-19	Gorgona, Colombia	G1 komatiite	ol, plag, cpx, sp, glass	0.259	0.067	3	1080	0.78
GOR 94-43	Gorgona, Colombia	G1 komatiite	ol, plag, cpx, sp, glass	0.243	0.055	4	1200	0.81

Table 2

Sample	Origin	Mineral	Modal (%)	$\delta^{60}\text{Ni}$ (‰)	± 2 s.d.	<i>n</i>	Ni ($\mu\text{g/g}$)	Mg#
C273Q (lherzolite)	Lake Enep, Cameroon	olivine	ol: 45% opx: 35% cpx: 15% sp: 5%	0.139	0.044	4	2870	n/a
C235A (lherzolite)	Lake Baronbi Mbo, Cameroon	orthopyroxene	opx: 25% ol: 60% cpx: 10% sp: 5%	-0.035	0.031	5	785	0.90
P13 (lherzolite)	Ngaoundere Plateau, Cameroon	olivine	ol: 65%	0.166	0.049	5	3150	0.89
		orthopyroxene	opx: 25%	-0.019	0.055	4	770	0.90
		clinopyroxene	cpx: 5%	2.834	0.108	3	455	0.94
			sp: 5%					
N12 (harzburgite)	Biu Plateau, Cameroon	clinopyroxene	ol: 55-60%	0.423	0.078	5	395	n/a
		garnet	opx: 40-45%	0.296	0.060	5	160	n/a

Table 3

Sample	Number	Type	Class	$\delta^{60}\text{Ni}$ (‰)	± 2 s.d.	<i>n</i>	Ni (wt.%)
<i>Chondrite meteorites</i>							
Allende	BM 1969.148	carbonaceous	CV3	0.242	0.073	9	1.35 ^a
Murchinson	BM 17016	carbonaceous	CM2	0.229	0.072	9	1.20 ^b
Ornans	BM 42474	carbonaceous	CO3	0.286	0.079	4	1.36 ^c
Orgueil	BM 36104	carbonaceous	CI1	0.180	0.036	4	1.14 ^d
Indarch	BM 86948	enstatite	EH4	0.274	0.087	9	1.11 ^a
Khaipur	BM 1985.M144	enstatite	EL6	0.292	0.084	9	1.29 ^a
Kernouve	BM 43400	ordinary	H6	0.372	0.075	4	1.97 ^b
Bremervorde	BM 33910	ordinary	H3	0.262	0.050	5	1.42 ^a
Baratta	BM 1925.1286	ordinary	L4	0.306	0.046	9	1.10 ^a
Bruderheim	BM 1967.256	ordinary	L6	0.513	0.071	5	1.22 ^e
Parnallee	BM 34792	ordinary	LL3	0.160	0.049	4	1.06 ^a
St Severin	BM 1866.493	ordinary	LL6	0.244	0.047	5	10.5 ^f
<i>Iron meteorites</i>							
Negrillos	USNM 1222	hexahedrite	IIA	0.312	0.032	6	5.41 ^g
North Chile	BM 1959.917	hexahedrite	IIA	0.362	0.045	6	5.59 ^h
Arispe	USNM 2638	coarse octahedrite	IC	0.203	0.064	5	6.77 ⁱ
Clark County	BM 1959.949	medium octahedrite	IIIF	0.299	0.051	6	7.02 ⁱ
Duel Hill	USNM 1048	fine octahedrite	IVA	-0.057	0.057	6	10.45 ^j
Gibeon	BM 1910.753	fine octahedrite	IVA	0.312	0.062	6	7.78 ^j
Sikhte-Alin	BM 1992.M37	coarse octahedrite	IIB	0.295	0.062	6	5.87 ^g
Charcas	BM 85075	medium octahedrite	IIIA	0.232	0.065	6	7.86 ^k
Henbury	BM 1932.1473	medium octahedrite	IIIA	0.292	0.067	6	7.47 ⁱ