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# 1 The non-chondritic Ni isotope composition of Earth's mantle

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10

## 11 ABSTRACT

12 Nickel is a major element in the Earth. Due to its siderophile nature, 93 % of Ni is hosted in the core and the Ni  
13 isotope composition of the bulk silicate Earth might inform on the conditions of terrestrial core formation.

14 Whether Earth's mantle is fractionated relative to the chondritic reservoir, and by inference to the core, is a  
15 matter of debate that largely arises from the uncertain Ni isotope composition of the mantle. We address this  
16 issue through high-precision Ni isotope measurements of fertile- to melt-depleted peridotites and compare  
17 these data to chondritic meteorites. Terrestrial peridotites that are free from metasomatic overprint display a  
18 limited range in  $\delta^{60/58}\text{Ni}$  (deviation of  $^{60}\text{Ni}/^{58}\text{Ni}$  relative to NIST SRM 986) and no systematic variation with  
19 degree of melt depletion. The latter is consistent with olivine and orthopyroxene buffering the Ni budget and  
20 isotope composition of the refractory peridotites. As such, the average Ni isotope composition of these  
21 peridotites ( $\delta^{60/58}\text{Ni} = 0.115 \pm 0.011 \text{ ‰}$ ) provides a robust estimate of the  $\delta^{60/58}\text{Ni}$  of the bulk silicate Earth.

22 Peridotites with evidence for melt metasomatism range to heavier Ni isotope compositions where the  
23 introduction of clinopyroxene appears to drive an increase in  $\delta^{60/58}\text{Ni}$ . This requires a process where melts do  
24 not reach isotopic equilibrium with buffering olivine and orthopyroxene, but its exact nature remains obscure.

25 Chondritic meteorites have variability in  $\delta^{60/58}\text{Ni}$  due to heterogeneity at the sampling scale. In particular, CI1  
26 chondrites are displaced to isotopically lighter values due to sorption of Ni onto ferrihydrite during parent body  
27 alteration. Chondrites less extensively altered than the CI1 chondrites show no systematic differences in  
28  $\delta^{60/58}\text{Ni}$  between classes and yield average  $\delta^{60/58}\text{Ni} = 0.212 \pm 0.013 \text{ ‰}$ , which is isotopically heavier than our  
29 estimate of the bulk silicate Earth. The notable isotopic difference between the bulk silicate Earth and  
30 chondrites likely results from the segregation of the terrestrial core. Our observations potentially provide a  
31 novel constraint on the conditions of terrestrial core formation but requires further experimental calibration.

32

33 **Keywords:** Ni mass-dependent isotope variations; bulk silicate Earth; peridotites; chondrites; core formation

34

35

## 36 1. Introduction

37

38 The segregation into a metallic core and silicate mantle is the largest differentiation event in Earth's history, yet  
39 the exact conditions under which metal-silicate segregation took place remain incompletely understood,  
40 despite a long history of elemental partitioning studies (cf., Wade and Wood, 2005; Siebert et al., 2013). Mass-  
41 dependent ("stable") isotope fractionation provides an alternative approach to investigate core formation (e.g.,  
42 Schoenberg and von Blanckenburg, 2006; Georg et al., 2007; Fitoussi et al., 2009; Polyakov, 2009). Establishing  
43 the relative isotopic compositions of the core and the bulk silicate Earth (BSE) is the first step in this approach.  
44 As the core is inaccessible for direct sampling, its isotopic composition cannot be determined directly. For  
45 refractory elements that are not isotopically fractionated during planetary accretion, however, the composition  
46 of the core can be estimated through a mass balance between the BSE and chondritic meteorites that are  
47 inferred to be representative of the bulk Earth.

48 The mass-dependent isotope systematics of a range of elements has been investigated to find a core  
49 formation signature, but results have so far been inconsistent and subject to multiple interpretations (see  
50 Bourdon et al., 2018 for a recent review). Nickel is the fifth most abundant element in the Earth and holds  
51 considerable promise as an isotopic tracer of core formation yet has received comparatively little attention to  
52 date. Its elemental distribution between the mantle and core has been pivotal in demonstrating high-pressure  
53 core formation on Earth (e.g., Li and Agee, 1996) and is optimal for its use as a core formation proxy. Nickel is  
54 sufficiently siderophile to yield a large potential isotopic difference between the BSE and chondrites but not to  
55 the extent that its mantle budget is significantly overprinted by a late-veener component (<5 % of mantle Ni  
56 derives from a late veneer addition corresponding to 0.6 % of the mass of the Earth). Compared to Fe, which  
57 has a similar core-mantle partition coefficient, Ni has the distinct advantage that it occurs in a single valence  
58 state in the mantle. This eliminates a significant layer of complexity compared to Fe, whose two valence states  
59 can induce significant isotope fractionation during mantle processes such as the disproportionation of Fe<sup>2+</sup> by  
60 bridgmanite (Williams et al., 2012) and partial melting (Weyer et al., 2005; Dauphas et al., 2009).

61 To use Ni isotopes as a tracer of core formation requires a comparison of well-constrained isotopic  
62 compositions of the BSE and chondritic meteorites. Clear deductions from published Ni data are obfuscated by  
63 much scatter but a recent compilation hints at an isotopically light BSE (Elliott and Steele, 2017). Whereas  
64 previous studies have reported relatively consistent Ni isotope compositions for chondrites and iron meteorites  
65 (Cook et al., 2007; Moynier et al., 2007; Cameron et al., 2009; Chernozhkin et al., 2016; Gall et al., 2017), the  
66 Ni isotope composition of the BSE is more contentious (Cameron et al., 2009; Gueguen et al., 2013; Gall et al.,  
67 2017). Much of the uncertainty in estimates of the composition of the BSE can arise from the inclusion of  
68 basalts and komatiites, which might be isotopically fractionated relative to their mantle source by the presently  
69 unconstrained olivine-melt fractionation factor. A detailed study of Ni isotope variation in fertile, non-  
70 metasomatised peridotites, which provide the best approximation of the BSE (Carlson and Ionov, 2019), is  
71 currently lacking.

72 In this contribution, we re-evaluate the Ni isotope composition of the BSE through high-precision isotope  
73 measurements of four carefully selected suites of mantle peridotites. These samples cover a wide range in  
74 degrees of melt depletion and are minimally affected by metasomatic overprint. For five of these  
75 unmetasomatised peridotites, we have also measured the Ni isotope composition of pristine olivine separates.

76 In addition, five peridotite samples with evidence for modal or cryptic metasomatism were included to  
77 specifically investigate the effects of melt-rock reactions in the mantle. We complement the peridotite dataset  
78 with measurements of chondritic meteorites to compare mantle- and chondrite Ni isotope compositions  
79 obtained using the same methodology.

80

81

## 82 **2. Peridotite and meteorite samples**

83

### 84 **2.1. Peridotite samples**

85 We focus on well-characterised orogenic peridotites from the Horoman (Japan) and Zabargad (Red Sea) massifs  
86 and Central-Asian off-cratonic peridotite xenoliths (Vitim and Tariat) to investigate Ni isotope variations in the  
87 mantle and obtain an improved estimate of the Ni isotope composition of the BSE. Many of these samples have  
88 been used previously to constrain the mass-dependent isotope composition of the BSE for e.g., Li, Mg, Ca, V, Cr  
89 and Fe (Weyer and Ionov, 2007; Pogge von Strandmann et al., 2011; Hin et al., 2017; Kang et al., 2017; Xia et  
90 al., 2017; Qi et al., 2019). There are several important reasons behind our choice of these sample sets. As  
91 weathering of peridotites has been shown to drive fractionation of Ni isotopes (e.g., Ratié et al., 2015; Spivak-  
92 Birndorf et al., 2018), freshness of the samples was a first prerequisite.

93 The second criterion was to minimise the effect of metasomatic overprints by selecting peridotites  
94 without petrographic evidence for metasomatism such as the introduction of secondary clinopyroxene, garnet  
95 or other phases. The lack of metasomatic perturbation of the selected samples is supported by chemical and  
96 radiogenic isotope evidence (e.g., Saal et al., 2001; Ionov et al., 2005; Carlson and Ionov, 2019). For example,  
97 fertile to moderately melt-depleted samples have primitive mantle-normalised (PM; Palme and O'Neill, 2014)  
98 flat to light rare earth element (LREE) depleted trace element patterns (Figure 1) and superchondritic  
99  $^{143}\text{Nd}/^{144}\text{Nd}$ . The most refractory (highest MgO content) samples show variable fluid-mobile element  
100 enrichment (e.g., Takazawa et al., 2000), indicative of minor cryptic metasomatism, yet still have  $\text{La}/\text{Sm}_{\text{PM}} \leq 1$   
101 and are not overprinted to the extent seen in cratonic xenoliths (supplementary Figure S1).

102 Furthermore, the majority of the peridotites have been previously measured for their Li isotope  
103 composition (Brooker et al., 2004; Pogge von Strandmann et al., 2011; Lai et al., 2015) so that we can explicitly  
104 avoid samples affected by kinetic fractionation resulting from diffusional disturbance during xenolith  
105 entrainment or as a result of melt percolation, which might possibly affect Ni isotope systematics in a similar  
106 manner to Mg (Pogge von Strandmann et al., 2011; see Figure 1).

107 Our set of peridotite samples includes garnet-, spinel- and plagioclase peridotites that record a wide range  
108 in degree of melt depletion (e.g., 37-49 wt.% MgO; Figure 1). This allows us to investigate the possible influence  
109 of melt depletion on the Ni isotope composition of refractory peridotites. Nevertheless, our collection still  
110 includes a large number of fertile samples, not well represented in previous Ni isotope studies, that provide the  
111 readiest estimate for the BSE.

112 Although the focus of this study is on non-metasomatised peridotites, we have included five samples with  
113 obvious evidence for melt metasomatism as indicated by the introduction of clinopyroxene or  $\text{La}/\text{Sm}_{\text{PM}} > 1$

114 (Figure 1), to assess the influence of melt-rock reactions on Ni isotope systematics. The metasomatised samples  
115 include a Zabargad lherzolite with modal clinopyroxene enrichment and high  $\delta^7\text{Li}$  (BZ-230). In addition, LREE  
116 enrichment in four Tariat xenoliths points to a more cryptic metasomatic overprint, and phlogopite is also  
117 present in one of these samples. A more detailed description of the peridotite samples is provided in the online  
118 supplementary material.

119

## 120 **2.2. Chondritic meteorites**

121 A diverse set of 25 chondritic meteorites of different petrological grades was measured for their Ni isotope  
122 composition. This sample set includes seven ordinary chondrites (LL3.6-LL6, L3.7-L4 and H4), eight enstatite  
123 chondrites (EH3-EH5 and EL6) and ten carbonaceous chondrites (CI1, CM2, CR2, CO3, CV3 and CK4). Small  
124 samples of the chondritic meteorites, weighing between 4 and 100 mg, were provided by the Natural History  
125 Museum (NHM; London); see Table 2 for identification numbers and dissolved weights. Larger pieces of three  
126 additional ordinary chondrites (Chelyabinsk, Kilabo and Buzzard Coulee) and a sample of carbonaceous  
127 chondrite Allende were obtained from meteorite dealers. Small chips from the interior of these meteorites  
128 were lightly crushed in an agate pestle and mortar before further processing.

129 The majority of the chondrites used in this study are observed falls, thus limiting the extent of terrestrial  
130 weathering and contamination. The four exceptions are Barratta (H4), Yilmia (EL6), Atlanta (EL6) and Kota-Kota  
131 (EH3). Of these meteorite finds, Barratta was recovered approximately 12 years after falling on Earth and is  
132 fresh with a well-preserved fusion crust (Mason and Wiik, 1966). Yilmia, another Australian find, is locally  
133 extensively weathered but retains fresh sections in the centre (Buseck and Holdsworth, 1972). The specimen in  
134 the NHM collection is derived from the centre and essentially unweathered. For Kota-Kota and Atlanta, we did  
135 not process bulk samples but microdrilled mounts of these meteorites to explicitly target the most pristine  
136 parts of the meteorite samples (recovery of ~5-10 mg sample material; Table 2). We have, however, specifically  
137 avoided meteorite finds with a long terrestrial residence time, such as finds from the Sahara and Arabian  
138 deserts or Antarctica.

139 As heterogeneous objects, Jarosewich (1990) recommends that a minimum of 10 g of chondrite material  
140 should be used for a representative chemical analysis. Due to the precious nature of meteoritic material, this is  
141 not practically possible and we have performed measurements on significantly smaller aliquots, as common in  
142 many studies. In order to assess the effect of a sampling bias on our Ni isotope measurements, we have  
143 measured two separate samples of CI1 chondrite Orgueil (both provided by the NHM). In addition, we have  
144 measured both a bulk sample (46.7 mg) of L3.7 chondrite Cenicerros and four subsamples microdrilled from two  
145 polished mounts (5-10 mg material; see Luu et al., 2019 and Table 2 for more details).

146

147

## 148 **3. Analytical techniques**

149

### 150 **3.1. Digestion and Ni purification**

151 The majority of the meteorite Ni isotope measurements were carried out on aliquots from larger sample  
152 dissolutions that were measured for Mg isotope composition by Hin et al. (2017) and Luu et al. (2019).  
153 Peridotite and additional meteorite samples were digested in HF-HNO<sub>3</sub> at 200 °C and high-pressure in PTFE  
154 bombs. Initially, several peridotite samples were digested at low pressure and 140 °C but this proved  
155 insufficient to break down spinel in spinel-rich samples. When residual spinel was present (e.g., in DTS-1), a  
156 new sample aliquot was digested at high pressure. Several Horoman peridotites did dissolve completely at low  
157 pressure and Ni data for low- and high-pressure digestions of DTS-1 (with and without residual spinel) yield  
158 indistinguishable results (Figure 2).

159 After digestion, an aliquot of each sample solution was equilibrated with a <sup>61</sup>Ni–<sup>62</sup>Ni double spike prior to  
160 further processing. The double spike was calibrated as described in Klaver and Coath (2019). Nickel was  
161 separated from the matrix using a two-step ion-exchange procedure. A brief outline of the purification  
162 procedure is presented below; additional information is provided in the online supplementary material. The  
163 first step employs high-aspect ratio columns with 2.5 mL AG50W-X12 resin used for Mg separation (Pogge von  
164 Strandmann et al., 2011). Nickel and Mg are co-eluted from this column in 2.00 M HNO<sub>3</sub> whereas most other  
165 major cations are effectively separated; Ti, Al and Fe are eluted with 0.5 M HF and Ca and Cr remain on the  
166 column. The Mg-Ni fraction only contains Mn, Co and K. Subsequent Ni purification was achieved using cationic  
167 resin with a mixed HCl-acetone eluent and dimethylglyoxime as a Ni-specific chelating agent (Wahlgren et al.,  
168 1970; Victor, 1986).

169 The use of dimethylglyoxime has been successfully used in other protocols for separating Ni (e.g.,  
170 Regelous et al., 2008; Chernonozhkin et al., 2015) but quantitative break-down of the organic Ni complex is  
171 potentially problematic and can affect the magnitude of instrumental mass fractionation during measurement  
172 (Klaver and Coath, 2019). Hence, we minimise the amount of dimethylglyoxime by using it only in a final small-  
173 volume (200 µL; 4.5 by 13 mm) column filled with AG50W-X4 resin. The Ni-Mg fraction from the first column  
174 was dissolved in 50 µL 10 M HCl to which 950 µL Romil SpS quality acetone was added while columns were  
175 conditioned with 1 mL 0.5 M HCl-95 % acetone. After loading, Mn, Co and any residual Fe were eluted with 600  
176 µL 0.5 M HCl-95 % acetone. Nickel was collected with 1.5 mL 0.5 M HCl-95 % acetone-0.1 M dimethylglyoxime  
177 and 0.5-1.0 mL 0.5 M HCl-95 % acetone; Mg and any other remaining matrix elements were rinsed off the  
178 column with 6 M HCl. The Ni fractions were collected in PFA beakers to which ~5 mL 18.2 MΩcm water was  
179 added to prevent the formation of volatile tetracarbonylnickel (Victor, 1986). Acetone was evaporated at 75 °C  
180 after which ~300 µL concentrated HNO<sub>3</sub> was added and the solutions were evaporated to dryness. Repeated  
181 treatment with concentrated HNO<sub>3</sub> and 30 % H<sub>2</sub>O<sub>2</sub> largely eliminated the organic residue until only a clear  
182 green speck of Ni nitrate was left. The samples were then re-dissolved in 0.3 M HNO<sub>3</sub> for measurement.  
183 Column yields are >90 %; total procedural blanks are 0.4-0.8 ng and thus negligible compared to the ~5 µg Ni  
184 used in the measurements.

185

### 186 **3.2. Mass spectrometry and data reduction**

187 Nickel isotope measurements were carried out using a Thermo Scientific Neptune multi-collector inductively-  
188 coupled plasma mass spectrometer (MC-ICP-MS; s/n 1020). Samples were introduced in 0.3 M HNO<sub>3</sub> with a 50

189  $\mu\text{L}/\text{min}$  capillary, PFA nebuliser and CETAC Aridus desolvating nebuliser (typical gas flows are  $\sim 5.5 \text{ L}/\text{min}$  Ar and  
 190  $\sim 5 \text{ mL}/\text{min}$   $\text{N}_2$ ). The Neptune was operated in medium resolution ( $m/\Delta m \geq 6000$ , 5-95 % peak height definition)  
 191 in order to resolve isobaric interferences, notably  $^{40}\text{Ar}^{18}\text{O}$  on  $^{58}\text{Ni}$  and minor oxide and argide complexes on  
 192 other Ni isotopes (see online supplementary material). Interference of  $^{58}\text{Fe}$  on  $^{58}\text{Ni}$  could not be resolved but  
 193 was corrected by monitoring  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$ . This correction was found to be robust at least up to  $^{56}\text{Fe}/^{60}\text{Ni} = 0.6$   
 194 while samples always had  $^{56}\text{Fe}/^{60}\text{Ni} < 0.15$  (supplementary Figure S7).

195 Samples were measured at a concentration of  $1 \mu\text{g}/\text{mL}$  Ni, which yielded a total Ni beam intensity (sample  
 196 plus double spike) of 50-85 V on default  $10^{11} \Omega$  amplifiers with an on-peak background of  $< 20 \text{ mV}$ . A single  
 197 measurement comprises 50 cycles of 4.2 s integration time, consuming  $\sim 400 \text{ ng}$  Ni, preceded by an on-peak  
 198 blank measurement of 15 cycles. Samples were bracketed with measurements of spiked reference material  
 199 NIST SRM 986 as to allow a second-order correction of non-exponential instrumental mass fractionation. Data  
 200 processing was carried out in an offline spreadsheet. After correction for the isobaric interference of Fe, an  
 201 outlier test was applied to exclude measurements outside 4 interquartile ranges of the median caused by  
 202 memory effects in the Aridus. A blank subtraction was not applied as it was found to have a detrimental effect  
 203 on the precision; blank corrected and uncorrected data proved identical within uncertainty with the latter  
 204 being more precise. The double spike inversion yielded the  $^{60}\text{Ni}/^{58}\text{Ni}$  of the sample that was expressed relative  
 205 to the two adjacent SRM 986 measurements as  $\delta^{60/58}\text{Ni}_{\text{SRM 986}}$  (hereafter written as  $\delta^{60/58}\text{Ni}$ , following Coplen,  
 206 2011):

$$208 \quad \delta^{60/58}\text{Ni}_{\text{SRM 986}} = \left[ \frac{^{60}\text{Ni}/^{58}\text{Ni}_{\text{sample}}}{\sqrt{^{60}\text{Ni}/^{58}\text{Ni}_{\text{SRM 986}}^{\#1} \times ^{60}\text{Ni}/^{58}\text{Ni}_{\text{SRM 986}}^{\#2}}} \right] - 1$$

209  
 210 Each sample was measured at least six times. We report the average  $\delta^{60/58}\text{Ni}$  and quote a  $2s_x$  precision that is  
 211 the standard error of the mean for the repeat measurements assuming homoscedasticity for each  
 212 measurement session. No measurements were excluded at this stage. The reproducibility of the analytical  
 213 protocol was evaluated through the repeated measurement of reference materials. Our in-house Bristol  
 214 Isotope Group Ni solution (BIG-Ni) was measured both directly and after processing through the ion-exchange  
 215 separation procedure, which yield indistinguishable means and an intermediate precision of  $\delta^{60/58}\text{Ni} = 0.078 \pm$   
 216  $0.014 \text{ ‰}$  ( $2s$ ,  $n = 29$ ) over the course of this study (Figure 2a). Additionally, repeated measurements of  
 217 reference materials JP-1 (dunite) and NIST SRM 361 (low alloy steel) yield  $\delta^{60/58}\text{Ni} = 0.124 \pm 0.011 \text{ ‰}$  ( $2s$ ,  $n = 12$ )  
 218 and  $-0.070 \pm 0.016 \text{ ‰}$  ( $2s$ ,  $n = 9$ ), respectively (Figure 2a). The pooled intermediate precision for BIG-Ni, JP-1  
 219 and SRM 361 is  $0.014 \text{ ‰}$ , which we use as the best estimate of the uncertainty in our measurements.  
 220 Indistinguishable values for processed and unprocessed BIG-Ni documents the robustness of the double spike  
 221 method in correcting for any non-quantitative chemical separation yields and potential matrix effects caused  
 222 by residual organic material from the dimethylglyoxime used to elute Ni (Klaver and Coath, 2019).

223 The double spike inversion explicitly assumes that sample and reference material lie on the same  
 224 exponential law fractionation line and that no mass-independent (or non-exponential law mass-dependent)

225 anomalies are present. For meteoritic material, this is not the case (see discussion in section 5.3.1.). Hence,  
226 chondrite  $\delta^{60/58}\text{Ni}$  data need to be corrected for the presence of nucleosynthetic anomalies relative to the  
227 Earth. We follow the approach described by Hu and Dauphas (2017) using mass-independent Ni data compiled  
228 from Regelous et al. (2008), Steele et al. (2012), Tang and Dauphas (2012), Tang and Dauphas (2014) and  
229 Render et al. (2018). Chondrites are corrected using measured data for the same meteorite or the average for a  
230 meteorite class (e.g., EH). No mass-independent Ni data are available for CK chondrites (Karoonda). The  
231 average mass-independent composition of CV chondrites is used for correction of Karoonda as the similar O  
232 isotope composition of these two chondrite classes suggests that they are derived from the same parent body  
233 (Greenwood et al., 2010). The magnitude of the correction for nucleosynthetic anomalies on  $\delta^{60/58}\text{Ni}$  is 0.002-  
234 0.003 ‰ for enstatite chondrites, 0.005-0.007 ‰ for ordinary chondrites, 0.005-0.016 ‰ for carbonaceous  
235 chondrites except CR chondrites Renazzo and Al Rais (0.022 ‰; Table 2). All meteorite  $\delta^{60/58}\text{Ni}$  data reported in  
236 Tables 1 and 2, shown in the figures and discussed in the text is corrected for mass-independent anomalies.

237

238

#### 239 4. Results

240

241 We obtain an intermediate precision of 0.014 ‰ (2s) on  $\delta^{60/58}\text{Ni}$  for BIG-Ni and reference materials JP-1 and  
242 SRM 361. This presents an improvement compared to previous double spike Ni studies that report a 2s  
243 intermediate precision of 0.045 ‰ (Gueguen et al., 2013) and 0.07 ‰ (Gall et al., 2012; Gall et al., 2017) for  
244 geological reference materials. Compared to these studies, measuring higher intensity ion beams and multiple  
245 repeats per sample results in better counting statistics but our careful identification, resolution and monitoring  
246 of small but significant isobaric interferences (see supplementary material) may also play a role in our  
247 improved intermediate precision. Our  $\delta^{60/58}\text{Ni}$  results for low alloy steel SRM 361 and peridotite reference  
248 materials JP-1, DTS-1, DTS-2 and PCC-1 are in excellent agreement with literature data (Figure 2).

249 The  $\delta^{60/58}\text{Ni}$  data for peridotites and chondritic meteorites are listed in Tables 1 and 2, respectively, and  
250 shown in Figure 3. Terrestrial peridotites display a range in  $\delta^{60/58}\text{Ni}$  from 0.041 to 0.147 ‰ where the lower end  
251 of this distribution is formed by three peridotites with  $\delta^{60/58}\text{Ni}$  between 0.041 and 0.075 ‰. The 22 fertile to  
252 refractory peridotites yield a mean of  $0.115 \pm 0.011$  ‰ ( $2s_x$ ). Metasomatised peridotites have on average  
253 higher  $\delta^{60/58}\text{Ni}$  (0.108 to 0.215 ‰) but only the heaviest sample, Zabargad lherzolite BZ-230, overlaps with the  
254 Ni isotope compositions for the cratonic xenoliths reported by Gall et al. (2017; see Figure 4)

255 Chondrite  $\delta^{60/58}\text{Ni}$  results range from 0.024 to 0.278 ‰. Our enstatite chondrite measurements are most  
256 homogeneous whereas the carbonaceous chondrites display the largest variation. CI1 chondrites have  
257 significantly lower  $\delta^{60/58}\text{Ni}$  than the other chondrites and two separate samples of Orgueil yield  $\delta^{60/58}\text{Ni}$  values  
258  $\sim 0.09$  ‰ apart. Allende (CV3) and Karoonda (CK4) have the isotopically heaviest compositions of the  
259 carbonaceous chondrites. For Cenicerros (L3.7), three out of four microdrilled subsamples (5-10 mg) have  
260 identical  $\delta^{60/58}\text{Ni}$  to the bulk chip while subsample #4 is around 0.04 ‰ lighter. The mean  $\delta^{60/58}\text{Ni}$  of the five  
261 measurements of Cenicerros, weighted by the mass of digested material, is  $0.196 \pm 0.006$  (Table 2). Means for  
262 the three chondrite classes are indistinguishable:  $\delta^{60/58}\text{Ni} = 0.213 \pm 0.026$  ‰ for ordinary chondrites ( $2s_x$ ;  $n = 7$ ),



263 0.208 ± 0.016 ‰ for enstatite chondrites (2s<sub>x</sub>; n = 8) and 0.215 ± 0.028 for carbonaceous chondrites (2s<sub>x</sub>; n = 7;  
264 excluding CI1 chondrites). Taken together, all chondrites excluding CI1 chondrites yield a mean δ<sup>60/58</sup>Ni of 0.212  
265 ± 0.013 ‰ (2s<sub>x</sub>; n = 22).

266  
267

## 268 5. Discussion

269

### 270 5.1. Ni isotope systematics in the mantle

271 Nickel isotope systematics in the mantle are relatively unexplored. The only study to date to report on the Ni  
272 isotope composition of a suite of peridotites is that of Gall et al. (2017), who found notable δ<sup>60/58</sup>Ni variations  
273 of >0.1 ‰ in peridotite xenoliths from the Tanzania and Kaapvaal cratons. Based on a correlation between  
274 δ<sup>60/58</sup>Ni and modal clinopyroxene content (Figure 4), Gall et al. (2017) interpreted the range in δ<sup>60/58</sup>Ni to result  
275 from melt depletion, arguing that non-modal melting depletes the peridotite residue in isotopically heavy  
276 clinopyroxene. Given the small leverage of clinopyroxene on the Ni budget of peridotites, such a relationship is  
277 surprising. As Ni is a compatible element and therefore not likely to be sensitive to melt-rock reactions, Gall et  
278 al. (2017) did not consider the potential effects of post-melting events. Yet, their Tanzanian xenolith samples  
279 cannot be simple melting residues and show clear evidence for cryptic and modal metasomatism (Figure 1 and  
280 supplementary Figure S1; Dawson and Smith, 1973; Gibson et al., 2013). Our peridotite dataset covers a wider  
281 range from fertile to variably melt-depleted peridotites that are largely free from metasomatic overprints,  
282 complemented with five samples with different types of metasomatic overprint (Figure 1), which allows us to  
283 re-assess the influence of melt depletion and melt-rock reactions on Ni isotope systematics.

284

#### 285 5.1.1. Ni fractionation during melt extraction

286 Fertile spinel- and garnet lherzolites from Vitim and Tariat have geochemical compositions overlapping with  
287 those inferred for the primitive mantle (Ionov et al., 2005; Ionov, 2007; Kang et al., 2017; Carlson and Ionov,  
288 2019) while harzburgites in the Horoman massif represent the pristine residues of up to 25 % melt extraction  
289 (Takazawa et al., 2000). This large variation in degree of melt depletion is manifest as a range of modal  
290 clinopyroxene contents from 18 % in the fertile samples to less than 1 % in the most refractory samples. We  
291 observe no variation in δ<sup>60/58</sup>Ni as a function of modal clinopyroxene content, nor with other indices of  
292 depletion such as whole rock Al<sub>2</sub>O<sub>3</sub> contents (Figure 4), which is in clear contrast with the conclusions reached  
293 by Gall et al. (2017). Olivine and orthopyroxene host >90% of Ni in peridotites. As both these phases are  
294 retained during melting, δ<sup>60/58</sup>Ni of the residue is expected to be buffered as long as the olivine-melt and  
295 orthopyroxene-melt isotope fractionation factors do not greatly deviate from unity.

296 To illustrate the effects of melting on Ni isotope systematics, we have modelled the variation in δ<sup>60/58</sup>Ni of  
297 the solid residues and extracted melts (Figure 5). Mineral-olivine Ni isotope fractionation factors (α<sub>mineral-olivine</sub>)  
298 are distilled from the mineral separate data of Gall et al. (2017), mineral-olivine Ni partition constants (D) are  
299 derived from Ni contents of phases in equilibrated fertile Vitim lherzolites (Ionov et al., 2005) and we employed  
300 a variable D<sub>melt-olivine</sub> (8-30; Hart and Davis, 1978). The olivine-melt Ni isotope fractionation factor is the main

301 unknown parameter in the modelling. Hence, we have explored a range of values for  $\alpha_{\text{melt-olivine}}$  and used the  
302 values that reproduce the range in Ni isotope compositions reported for natural basalts. All modelling  
303 parameters are given in supplementary Table S4. An elemental and isotopic mass balance was applied to a  
304 pMELTS equilibrium melting model using a primitive mantle starting composition (Palme and O'Neill, 2014) to  
305 yield the  $\delta^{60/58}\text{Ni}$  of melt and residue, which is compared to the observed variations in peridotites (this study;  
306 Gall et al., 2017) and basalts (Cameron et al., 2009; Gueguen et al., 2013; Chernozhkin et al., 2015).

307 Modelling confirms our inference that Ni isotopes do not noticeably fractionate in the mantle during melt  
308 depletion (Figure 5). The Ni isotope composition of melts is predominantly dependent on  $\alpha_{\text{melt-olivine}}$  and the  
309 variation in natural basalts constrains  $\alpha_{\text{melt-olivine}}$  to lie between 0.99985 and 1.00015 (Figure 5). Over this range  
310 in  $\alpha_{\text{melt-olivine}}$ , the composition of residual peridotite remains constant within our level of precision ( $\delta^{60/58}\text{Ni}$   
311  $<0.015\text{‰}$ ) up to very high degrees of melting. The  $\delta^{60/58}\text{Ni}$  of residual peridotite is insensitive to the value of  
312  $\alpha_{\text{clinopyroxene-olivine}}$ . Gall et al. (2017) report a very isotopically heavy clinopyroxene composition in one sample  
313 ( $\delta^{60/58}\text{Ni} +2.8\text{‰}$ ) and even using such an extreme  $\alpha_{\text{clinopyroxene-olivine}}$  barely affects the Ni isotope composition of  
314 the residue as that is still dominated by olivine and orthopyroxene. A significant decrease in  $\delta^{60/58}\text{Ni}$  as the  
315 result of melt extraction, as proposed by Gall et al. (2017), can only be reproduced by adopting an  $\alpha_{\text{melt-olivine}}$   
316 that is an order of magnitude higher (1.001), which would result in very heavy Ni isotope compositions of  
317 mantle melts ( $\delta^{60/58}\text{Ni} >1\text{‰}$ ). This is clearly inconsistent with the data for natural basalts and hence we  
318 conclude that melt depletion does not fractionate Ni isotopes in the mantle and that the  $\delta^{60/58}\text{Ni}$  variations in  
319 the xenolith samples of Gall et al. (2017) results from a different process.

320

### 321 *5.1.2. The effects of metasomatism*

322 Peridotite samples derived from the subcontinental lithospheric mantle often display evidence for interaction  
323 with percolating melts and fluids, leading to enrichment in incompatible elements and (re-)introduction of  
324 phases such as clinopyroxene and hydrous minerals (e.g., Ionov et al., 2002; Grégoire et al., 2003; Simon et al.,  
325 2003; Pearson et al., 2014). The xenoliths measured for  $\delta^{60/58}\text{Ni}$  by Gall et al. (2017) have La/Sm and La  
326 contents higher than the primitive mantle (Figure 1 and supplementary Figure S1), which contrasts with their  
327 melt-depleted major element composition and suggests metasomatism by LREE-enriched melts. In addition,  
328 some of these samples have unusually high garnet and/or pyroxene contents while others contain late-stage  
329 phlogopite and ilmenite (Dawson and Smith, 1973; Gibson et al., 2013). We have measured four Tariat  
330 xenoliths and one Zabargad sample with clear evidence for metasomatic enrichment to investigate its effect on  
331 Ni isotope systematics. The metasomatised Tariat xenoliths have LREE-enriched compositions, in combination  
332 with the introduction of phlogopite in sample Mo4230-16, that results from silicate- and carbonatite melt  
333 metasomatism (Kang et al., 2017; Carlson and Ionov, 2019). The hand specimen of Zabargad Iherzolite BZ-230 is  
334 enriched in clinopyroxene, which occurs in clusters that contain up to 30 % clinopyroxene, and has an unusually  
335 heavy Li isotope signature, but no obvious LREE enrichment (Brooker et al., 2004). Three out of four  
336 metasomatised Tariat samples in our dataset have marginally higher  $\delta^{60/58}\text{Ni}$  than the pristine peridotites  
337 (Figure 3) but only the clinopyroxene-enriched Zabargad Iherzolite has a composition ( $0.215\text{‰}$ ) that overlaps  
338 with the cratonic xenoliths of Gall et al., (2017; see Figure 4). In combination with the correlation between

339 modal clinopyroxene and  $\delta^{60/58}\text{Ni}$  found by Gall et al. (2017), this suggests that Ni isotope systematics of  
340 peridotites are sensitive to the introduction of metasomatic clinopyroxene.

341 Clinopyroxene was found to be the isotopically heaviest phase in peridotite xenoliths ( $\delta^{60/58}\text{Ni}$  up to 2.8  
342 ‰) by Gall et al. (2017). Equilibration between percolating melts and refractory peridotite is not expected to  
343 significantly alter the Ni isotope composition of the peridotite as olivine and orthopyroxene will dominate the  
344 Ni budget and hence buffer  $\delta^{60/58}\text{Ni}$ , analogous to the arguments against Ni fractionation during melting in the  
345 previous section. Trace element and Sr-Nd isotope evidence, however, indicates that metasomatic  
346 clinopyroxene is often not in equilibrium with the other phases in the peridotite (e.g., Grégoire et al., 2003;  
347 Simon et al., 2003; Carlson et al., 2004; Simon et al., 2007). In such a scenario, isotopically heavy clinopyroxene  
348 can crystallise from a percolating melt without reaching equilibrium with the other phases and thus elevate the  
349 bulk  $\delta^{60/58}\text{Ni}$  of the xenolith. Due to the low Ni content of metasomatic clinopyroxene (Gibson et al., 2013),  
350 however, more than 20 % of isotopically heavy clinopyroxene (2.8 ‰) has to be added to elevate  $\delta^{60/58}\text{Ni}$  of the  
351 peridotite by 0.1 ‰, which is clearly in excess of the clinopyroxene modal abundances in the Gall et al. (2017)  
352 samples (1-3 % modal clinopyroxene; Figure 4). Hence, the disequilibrium introduction of clinopyroxene drives  
353 a change in  $\delta^{60/58}\text{Ni}$  in the right direction but the variation in peridotites cannot be explained by the current  
354 data. The significant difference in  $\delta^{60/58}\text{Ni}$  of clinopyroxene separates of Gall et al. (2017), however, might point  
355 towards an even larger heterogeneity of clinopyroxene  $\delta^{60/58}\text{Ni}$  in metasomatised peridotites, which requires  
356 further study to substantiate. We conclude that the correlation between modal clinopyroxene and  $\delta^{60/58}\text{Ni}$  in  
357 metasomatised peridotites reflects a disequilibrium process where clinopyroxene is introduced without fully re-  
358 equilibrating with the solid residue. Hence,  $\delta^{60/58}\text{Ni}$  in peridotites may be more susceptible to metasomatic  
359 alteration than previously thought, yet the exact nature of the processes causing Ni isotope fractionation in the  
360 mantle remain poorly constrained.

### 361 362 *5.1.3. Light Ni isotope compositions*

363 Three peridotite samples have lower  $\delta^{60/58}\text{Ni}$  than the majority of the samples (Figure 3). Dunite reference  
364 material DTS-1 is also characterised by a light Ni isotope composition (-0.082 ‰) that is distinct from its  
365 counterpart DTS-2, which also has a strikingly different Ni content (2360 versus 3780 ppm for DTS-1 and -2,  
366 respectively). Inhomogeneity and contamination of reference materials can be an issue and as we have no  
367 details on the processing of DTS-1, we exclude it from the subsequent discussion.

368 Weathering of ultramafic lithologies drives a decrease in  $\delta^{60/58}\text{Ni}$  in the solid residue (Ratié et al., 2015;  
369 Spivak-Birndorf et al., 2018), which is consistent with an isotopically heavy riverine flux and seawater  
370 composition (Cameron and Vance, 2014). This process will modify whole rock  $\delta^{60/58}\text{Ni}$  but should not affect the  
371 composition of unaltered olivine crystals, the main host of Ni in peridotites. If the light Ni isotope composition  
372 was already acquired in the mantle and the peridotites attained isotopic equilibrium, the Ni isotope  
373 composition of olivine is expected to mirror that of the bulk sample. Hence, to distinguish weathering from  
374 high-temperature processes as the cause of the light isotope compositions, we measured pristine handpicked  
375 olivine separates from the low- $\delta^{60/58}\text{Ni}$  samples and two samples with normal  $\delta^{60/58}\text{Ni}$  (Figure 6).

376 Olivine in all samples has similar  $\delta^{60/58}\text{Ni}$  to the bulk sample, which is consistent with olivine dominating  
377 the Ni budget in peridotites. The light isotope composition of the three samples is mirrored by low  $\delta^{60/58}\text{Ni}$  in  
378 olivine separates, thus clearly ruling out weathering as the processes responsible for the shift in  $\delta^{60/58}\text{Ni}$ .  
379 Instead, these peridotites appear to have equilibrated at lower bulk  $\delta^{60/58}\text{Ni}$ , which strongly points towards a  
380 high-temperature process that modified the Ni isotope composition in the mantle. There are few clues to the  
381 nature of this process as the low- $\delta^{60/58}\text{Ni}$  samples are not distinct in any lithophile element systematics, as such  
382 effectively ruling out any form of silicate melt metasomatism. For instance, disequilibrium introduction of  
383 isotopically light orthopyroxene (Gall et al., 2017) should have been apparent from modal abundances and an  
384 elevated whole rock  $\text{SiO}_2/\text{MgO}$ , neither of which is observed.

385 The lack of any systematic variation in lithophile elements could point to a role for sulfide mobility, which  
386 can be decoupled from silicate melt metasomatism (e.g., van der Meer et al., 2017). The introduction of  
387 isotopically light sulfides (Gueguen et al., 2013; Hofmann et al., 2014) could lower  $\delta^{60/58}\text{Ni}$  while leaving  
388 lithophile elements unaffected. Tentative evidence for this process is provided by S contents that are  
389 significantly higher (~610 ppm) than expected for the degree of depletion in low- $\delta^{60/58}\text{Ni}$  Zabargad sample BZ-  
390 241 (Brooker et al., 2004). No S abundance data are available for the Horoman samples, but petrographic and  
391 Pb isotope evidence suggest that sub-seafloor hydrothermal alteration in a mid-oceanic ridge setting has  
392 introduced Ni-rich sulfides in the Horoman peridotites (Ranaweera et al., 2018). The introduction of isotopically  
393 light pentlandite can elevate S contents and lower  $\delta^{60/58}\text{Ni}$  but need not lead to a noticeable increase in the  
394 abundance of lithophile elements. Adding 0.04 % pentlandite (~35 wt.% Ni,  $\delta^{60/58}\text{Ni} = -1 \text{‰}$ ), consistent with  
395 modal sulfide abundances (Ranaweera et al., 2018), and subsequent re-equilibration with the peridotite can  
396 account for the observed decrease in  $\delta^{60/58}\text{Ni}$  of ~0.07 ‰. As such, sulfide metasomatism is the best candidate  
397 to explain a decrease in  $\delta^{60/58}\text{Ni}$  in these peridotites.

398

## 399 **5.2. Ni isotope systematics of chondrites**

400 The chondritic meteorites in this study display a significant degree of Ni isotope heterogeneity. Although there  
401 is no systematic difference between the range and average  $\delta^{60/58}\text{Ni}$  of ordinary and enstatite chondrites,  
402 carbonaceous chondrites are notably more heterogeneous (Figure 3). In particular, CI1 type chondrites have  
403 significantly lower and more variable  $\delta^{60/58}\text{Ni}$  than other chondrite groups. When CI1 chondrites are excluded  
404 (see discussion in 5.2.1.), however, the mean  $\delta^{60/58}\text{Ni}$  of carbonaceous chondrites is indistinguishable from  
405 enstatite and ordinary chondrites. Nevertheless, there is variation in  $\delta^{60/58}\text{Ni}$  outside analytical uncertainty  
406 within all chondrite classes. Previous studies have attributed Ni isotope heterogeneity in chondrites to variable  
407 proportions of isotopically heavy metal (Gall et al., 2017) or as the result of sorting of isotopically distinct  
408 silicate, metal and sulfide phases during accretion of the chondrite parent bodies (Moynier et al., 2007). We  
409 find no obvious correlation between Ni or metal content (Figure 7a) but note that metal separates from  
410 chondrites (Cook et al., 2007; Moynier et al., 2007) display a much larger variation than bulk chondrites (Figure  
411 7a). Below, we will investigate processes that may contribute to the observed Ni isotope variation in  
412 chondrites.

413

414 *5.2.1. Aqueous alteration on the CI parent body*

415 Petrological type 1 carbonaceous chondrites have experienced the largest extent of low-temperature aqueous  
416 alteration on their parent bodies (e.g., Richardson, 1978; Endress and Bischoff, 1993). Isotopic exchange with  
417 fluids is widely considered to be responsible for the heavier O isotope composition of CI1 meteorites compared  
418 to other carbonaceous chondrite types (Figure 7b; Clayton and Mayeda, 1999). The Mg isotope composition of  
419 CI1 chondrites is also shifted to heavier values compared to petrological type 2-6 chondrites (Hin et al., 2017),  
420 showing an overall consistent sense of fractionation caused by aqueous alteration. Nickel is a reasonably fluid-  
421 mobile element that is isotopically fractionated during weathering in the terrestrial environment where the  
422 alteration of olivine to phyllosilicates causes a decrease in  $\delta^{60/58}\text{Ni}$  (Ratié et al., 2015; Spivak-Birndorf et al.,  
423 2018). Hence, alteration to a phyllosilicate-dominated mineralogy during aqueous alteration on the CI parent  
424 body can help explain the overall lower  $\delta^{60/58}\text{Ni}$  in CI1 chondrites

425 Not only are the values of  $\delta^{60/58}\text{Ni}$  in CI1 chondrites low, but they are quite variable between different  
426 dissolution of the same meteorite (see Table 2, Steele et al., 2012 and Gall et al., 2017 for independent  
427 measurements of Orgueil that span 0.16 ‰). This marked isotopic variability echoes order of magnitude  
428 variation in Ni content in  $\sim 100\ \mu\text{m}$  fragments of CI1 chondrites (Morlok et al., 2006). The elemental  
429 heterogeneity in Ni exceeds that of Fe and in six large fragments of Orgueil, weighing  $>0.6\ \text{g}$ , a variation of  
430 more than 10 % in Ni content and  $>20\ \%$  in Fe/Ni was found by Barrat et al. (2012). The pronounced elemental  
431 and isotopic variability in Ni is likely related to the role of ferrihydrite, a phase that strongly adsorbs and  
432 isotopically fractionates Ni onto its surface (Eickhoff et al., 2014; Wasylenki et al., 2015). Ferrihydrite is a  
433 common fine-grained matrix phase that occurs intergrown with phyllosilicates in CI1 chondrites, although its  
434 abundance is highly variable (e.g., Tomeoka and Buseck, 1988; Bland et al., 2004; King et al., 2015). Nickel and S  
435 contents correlate with the presence of ferrihydrite as a result of surface adsorption (Tomeoka and Buseck,  
436 1988; Morlok et al., 2006). Experimental studies indicate that the adsorption of Ni onto ferrihydrite is  
437 associated with a fractionation of  $\sim 0.35\ \%$  in  $\delta^{60/58}\text{Ni}$  at room temperature (Wasylenki et al., 2015; Gueguen et  
438 al., 2018). As the abundance of ferrihydrite was found to vary from 2 to 5 % in different subsamples of Orgueil  
439 (Bland et al., 2004; King et al., 2015), it is not surprising that we find both low and variable  $\delta^{60/58}\text{Ni}$  in our  
440 measurements of Orgueil. Given the highly specific role of ferrihydrite in influencing the Ni isotope composition  
441 of CI1 chondrites, we do not include them in our average composition of carbonaceous chondrites.

442  
443 *5.2.2. Ni diffusion during parent body metamorphism*

444 Parent body metamorphism causes notable redistribution of Ni between silicate, Ni-bearing sulfide and metal  
445 phases during aqueous and thermal processing (e.g., Rubin, 1990; Huss et al., 2006). Fractionation of Ni  
446 isotopes can occur on a  $\mu\text{m}$ - to mm-scale during diffusive transport of Ni between phases in response to  
447 changing equilibrium conditions. For example, Ni is redistributed between kamacite and taenite grains but, due  
448 to sluggish kinetics, does not reach equilibrium as illustrated by characteristic “M-shaped” Ni concentration  
449 profiles in taenite in chondrites (e.g., Wood, 1967). Modelling predicts that these frozen-in diffusion profiles  
450 are accompanied by kinetic fractionation of Ni isotopes (Dauphas, 2007; Watson et al., 2016), which is  
451 supported by up to 0.8 ‰ variations in  $\delta^{60/58}\text{Ni}$  in microdrilled iron meteorites that display similar diffusion

452 profiles (Cook et al., 2007; Chernozhkin et al., 2016). Moreover, a similar range of  $\sim 0.8$  ‰ in  $\delta^{60/58}\text{Ni}$  is  
453 observed in metal grains separated from ordinary chondrites by Moynier et al. (2007), which suggests that local  
454 Ni isotope disequilibrium is indeed prevalent in metal-bearing chondrites. The effects of kinetic fractionation in  
455 meteoritic metal are an order of magnitude larger than the observed variation within bulk ordinary and  
456 enstatite chondrites (Figure 7) and could contribute to scatter on the sampling scale. Whilst redistribution,  
457 and the potential for kinetic fractionation, of Ni between different meteoritic components during thermal  
458 metamorphism is best documented for ordinary chondrites (Rubin, 1990), it is likely to be significant in creating  
459 isotopic heterogeneity within chondrites more generally. For instance, perryite, a Ni silicide phase, disappears  
460 from the matrix of enstatite chondrites and Ni is partitioned into other phases including kamacite during  
461 thermal metamorphism on the enstatite chondrite parent body (Reed, 1968; Huss et al., 2006). Imperfect  
462 sampling of such heterogeneity can increase the variability in Ni isotope measurements of chondrites. To gauge  
463 the effect of these processes on measurements of samples the size typically used in this study, we compared  
464 the composition of a bulk sample of L3.7 chondrite Ceniceros to four subsamples that were microdrilled from  
465 two polished mounts. Three out of four microdrilled subsamples have a Ni isotope composition identical to the  
466 bulk chip whereas one subsamples is 0.04 ‰ lighter (Figure 3).

467

### 468 **5.3. Ni isotope fractionation during planetary differentiation**

#### 469 *5.3.1. The Ni isotope composition of Earth's building blocks*

470 Nucleosynthetic (mass-independent) Ni isotope anomalies have been clearly established in iron meteorites,  
471 bulk chondrites and CAIs (e.g., Regelous et al., 2008; Steele et al., 2011; Steele et al., 2012; Tang and Dauphas,  
472 2012; Render et al., 2018; Nanne et al., 2019; see Figure 8a). As these nucleosynthetic anomalies are not  
473 modified during the physicochemical processes of accretion and differentiation of the Earth, they serve as the  
474 most reliable geochemical proxy for the nature of the material accreting to from the Earth. Enstatite chondrites  
475 have a mass-independent Ni isotope composition that is the closest match to the Earth (Figure 9a). A similar  
476 picture emerges from all elements that have been investigated for nucleosynthetic anomalies (e.g., O, Cr, Ti,  
477 Mo, Ru, Nd); from an isotopic perspective, the Earth is most similar, yet not an exact match, to enstatite  
478 chondrites (Warren, 2011; Dauphas, 2017). In particular, the fact that both lithophile and (highly) siderophile  
479 elements best match with enstatite chondrites provides key evidence that the nature of accreting material did  
480 not change significantly during the formation of the Earth and is unlikely to be a fortuitous mixture between  
481 ordinary chondrites and CI chondrites (Dauphas, 2017). Recent high-precision Mo isotope measurements have  
482 been argued to allow some carbonaceous material in the later phases of accretion (Budde et al., 2019) but  
483 clearly exclude the possibility of a  $\sim 2:1$  ordinary chondrite-CI chondrite mixture that might be permissible  
484 based on Ni isotope systematics alone (Figure 8a). For this reason, we take enstatite chondrites as the best  
485 proxy for the Ni isotopic composition of the building blocks of the Earth and explicitly compare the  $\delta^{60/58}\text{Ni}$  of  
486 the bulk silicate Earth to average enstatite chondrites. It must be noted that using a bulk chondrite value,  
487 excluding only the altered CI1 chondrites, makes no difference within uncertainty to any of the conclusions  
488 reached here.

489

### 490 5.3.2. The non-chondritic Ni isotope compositions of the BSE

491 The Ni isotope composition of the BSE is more contentious than that of chondrites (Figure 8b). Earlier  $\delta^{60/58}\text{Ni}_{\text{BSE}}$   
492 estimates were based on a small number of measurements of peridotitic and basaltic reference materials  
493 (Cameron et al., 2009; Steele et al., 2011; Gueguen et al., 2013; Elliott and Steele, 2017). The mantle hosts  
494 99.97 % of Ni in the BSE and hence dominates its isotopic composition. Including basalts or komatiites, which  
495 might be fractionated relative to their mantle source depending on the at present unconstrained value of  $\alpha_{\text{melt-}}$   
496  $\text{olivine}$  (Figure 5), can thus bias the estimated average  $\delta^{60/58}\text{Ni}_{\text{BSE}}$ . This is compounded by potential inhomogeneity  
497 of reference materials and analytical artefacts in the measurement of low-Ni samples, as suggested by the  
498 different  $\delta^{60/58}\text{Ni}$  values reported for USGS reference material BHVO-2 with means varying outside quoted  
499 uncertainties by  $\sim 0.2$  ‰ (Cameron et al., 2009; Gall et al., 2012; Gueguen et al., 2013; Chernonozhkin et al.,  
500 2015; Render et al., 2018). In addition, including isotopically light dunite DTS-1 might skew the average towards  
501 lower  $\delta^{60/58}\text{Ni}$ .

502 Gall et al. (2017) performed the first more systematic study of Ni isotopes in peridotites yet their sample  
503 set included several strongly metasomatised peridotites that may not be representative of the BSE and that  
504 biased their estimate of  $\delta^{60/58}\text{Ni}_{\text{BSE}}$  towards heavier isotope compositions ( $0.23 \pm 0.06$  ‰). By measuring a large  
505 suite of fertile and variably melt-depleted peridotites and explicitly investigating the effects of modal- and  
506 cryptic metasomatism on Ni isotope systematics, we have been able to provide a more precise and potentially  
507 more representative estimate of the Ni isotope composition of the BSE. Based on the absence of detectable  
508 fractionation as a function of degree of melt depletion, we take the average of all non-metasomatised  
509 peridotites to be representative of the BSE:  $\delta^{60/58}\text{Ni}_{\text{BSE}} = 0.115 \pm 0.011$  ‰. As we observe no systematic  
510 variation in  $\delta^{60/58}\text{Ni}$  between different tectonic settings, facies (plagioclase, spinel and garnet) and degree of  
511 depletion (Figure 4) in the non-metasomatised peridotite samples, this is assumed to be a robust estimate of  
512 the composition of the BSE. Our average is in good agreement with published data for unmetasomatised  
513 peridotites (Figure 3); the discrepancy with previous estimates of the composition of the BSE mainly lies in the  
514 exclusion of basalts, komatiites and metasomatised peridotites.

515 Previous studies lacked the precision to resolve a difference in  $\delta^{60/58}\text{Ni}$  between the BSE and chondrites  
516 but hinted towards and isotopically light BSE (Figure 8a). By compiling all published data and optimistically  
517 using a  $2\sigma$  uncertainty of the different reservoirs, Elliott and Steele (2017) suggested that the BSE has lower  
518  $\delta^{60/58}\text{Ni}$  than the chondritic reservoir. Our study substantiates their speculative inference and, for the first time,  
519 documents a notable difference in  $\delta^{60/58}\text{Ni}$  between the BSE and Earth's building blocks (Figure 8a). Relative to  
520 enstatite chondrites, the BSE is lighter by  $0.092 \pm 0.027$  ‰. The observed difference is statistically significant;  
521 comparing all data for chondrites (excluding CI1) and peridotites (see Figure 3) through a Mann-Whitney  $U$  test  
522 indicates that the probability that the two groups are identical is  $\ll 0.01$ .

523

### 524 5.3.3. A core formation signature?

525 The notable non-chondritic Ni isotope composition of the BSE likely results from an isotopic fractionation event  
526 on a planetary scale during the accretion and early differentiation of the Earth. Two main processes that can  
527 shape the isotopic composition of the bulk Earth and its major reservoirs (core, BSE, atmosphere) are vapour

528 loss during planetary accretion (e.g., Poitrasson et al., 2004; Pringle et al., 2014; Hin et al., 2017) and core-  
529 mantle segregation (see Bourdon et al., 2018 for a recent review). Fractionation due to vapour loss will leave  
530 the bulk planet isotopically heavy, as for instance argued for Mg, Si and Cu (Georg et al., 2007; Savage et al.,  
531 2015; Hin et al., 2017). Vapour loss during accretion can therefore not account for the isotopically light Ni  
532 composition of the BSE and any evaporative fractionation of Ni would only result in an even larger difference in  
533  $\delta^{60/58}\text{Ni}$  between the BSE and the core. The magnitude of evaporative fractionation of Ni, however, is believed  
534 to be very small as modelling by Hin et al. (2017) predicts  $<0.01\text{‰}$  fractionation for Fe, which has a similar  
535 50 % condensation temperature (Lodders, 2003). Ruling out evaporative fractionation leaves core formation as  
536 the main candidate to have fractionated Ni on a planetary scale.

537 An isotopically enstatite chondrite bulk Earth with a mass distribution where 93 % of the Ni is hosted in  
538 the core (McDonough, 2014) gives a difference in  $\delta^{60/58}\text{Ni}$  between the BSE and core, denoted as  $\Delta^{60/58}\text{Ni}_{\text{CORE-BSE}}$ ,  
539 of  $0.099 \pm 0.029\text{‰}$ . Whether equilibrium isotope fractionation between the metallic core and silicate mantle  
540 can account for the observed difference is not clear due to the absence of comprehensive constraints from  
541 natural samples or experimental studies. A study of Ni isotopes in stony-iron meteorites yielded opposing signs  
542 for metal-silicate fractionation in mesosiderites and pallasites, suggesting that kinetic fractionation dominate  
543 over equilibrium effects (Chernonozhkin et al., 2016). The slow cooling of such samples allows subsolidus  
544 diffusion of Ni and associated non-equilibrium fractionation, making stony-iron meteorites inappropriate  
545 materials to study equilibrium metal-silicate fractionation.

546 Lazar et al. (2012) performed subsolidus experiments to determine the Ni isotope fractionation factor  
547 between Ni metal and Ni-talc. Although these experiments are clearly not representative of the conditions of  
548 terrestrial core formation, they provide the only available experimental constraint on Ni fractionation between  
549 metal and silicate. The Lazar et al. (2012) experiments suggests that the metal phase preferentially hosts the  
550 heavier isotopes of Ni, which is thus consistent with our observation of an isotopically light BSE, yet the  
551 magnitude of fractionation is significantly smaller than the observed  $\Delta^{60/58}\text{Ni}_{\text{CORE-BSE}}$  (Figure 9). At reasonable  
552 temperatures for terrestrial core formation (in excess of 2500 °C; e.g., Wade and Wood, 2005; Siebert et al.,  
553 2013; Fischer et al., 2015), the experimental calibration of Lazar et al. (2012) suggests negligible ( $<0.02\text{‰}$ )  
554 fractionation of Ni isotopes. Given how far removed from natural conditions the Lazar et al. (2012) experiments  
555 are, it is difficult to judge the significance of the discrepancy between the experimental constraints and  
556 observed  $\Delta^{60/58}\text{Ni}_{\text{CORE-BSE}}$ . Superliquidus metal-silicate equilibrium experiments are required to gain a better  
557 understanding of metal-silicate fractionation of Ni as subtle compositional effects might influence its  
558 magnitude. A dependence of metal-silicate isotopic fractionation factors on the presence of minor alloying  
559 elements in the metal phase has been proposed for Fe (Shahar et al., 2015; Elardo and Shahar, 2017), although  
560 these results are controversial (cf., Poitrasson et al., 2009; Hin et al., 2012; Liu et al., 2017). Similar  
561 compositional effects might influence the isotopic fractionation of Ni, making this a potentially interesting  
562 avenue to explore through experimental studies. In any case, our demonstration of a notably non-chondritic Ni  
563 isotope composition of the BSE provides an interesting new constraint on the conditions of terrestrial core  
564 formation, but significantly more experimental work is required to exploit this observation.

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## 567 **7. Conclusions**

568 We present a high-precision Ni isotope dataset for terrestrial peridotites and chondritic meteorites. The main  
569 findings of this work can be summarised as follows:

- 570 1) Mantle peridotites have a limited range in  $\delta^{60/58}\text{Ni}$  and do not exhibit systematic variation with degree  
571 of melt depletion. This is consistent with olivine and orthopyroxene dominating the Ni budget of  
572 residual peridotite, thus buffering the isotope composition. The composition of the BSE is constrained  
573 at  $\delta^{60/58}\text{Ni} = 0.115 \pm 0.011 \text{ ‰}$ .
- 574 2) Melt-metasomatised peridotites may show isotopically heavier compositions. Disequilibrium  
575 processes are required to increase  $\delta^{60/58}\text{Ni}$ , which is otherwise buffered by olivine and orthopyroxene.  
576 The introduction of isotopically heavy clinopyroxene can drive an increase in  $\delta^{60/58}\text{Ni}$ , but the exact  
577 nature of this process remains obscure.
- 578 3) Chondritic meteorites have more variable  $\delta^{60/58}\text{Ni}$ , mainly as the result of heterogeneity at the  
579 sampling scale likely caused by parent body processes. Aqueous alteration and sorption of Ni onto  
580 ferrihydrite are responsible for the markedly isotopically light compositions of CI1 chondrites. All other  
581 chondrites have notably higher  $\delta^{60/58}\text{Ni}$  than the BSE with a mean of  $0.212 \pm 0.013 \text{ ‰}$ .
- 582 4) The difference in  $\delta^{60/58}\text{Ni}$  between the BSE and chondrites is of the wrong sign to be caused by vapour  
583 loss during accretion and therefore likely results from terrestrial core formation. Experimental  
584 rationalisation is required to put the observation of an isotopically light BSE into context.

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586

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825

826

827 **TABLE CAPTIONS**

828

829 **Table 1.**  $\delta^{60/58}\text{Ni}$  data for peridotites and geological reference materials. Data sources for Ni,  $\text{Al}_2\text{O}_3$  and modal  
830 clinopyroxene contents are given in supplementary Table S1.

831

832 **Table 2.**  $\delta^{60/58}\text{Ni}$  data for chondritic meteorites.

833

834

### 835 **FIGURE CAPTIONS**

836

837 **Figure 1.** Compositional characterisation of the peridotite samples measured for their Ni isotope composition  
838 in this study: a) MgO versus primitive mantle-normalised La/Sm; b)  $\delta^{25}\text{Mg}$  versus  $\delta^7\text{Li}$ . Open symbols depict  
839 metasomatised peridotites. The major and trace element composition of the primitive mantle (PM) is from  
840 Palme and O'Neill (2014); the Li and Mg isotope compositions of the PM are taken from Pogge von Strandmann  
841 et al. (2011) and Hin et al. (2017), respectively. Also shown as dark grey squares in a) are the compositions of  
842 xenoliths measured for Ni isotope composition by Gall et al. (2017) and other cratonic xenoliths (small grey  
843 circles). Data sources for the peridotite samples and cratonic xenoliths are listed in supplementary Table S1;  
844 the field for peridotite xenoliths and Li-Mg diffusion model in b) are from Pogge von Strandmann et al. (2011).

845

846 **Figure 2.**  $\delta^{60/58}\text{Ni}$  data relative to NIST SRM 986 for our in-house BIG-Ni solution and geological reference  
847 materials; a) intermediate precision for BIG-Ni (open symbols: BIG-Ni processed through the chemical  
848 separation procedure together with samples), dunite JP-1 and low alloy steel SRM 361. The lighter shaded bar  
849 displays the 2s and the darker shaded bar the  $2s_x$  precision. Processed- and unprocessed aliquots of BIG-Ni  
850 have identical means; b) comparison of geological reference materials to published results. Our data are in  
851 excellent agreement with published values yet more precise. High- and low-pressure digestions of DTS-1, the  
852 latter with minor residual spinel, yield indistinguishable  $\delta^{60/58}\text{Ni}$ .

853

854 **Figure 3.**  $\delta^{60/58}\text{Ni}$  data for the measured peridotites and chondritic meteorites. Open symbols for peridotites  
855 represent samples affected by clear modal- or cryptic metasomatism. The open circles below the sample  
856 groups are published data for peridotites and chondritic meteorites (Cameron et al., 2009; Steele et al., 2012;  
857 Gueguen et al., 2013; Chernonozhkin et al., 2016; Gall et al., 2017). For ordinary chondrite Cenicerros (L3.7),  
858 both a bulk sample and four microdrilled subsamples were measured (see main text); the latter are shown as  
859 smaller. Error bars are 2s intermediate precision for reference materials measured in this study; shaded fields  
860 represent the 95% confidence interval for the sample groups. For the peridotites, the metasomatised samples  
861 and DTS-1 are excluded from the mean; CI1 chondrites (stars) are excluded from the carbonaceous chondrite  
862 mean.

863

864 **Figure 4.**  $\delta^{60/58}\text{Ni}$  versus indices of degree of melt depletion: whole rock  $\text{Al}_2\text{O}_3$  content (a) and modal  
865 clinopyroxene (b) for peridotites from this study and Gall et al. (2017). Data sources are listed in the online



866 supplementary material. Open symbols are peridotites affected by cryptic- or modal and the shaded green bar  
867 depicts the  $\delta^{60/58}\text{Ni}$  of the BSE as determined in this study. The  $\text{Al}_2\text{O}_3$  and modal clinopyroxene contents of the  
868 primitive upper mantle (PM) are from Palme and O'Neill (2014) and Walter (2014), respectively. Error bars are  
869 2s for the Gall et al. (2017) data and smaller than symbol size for peridotites from this study.

870

871 **Figure 5.** Equilibrium melting of a primitive mantle source (Palme and O'Neill, 2014) with a  $\delta^{60/58}\text{Ni}$  of our new  
872 BSE estimate, using mineral-olivine Ni isotope fractionation factors from Gall et al. (2017) and mineral-olivine  
873 Ni partition coefficients derived from equilibrated fertile Vitim lherzolites (Ionov et al., 2005). As  $\alpha_{\text{melt-olivine}}$  is  
874 not constrained, the grey fields show modelled melt and residue compositions with  $D_{\text{olivine-melt}}$  and  $\alpha_{\text{melt-olivine}}$   
875 varying from 8-30 and 0.99985-1.00015, respectively. All modelling parameters are given in supplementary  
876 Table S4. Modelled melt  $\delta^{60/58}\text{Ni}$  compositions are compared to literature data for basalts (Cameron et al.,  
877 2009; Gueguen et al., 2013; Chernonozhkin et al., 2015). Symbols for peridotite data, excluding the  
878 metasomatised and anomalously light samples, are as in previous figures; data from Gall et al. (2017) are  
879 shown as grey squares.

880

881 **Figure 6.** Comparison of whole rock (WR) versus olivine  $\delta^{60/58}\text{Ni}$  for five Horoman and Zabargad peridotites that  
882 include the anomalously light samples. The isotopically light compositions of these bulk peridotites is mirrored  
883 by pristine olivine separates, arguing against weathering or sample contamination as the cause of the lower  
884  $\delta^{60/58}\text{Ni}$ . See main text for further discussion.

885

886 **Figure 7.** Ni isotope variation in chondrites. a) lack of systematic variation of  $\delta^{60/58}\text{Ni}$  with Ni content;  
887 uncertainties are smaller than symbol size for our data. Literature data for ordinary (grey circles), enstatite  
888 (grey squares) and carbonaceous (grey diamonds) chondrites (Cameron et al., 2009; Steele et al., 2012;  
889 Chernonozhkin et al., 2016; Gall et al., 2017) are shown for comparison. Sources of Ni concentration data are  
890 listed in supplementary Table S1. The Ni isotope composition of metal separates from chondrites (Cook et al.,  
891 2007; Moynier et al., 2007) is shown as open circles on the right. Moynier et al. (2007) report their data relative  
892 to an Alfa Aesar Ni solution that has not been calibrated against SRM 986 and no data for other reference  
893 materials are given. In order to estimate the bias in the Moynier et al. (2007) data, we compared their results  
894 for iron meteorites Sikhote Alin and Gibeon to published values (Cook et al., 2007; Gueguen et al., 2013;  
895 Chernonozhkin et al., 2016; Gall et al., 2017) and found a systematic offset of +0.089 ‰. We have therefore  
896 corrected their metal separate data down by 0.089 ‰, which results in a translation of all  $\delta^{60/58}\text{Ni}$  values but  
897 does not affect the magnitude of the variation found by Moynier et al. (2007); b) mass-dependent O ( $\delta^{18}\text{O}$ )  
898 versus Ni isotope composition ( $\delta^{60/58}\text{Ni}$ ) of carbonaceous chondrites; grey box shows the range of enstatite (EC)  
899 and ordinary chondrite compositions (OC). Oxygen isotope data are from Clayton and Mayeda (1999). A  
900 general covariation in  $\delta^{18}\text{O}$  and  $\delta^{60/58}\text{Ni}$  with degree of parent body low-temperature aqueous alteration  
901 (petrological type is colour coded) is observed.

902

903 **Figure 8.** a) Nucleosynthetic (mass-independent) Ni anomalies of chondrites relative to the Earth. Data for the  
904 chondrite classes are compiled from Regelous et al. (2008), Steele et al. (2012), Tang and Dauphas (2012, 2014)  
905 and Render et al. (2018); the value for the Earth is from Steele et al. (2012) and the CAI array from Render et al.  
906 (2018). The shaded fields show the composition of carbonaceous (CC) and non-carbonaceous (NC) type iron  
907 meteorites (Steele et al., 2011; Nanne et al., 2019). The Earth is most similar to enstatite chondrites; see text  
908 for discussion; b) The  $\delta^{60/58}\text{Ni}$  composition of the bulk silicate Earth (BSE) versus that of chondritic meteorites  
909 from this study (enstatite chondrites only; black rectangle) and the literature (Cameron et al., 2009; Steele et  
910 al., 2011; Steele et al., 2012; Gall et al., 2017). This study has sufficient resolution to provide the first robust  
911 evidence that the BSE is isotopically light compared to the chondritic reservoir (top-left side of the diagram),  
912 thus corroborating the inference by Elliott and Steele (2017) that was based on a compilation of literature data.  
913

914 **Figure 9.** Experimental constraints on metal-silicate Ni isotope fractionation compared to the observed  
915  $\Delta^{60/58}\text{Ni}_{\text{CORE-BSE}}$ . The blue diamonds are subsolidus experiments between Ni metal and talc from Lazar et al.  
916 (2012); the blue shaded field shows their regression that excludes the experiment at 950 °C. The red shaded  
917 bar at 2500-3500 °C depicts plausible temperatures of core-mantle equilibration. See text for discussion.  
918