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1 Residual liquid from deep magma ocean crystallization in the source of
2 komatiites from the ICDP drill core in the Barberton Greenstone Belt

3

4 Boyet M.¹, Garçon M.¹, Arndt N.², Carlson R.W.⁴, Konc Z.¹

5

6 ¹ Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et
7 Volcans, F-63000 Clermont-Ferrand, France

8

9 ² ISTERre, UMR 5275, CNRS, Université Grenoble-Alpes, BP 53, FR-38041 Grenoble
10 CEDEX 09, France

11

12 ³ Carnegie Institution for Science, Earth and Planets Laboratory, 5241 Broad Branch
13 Road, NW, Washington DC 20015-1305, United States

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23 ABSTRACT

24 Komatiites and sedimentary rocks sampled during the International Continental
25 Drilling Program (BARB1-2-3-4-5) in the Barberton greenstone belt, South Africa,
26 were analyzed for ¹⁴⁶Sm-¹⁴²Nd systematics. Resolved negative $\mu^{142}\text{Nd}$ values (down
27 to -7.7 ± 2.8) were identified in komatiites from the 3.48 Ga Komati Formation and
28 this signature correlates with low Hf/Sm ratios measured in these samples. The
29 negative $\mu^{142}\text{Nd}$ point to a source with subchondritic Sm/Nd ratio which formed
30 during the Hadean. No analytically resolvable ¹⁴²Nd anomalies were measured in
31 crustal detritus-rich, Si-rich, Ca-Fe-rich sediments and cherts from the Buck Reef
32 (3.42 Ga) and the Fig Tree Group (3.23-3.28 Ga). Our new measurements are
33 incorporated into a larger set of ¹⁴⁷Sm-¹⁴³Nd and ¹⁷⁶Lu-¹⁷⁶Hf data to better understand

34 the $^{142,143}\text{Nd}$ - ^{176}Hf isotope signatures in the mantle source at the time of komatiite
35 crystallization. Our calculations show that the $^{142,143}\text{Nd}$ - ^{176}Hf isotope signatures and
36 Hf/Sm ratios cannot be produced by recycling into the komatiite source of detrital
37 sediments like those sampled in the Barberton area. Only cherts have the required
38 trace element characteristics – low Hf/Sm, radiogenic $\epsilon^{176}\text{Hf}$ –but the trace element
39 concentrations in the cherts are so low that unrealistic amounts of chert would need to
40 be added.

41 We propose a four-stage model for the formation of these rocks. Negative $\mu^{142}\text{Nd}$ and
42 low Hf/Sm ratios developed during the crystallization of a deep magma ocean soon
43 after Earth accretion. The material that ultimately became the source of komatiites
44 was a residual liquid produced by 50% crystallization leaving a
45 bridgmanite/ferropericlasite/Ca-perovskite cumulate. The Lu-Hf and Sm-Nd isotope
46 systems were decoupled at this stage. After extinction of ^{146}Sm around 4 Ga,
47 parent/daughter ratios fractionated during a melt extraction event. With this model we
48 explain the positive $\epsilon^{176}\text{Hf}$ and slightly negative $\epsilon^{143}\text{Nd}$ in these samples. The 3.55 Ga
49 Schapenburg komatiites in another part of the Barberton belt share similar chemical
50 signatures, supporting our model of fractionation in a deep magma ocean early in
51 Earth history.

52

53

54 1. INTRODUCTION

55

56 Short- and long-lived radiogenic isotope systems provide strong constraints on the
57 composition, chemical differentiation and dynamics of the mantle. Studies of Archean
58 samples provide key information on the timing and processes that drove the evolution
59 of the early mantle and formation of the first crust (e.g. Carlson et al., 2019).
60 Particularly important are komatiites – ultramafic volcanic rocks found mainly in
61 Archean greenstone belts. Convincing petrological evidence indicates that these rocks
62 were derived from the deep mantle, and they therefore yield valuable information on
63 part of the early mantle that is rarely accessible (Ohtani, 1984; Herzberg, 1992; Arndt
64 et al., 2008).

65

66 The 3.5-3.0 Ga Barberton greenstone belt (BGB) in South Africa, together with the
67 Pilbara in Australia, contain the best-preserved examples of old volcanic and
68 sedimentary rocks (Lowe and Byerly, 1999; Arndt et al. 2008). The preservation of
69 primary chemical and isotopic signatures during metamorphic recrystallization has
70 been the subject of numerous studies for Barberton komatiites (e.g. Gruau et al., 1990,
71 1992; Lécuyer et al., 1994; Lahaye et al., 1995). One way to evaluate the degree of
72 metamorphic resetting of isotope systematics is through the use of the isochron
73 method. If the isochron age for a set of samples agrees with the age of the formation,
74 the initial isotope composition can more convincingly be used as a proxy of the source
75 composition. Short-lived radiogenic isotope systematics are less sensitive to post-
76 crystallization modification that occurs after the extinction of the parent isotope and
77 thus better record early Earth events. This is the case of the short-lived ^{146}Sm - ^{142}Nd
78 ($T_{1/2}=103$ Ma) system which records magmatic processes (melting/crystallization)
79 during the Hadean.

80

81 Here we present new results on the ^{146}Sm - ^{142}Nd isotope systematics of Barberton
82 komatiites from the Komati Formation and surrounding sedimentary rocks (mudstone,
83 sandstone) from the Fig Tree Group and Buck Reef cherts from the Kromberg
84 Formation sampled during the International Continental Drilling Program (ICDP,
85 Arndt et al., 2010). All these samples were analyzed previously for ^{147}Sm - ^{143}Nd and
86 ^{176}Lu - ^{177}Hf systematics (Blichert-Toft et al., 2015; Garçon et al., 2017). Previous
87 published combined studies of lithophile trace element isotope systematics
88 (^{146}Sm , ^{147}Sm - $^{142,143}\text{Nd}$ and ^{176}Lu - ^{176}Hf) on Barberton komatiitic lavas suggest a
89 source with non-chondritic relative abundances of refractory lithophile elements, and
90 that this source formed during the Hadean, as early as 4.4 Ga (Blichert-Toft et al.,
91 2004; Puchtel et al., 2013). More recent ^{147}Sm - ^{143}Nd and ^{176}Lu - ^{177}Hf isotope studies
92 of Barberton komatiites suggested that the komatiite source was characterized by
93 subchondritic Sm/Nd and superchondritic Lu/Hf ratios (Blichert-Toft et al., 2015).
94 This signature could result from the recycling of sediments in the mantle source of the
95 komatiites or, alternatively, from the crystallization of a deep magma ocean (Blichert-
96 Toft et al., 2015; Puchtel et al., 2016). In order to better understand the entire history
97 of mantle processes at the origin of Barberton komatiites, results from the three
98 systematics $^{146-147}\text{Sm}$ - $^{142,143}\text{Nd}$ and ^{176}Lu - ^{176}Hf are discussed together.

99

100

101 2. SAMPLES ANALYZED IN THIS STUDY

102

103 Seven komatiites were selected from drill cores BARB1 and BARB2 obtained during
104 the ICDP drilling project in the Komati Formation in the Onverwacht Group of the
105 Barberton Belt (Arndt et al., 2010). A description of the samples is given in Coetze
106 (2014) and Blichert-Toft et al. (2015). The seven selected samples have been
107 previously analyzed for ^{176}Lu - ^{176}Hf and ^{147}Sm - ^{143}Nd systematics by Blichert-Toft et
108 al. (2015). They all belong to the Al-depleted group as defined by Robin-Popieul et al.
109 (2012): they have low Al/Ti, relatively high concentrations of incompatible elements
110 and rare earth element patterns (REE) depleted in heavy REE with (Gd/Yb)_n between
111 1.21 and 1.32 when normalized to the primitive mantle Gd/Yb ratio. Two samples
112 classified as hyaloclastite (BARB1 GC/9 and BARB1 GC/34) have high loss of
113 ignition (LOI = 13.1 and 10.1 wt%, respectively) whereas other samples have LOI in
114 the range 1.8-7.5 wt%.

115

116 The komatiites of the Onverwacht Group are divided into seven formations and are
117 overlain by the Fig Tree (3.26–3.23 Ga; Kröner et al., 1991; Byerly et al., 1996) and
118 Moodies Groups (3.23-3.21 Ga; Heubeck et al., 2013) which mostly consist of
119 conglomerate, sandstone, shale, banded chert, banded iron formation and dacitic
120 volcanic rocks. In the subduction-accretion model for this region, the Fig Tree and
121 Moodies Groups could represent the fill of an evolving foreland basin fed by the
122 erosion products of an orogenic complex (Lowe and Byerly, 1999). The analyzed
123 sediment samples are mudstones and sandstones from ICDP cores BARB 4 and
124 BARB 5 drilled in the Mapepe formation of the Fig Tree group. Based on the major
125 and trace element compositions of these sediments, 3 groups were defined: crustal
126 detritus-rich, Si-rich, and Ca-Fe-rich sediments (Garçon et al., 2017). In addition, two
127 samples of chert from ICDP core BARB 3 drilled in a basal member of the Kromberg
128 Formation in the Onverwacht group (Buck reef cherts, 3.42 Ga; Kröner et al., 1991)
129 were analyzed for ^{142}Nd in this study. All sediments were previously analyzed for
130 ^{147}Sm - ^{143}Nd and ^{176}Lu - ^{176}Hf isotopic systematics by Garçon et al. (2017). The Si-rich
131 sediments from Fig Tree and the cherts from Buck reef show unusually high $\epsilon^{176}\text{Hf}$ as
132 required to explain the superchondritic Lu-Hf isotopic signatures of the Barberton

133 komatiites in the model involving sediment recycling in the mantle source of
134 komatiites (Blichert-toft et al., 2015).

135

136

137 3. PREVIOUS ISOTOPE STUDIES OF BARBERTON KOMATIITES

138 Isotopic studies of Barberton komatiites have been undertaken for at least the last four
139 decades including some of the earliest geochronological studies using the Sm-Nd
140 system (Hamilton et al., 1979). Early Sm-Nd studies (Hamilton et al., 1979; Jahn et
141 al., 1982, Gruau et al., 1990, 1992, Lecuyer et al., 1994, etc) found that initial
142 $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for the komatiites scattered considerably to both sub- and
143 superchondritic values. More recent analyses by Puchtel et al. (2013, 2016) of
144 carefully sampled, relatively fresh komatiites yielded internally consistent data.
145 However these samples may have a very small range of parent/daughter ratios and the
146 isochron method cannot be applied to make sure the isotopic systems have remained
147 closed since the formation age of the komatiites (e.g. Schapenburg komatiites). A
148 summary of $^{146,147}\text{Sm}-^{142,143}\text{Nd}$ and $^{176}\text{Lu}-^{176}\text{Hf}$ data obtained recently on komatiite
149 samples from the Onverwacht Group (3.55 Ga Schapenburg belt, 3.48 Ga Komati
150 formation, and 3.3 Ga Weltevreden) is presented in Figures 1 and 2. This includes
151 ^{143}Nd and ^{176}Hf results previously analyzed by Blichert-toft et al. (2015) on the same
152 samples as those analyzed for ^{142}Nd in this study (orange circles with red borders in
153 Figures 1 and 2). All data on the $^{146}\text{Sm}-^{142}\text{Nd}$ systematics measured on Barberton
154 komatiites are also presented.

155

156 **3.1. $^{147}\text{Sm}-^{143}\text{Nd}$ systematics**

157 Samples from the 3.48 Ga Komati (ICDP and outcrop samples, 45 whole-rocks
158 samples in total) have initial $\epsilon^{143}\text{Nd}$ between -4 and +4 but 60% of the samples have
159 slightly positive initial $\epsilon^{143}\text{Nd}$ up to +1 and the mean value of the 45 measurements is
160 equal to +0.5 (Figure 1A). Blichert-Toft et al. (2015) report conflicting results for
161 whole-rock komatiite samples and clinopyroxene separates. Initial $\epsilon^{143}\text{Nd}$ calculated
162 on clinopyroxene separated from two komatiite samples are negative (around -2)
163 whereas a separate from a third sample gives a different value with $\epsilon^{143}\text{Nd} = +2$.
164 Whole-rock data scatter from -2 to +2 in core samples and from -4 to +4 in outcrop
165 samples. Blichert-Toft et al. (2015) suggest that the negative initial $\epsilon^{143}\text{Nd}$ measured

166 in the clinopyroxene separates is representative of the source and propose that at least
167 part of positive values measured in whole-rock results from disturbance during later
168 hydrothermal alteration or metamorphism. ICDP komatiite samples analyzed in this
169 study for the ^{146}Sm - ^{142}Nd systematics are presented in a ^{147}Sm - ^{143}Nd isochron plot in
170 Figure 3A (data from Blichert-Toft et al., 2015). With a MWSD value of 22.0, the
171 regression yields a non-statistically significant result. However the ^{147}Sm - ^{143}Nd age is
172 in agreement with the accepted age of 3.48 Ga for this formation. The initial $\epsilon^{143}\text{Nd}$
173 calculated from the regression is $+0.3 \pm 3.3$ and individual samples range from -1.0 to
174 1.8 when recalculated at 3.48 Ga (mean value = $+0.4 \pm 1.9$, 2SD).

175

176 Komatiite samples from Schapenburg belt, a segment of the Barberton belt (3.55 Ga)
177 yield initial $\epsilon^{143}\text{Nd}$ between +1.7 and +2.7 (Puchtel et al., 2016), and samples of
178 slightly younger (3.3 Ga) Weltevreden komatiites have initial $\epsilon^{143}\text{Nd}$ from 0 to +2
179 (Blichert-Toft et al., 2015; Puchtel et al., 2013) (Figure 1).

180

181

182 **3.2. ^{176}Lu - ^{176}Hf systematics**

183 The Komati Formation data scatter widely on a Lu-Hf isochron diagram with an
184 MSWD of 122 for the whole dataset (Blichert-Toft et al., 2015). Considering only the
185 samples from the IDCP drill cores reduces the isochron scatter considerably, but
186 results in a young age (2941 ± 41 Ma, MSWD =30) and negative initial $\epsilon^{176}\text{Hf}$ of -1.5
187 ± 0.8 . Calculating the initial $\epsilon^{176}\text{Hf}$ of the individual ICDP whole-rock measurements
188 at the igneous age of 3.48 Ga provides a range from -3.2 to +3.9 with a mean value of
189 $+1.4 \pm 3.5$ (2SD) (Figure 1). The mean $\epsilon^{176}\text{Hf}$ considering outcrop samples is equal to
190 $+2.3 \pm 3.9$ (3 extreme values were removed, Blichert-Toft et al., 2015; Puchtel et al.,
191 2013). In contrast, the initial $\epsilon^{176}\text{Hf}$ of three clinopyroxene separates from the
192 komatiites ranged from +2.5 to +5.9 (Blichert-Toft et al., 2015), which overlaps with
193 the initial $\epsilon^{176}\text{Hf}$ determined for the whole-rock samples from which these
194 clinopyroxenes were separated, but contrasts with the negative initial $\epsilon^{143}\text{Nd}$
195 calculated for the same clinopyroxenes. Data obtained for the ^{176}Lu - ^{177}Hf systematics
196 for samples analyzed in this study are presented in Figure 3B (data from Blichert-Toft
197 et al., 2015). The ^{176}Lu - ^{177}Hf age calculated using all samples is clearly too young
198 (3062 ± 70 Ma, cf. supplementary Figure 1). However the slope is strongly influenced

199 by sample GC/34A which has the lowest Lu/Hf ratio. Excluding this sample gives an
200 older age of 3363 ± 213 Ma (MSWD = 4, Figure 3B) which is, within uncertainties, in
201 agreement with the formation age of the studied komatiites.

202 Schapenburg and Weltevreden komatiites have strongly positive $\epsilon^{176}\text{Hf}$ with mean
203 values at +5.5 and +7, respectively (Figure 1).

204

205

206 **3.3. ^{146}Sm - ^{142}Nd systematics**

207 Data for $^{142}\text{Nd}/^{144}\text{Nd}$ from Caro et al. (2006) and Puchel et al. (2013, 2016) for
208 komatiites from the 3.48 Ga Komati Fm, 3.55 Ga Schapenburg belt and 3.27 Ga
209 Weltevreden area are reported in Figure 2. Puchtel et al. (2016) report deficits in
210 ^{142}Nd in the 3.55 Ga Schapenburg komatiites with a mean $\mu^{142}\text{Nd}$ of -4.9 ± 2.8 (2SD,
211 8 samples). In contrast, no clearly resolved deviation relative to the terrestrial standard
212 has been reported so far in other Barberton komatiites. Among the four Komati
213 Formation samples measured by Caro et al. (2006), two are classified as tholeiitic
214 basalts and two as komatiitic basalts. The mean $\mu^{142}\text{Nd}$ for these samples is -0.7 ± 2.1
215 when calculated relative to the AMES Nd standard. Puchtel et al. (2013) obtained an
216 average $\mu^{142}\text{Nd}$ of 0.0 ± 4.8 (2SD) for four other komatiites from the Komati
217 Formation, and $\mu^{142}\text{Nd}$ of $+2.2 \pm 7.1$ (2SD) for four Al-undepleted Weltevreden
218 komatiites. A meta-tholeiite sample of the Komati Formation analyzed by Schneider
219 et al. (2018) has a small deficit in ^{142}Nd with a $\mu^{142}\text{Nd}$ of -5.4 ± 3.7 .

220

221

222 **4. METHODS**

223

224 Komatiite samples were digested and processed following the dissolution and
225 chemical separation protocols developed by Boyet and Carlson (2005, 2006) and
226 slightly modified by Rizo et al. (2011). Samples were dissolved using a 3:1 mixture of
227 HF-HNO₃ ultra-pure acids within Savillex Teflon beakers and placed on the hotplate
228 at 120 °C for 48 hours. To expel the fluorides, komatiites were treated with 7M HNO₃
229 and ultra-pure HClO₄. After evaporation to dryness, they were taken up in 6M HCl
230 and replaced closed onto the hotplate at 90 °C. Once clear sample solutions in HCl
231 were obtained, Nd fractions were separated using a three-step method: (i.) a cation-

232 exchange column –with AG50W-X8 resin– using 2.5M and 4M HCl to collect middle
233 to light rare earth elements (REE) from the bulk rock; (ii.) two consecutive passes
234 through pressurized cation-exchange columns using 2-methylactic acid (0.2M and pH
235 = 4.7) to collect Nd and eliminate Ce with the majority of the Sm (and Pr), which
236 together produce isobaric interferences on ^{142}Nd , ^{144}Nd , ^{148}Nd and ^{150}Nd . (iii.) Finally,
237 separation was completed by using Ln-Spec resin (50-100 microns) with 0.2M HCl to
238 purify the collected Nd and remove all the residual Sm. The reference basalt BHVO-2
239 was dissolved and purified using the same analytical protocol.

240

241 Sediments were dissolved in Savillex Teflon beakers using ammonium bifluoride
242 (NH_4HF_2) at 230°C for 12 hours following the procedure described in Zhang et al.,
243 (2012). Here Ce is separated from other REE once it is oxidized to Ce^{4+} . Details on
244 this technique are found in Garçon et al. (2018). The LREE cut was dissolved in 10N
245 HNO_3 + 20 mM NaBrO_3 . The concentrated nitric solution containing trivalent LREEs
246 was eluted on Ln-Spec resin (50-100 μm) while Ce(IV) remained adsorbed on the
247 column. This step was performed twice. The Nd cut was then processed through a fine
248 Ln-Spec resin (25-50 μm) using 0.2N to 0.25N HCl as eluents to isolate Nd. Finally,
249 the Nd cut was purified on a cation resin AG50W-X8 (200-400 mesh) using 2N
250 HNO_3 and 2.5N to 6N HCl to remove the residual traces of Ba and NaBrO_3 . Total
251 procedural blanks for Nd were negligible (15 pg) given that typical sample sizes
252 allowed separation of hundreds of ng of Nd.

253

254 The Nd isotopic composition was analyzed as positive metal ion (Nd^+) on the Thermo
255 Scientific Triton Thermal Ionization Mass Spectrometers (TIMS) at the Laboratoire
256 Magmas et Volcans (LMV) in Clermont-Ferrand (France) and at the Earth and Planets
257 Laboratory in Washington D.C. (USA) using double zone-refined rhenium filaments.
258 Measurements were carried out using a two-line acquisition procedure with 3 sec.
259 pause between line 1 and line 2 in which the Faraday cups were centered successively
260 on masses 145 and 143. Measurement corresponds to blocks of 20 cycles each with 8
261 sec. integration time using amplifier rotation for a total of 540 cycles. Measured Nd
262 isotope ratios were corrected for mass fractionation using the exponential law and
263 $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Interferences coming from Ce at mass 142 and Sm at masses
264 144, 148, and 150 were measured at mass 140 and 147 for Ce and Sm, respectively.
265 Most sediment samples were measured using a 4-line routine allowing the

266 measurements of all isotope ratios dynamically (Garçon et al., 2018). Calculations
267 were performed offline using the Matlab routine presented in Garçon et al. (2018).
268 Two dynamic $^{142}\text{Nd}/^{144}\text{Nd}$ ratios were obtained with this method and the average
269 value is reported here. Each run was thoroughly examined and the four criteria
270 described by Garçon et al. (2018) were applied. Ratios were corrected for the drift
271 (fractionation rate) as described in Garçon et al. (2018) and the runs were stopped
272 when $^{146}\text{Nd}/^{144}\text{Nd}$ reached 0.724. All results presented in Table 1 are runs
273 characterized by normal, smooth and slow evolution of the $^{146}\text{Nd}/^{144}\text{Nd}$ ratio. The
274 mass fractionation rate was always below the threshold limit of 0.4 ppm/s proposed
275 by Roth et al. (2014).

276

277 Komatiite samples were measured in two different analytical sessions spaced 2
278 months apart. Sediments were measured during 5 sessions (#3 to #7). The terrestrial
279 neodymium standard JNdi-1 was measured 4 to 10 times each session using
280 the same acquisition procedure as for the samples (Table 1). The external
281 reproducibility (2SD) on the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio is between 3.5 and 6.2 ppm for these 7
282 sessions. A similar range is obtained on the other Nd isotope ratios, except for
283 $^{150}\text{Nd}/^{144}\text{Nd}$ that is up to 31 ppm in session 6. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios measured for the
284 JNdi-1 standard are in the range 0.512097 to 0.512104, in perfect agreement with the
285 accepted value of 0.512099 ± 0.000005 (Garçon et al., 2018).

286

287 Samples (komatiites, sediments and BHVO-2) were measured between 1 and 5 times.
288 They are either different measurements of the same load (called re-run in Table 1),
289 different rhenium filaments (called re-load) or different dissolutions and chemical
290 procedures of the same sample (called duplicate). Generally, $^{142}\text{Nd}/^{144}\text{Nd}$ isotope
291 ratios measured on samples are expressed in μ -units ($\mu^{142}\text{Nd} =$
292 $[(^{142}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{142}\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}] - 1 \times 10^6$) and calculated relative to the average
293 value obtained for the JNdi-1 standard (assumed to be equal to the modern terrestrial
294 value, $\mu^{142}\text{Nd} = 0$) in the given TIMS session. Results are compiled in Table 1 and
295 plotted in Figure 2.

296

297

298 5. RESULTS

299

300 Komatiite samples have $\mu^{142}\text{Nd}$ values ranging from -2.2 ± 5.2 to -7.7 ± 2.8 (2SD)
301 (Figure 2). These values are barely resolved from the JNdi-1 terrestrial standard when
302 2 SD uncertainties are considered, but all our samples have negative $\mu^{142}\text{Nd}$. Most of
303 samples were measured several times and results are in good agreement. There is no
304 correlation between Ce and Sm interferences and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios. The average
305 $\mu^{142}\text{Nd}$ for all komatiites is -4.0 (2SD = 4.1; 2SE = 1.5). The modern basalt from
306 Hawaii, BHVO-2, has a $\mu^{142}\text{Nd} = -1.3 \pm 3.9$ and is thus not resolved from the JNdi
307 standard value. We note that for 3 out of 7 samples, our measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios
308 are in perfect agreement with those of Blichert-Toft et al. (2015) with a difference
309 lower than 5 ppm. Compared to the data from Blichert-Toft et al. (2015), sample
310 BARB1 GC/4 shows a difference of 64 ppm and the difference is even larger for
311 BARB1 GC/34A, BARB2 GC/1 and GC/6 with differences of 159 ppm, -212 ppm
312 and 493 ppm, respectively. Although we did not use the same dissolution technique
313 (Parr bomb in Blichert-Toft et al. (2015) vs. Savillex beakers on hot plate in this
314 study), the variable results are unlikely to be due to the mineralogy of these samples
315 because komatiites are not expected to contain mineral phases that require high
316 pressure and temperatures for dissolution. Results of incomplete sample dissolution
317 have been highlighted by Blichert-Toft et al. (2004) for the Lu-Hf systematics where
318 zircon would have a significant influence if it were present in the sample. Here we
319 suspect instead a powder heterogeneity with variable amounts of secondary minerals
320 like amphibole and titanite that are important REE carriers. A small change of 5% in
321 the Sm/Nd ratio is sufficient to explain the largest difference in $^{143}\text{Nd}/^{144}\text{Nd}$ observed
322 for BARB2 GC/6.

323

324 Our data for komatiites from ICDP cores BARB 1 and BARB 2 in the Komati
325 Formation show deficits in ^{142}Nd . These, like the Schapenburg komatiites, are Al-
326 depleted; they both display depletion in HREE relative to MREE ($1.3 < (\text{Gd}/\text{Yb})_{\text{N}}$,
327 $\text{CHUR} < 1.6$) associated with low Hf/Sm ratios (< 0.6 compared to ≈ 0.7 for the Bulk
328 Silicate Earth, Palme and O'Neil, 2014). Weltevreden komatiites, in contrast, are
329 strongly depleted in LREE relative to HREE (Stiegler et al, 2012; Puchtel et al.,
330 2013). The $^{142}\text{Nd}/^{144}\text{Nd}$ ratios expressed in μ -units show a positive correlation with
331 Hf/Sm (Figure 4). Samples with the lowest $^{142}\text{Nd}/^{144}\text{Nd}$ ratios have the lowest Hf/Sm
332 values, except sample BARB1 GC/34A which falls off of this correlation. GC/34A is

333 the hyaloclastite with the highest LOI (13.1 %). Its $^{176}\text{Lu}/^{177}\text{Hf}$ ratio is very low
334 (0.01181) in comparison to other studied samples (0.02420-0.03075) (Blichert-Toft et
335 al., 2015). These features suggest that the trace element compositional characteristics
336 of this sample have been modified during metamorphism or hydrothermal alteration.

337

338 Sediments show a larger variability in $\mu^{142}\text{Nd}$ with reproducibility (2SD) exceeding 5
339 ppm for 7 samples (Table 1 and Figure 2). We interpret this variability as reflective of
340 the fact that sediments contain components with distinct sources and hence powder
341 heterogeneity would translate into variability in isotopic composition. This possibility
342 is supported by the large variability seen in $^{143}\text{Nd}/^{144}\text{Nd}$ in different measurements of
343 the same sample (see Table 1). Considering the average of all measurements
344 performed for each sediment, none of the sediments show a resolved ^{142}Nd anomaly
345 even if most of the values are negative. Similarly, when gathered by sediment types,
346 none of the 4 groups (crustal detritus-rich sediments, Si-rich sediments, Ca-, Fe-rich
347 sediments and cherts) show a resolvable ^{142}Nd anomaly. Crustal detritus-rich, Si-rich,
348 Ca-Fe-rich sediments, and cherts have average $\mu^{142}\text{Nd}$ equal to 2.0 ± 7.3 , -4.2 ± 10.1 ,
349 -1.8 ± 4.2 , 1.7 ± 12.6 , respectively. Errors (2SD) are higher than those calculated on
350 magmatic samples (komatiites and BHVO-2) and do not strictly reflect analytical
351 error but mostly sample heterogeneity.

352

353

354 6. DISCUSSION

355

356 **6.1. Sm-Nd and Lu-Hf systematics of komatiites do not support recycling of** 357 **sedimentary material into the komatiite source**

358 Komatiites from ICDP cores BARB1 and BARB2 (Komati Formation) have negative
359 $\mu^{142}\text{Nd}$ values, a signature that reflects an early-formed source with subchondritic
360 Sm/Nd ratio. Blichert-Toft et al. (2015) inferred a source with subchondritic Sm/Nd
361 from the negative initial $\epsilon^{143}\text{Nd}$ in the Komati clinopyroxene data but their whole rock
362 initial $\epsilon^{143}\text{Nd}$ data range from negative to positive values. In contrast, the majority of
363 initial $\epsilon^{176}\text{Hf}$ reported by Blichert-Toft et al. (2015) provides positive values, up to
364 +5.9. These values are indicative of a source characterized by superchondritic Lu/Hf
365 formed early in Earth's history. These results suggest a decoupling of the Sm/Nd and

366 Lu/Hf isotope systems compared to that expected for melting in the upper mantle and
367 observed in most mantle-derived magmas throughout Earth history.

368

369 In a $\epsilon^{176}\text{Hf}$ - $\epsilon^{143}\text{Nd}$ diagram, modern mantle-derived rocks such as mid-ocean ridge
370 basalts and ocean island basalts - MORB and OIB - plot along a trend named the
371 mantle array *i.e.* the Sm/Nd and Lu/Hf isotope systems are coupled. This positive
372 correlation reflects the common behaviors of the daughter elements (Hf and Nd) that
373 are more incompatible than the parents (Lu and Sm) during magmatic processes
374 (melting, crystallization) occurring in the upper mantle. Chauvel et al. (2008)
375 demonstrated that the slope of the mantle array is well reproduced by the melting of a
376 depleted peridotitic source contaminated by old oceanic crust and sediments derived
377 from the erosion of subaerial continental crust. Volcanic arc lavas tend to fall off this
378 correlation because they have slightly more radiogenic Hf isotope ratios relative to
379 MORB and OIB. This signature is caused by transfer during subduction of surface
380 material (sediments or altered oceanic crust) into the mantle wedge where melting
381 takes place (Chauvel et al., 2009). The major carrier of Hf in continental crust is
382 zircon, a mineral particularly resistant to weathering. Weathering and erosion
383 fractionate the Lu/Hf ratio such that fine-grained sediments have high Lu/Hf ratios
384 due to selective removal of coarse-grained zircon. Over time, these sediments develop
385 radiogenic Hf isotopic compositions but the Sm/Nd ratio is not modified because both
386 elements are carried in the same mineral phases.

387

388 The nature of early crust (mafic vs. felsic) and the evolution of its composition
389 through time are widely discussed (Carlson et al., 2019 and references therein).
390 Erosion products of a mafic crust devoid of zircons should not record decoupling of
391 parent/daughter ratios for the Sm-Nd and Lu-Hf isotope systematics. The study by
392 Garçon et al. (2017) of Barberton metasedimentary rocks drilled in the Fig Tree
393 Group provides a good overview of the composition of the eroded crust in the
394 Barberton area. The Fig Tree Group is younger than the Komati komatiites, but
395 contains sediments derived from crustal terranes that were present at the surface
396 during komatiitic volcanism. Crustal detritus-rich sediments from Fig Tree (see
397 Garçon et al., 2017) are the most suitable samples to estimate the composition of the
398 crust in the Barberton area. They show no significant decoupling of their Sm-Nd and

399 Lu-Hf isotope systematics at the time of deposition. Therefore, the incorporation of
400 such sediments alone into the komatiitic mantle source cannot explain the
401 superchondritic Lu-Hf isotopic signatures measured in most Barberton komatiites
402 (Figure 1B). In contrast, Si-rich sediments from Fig Tree have slightly negative
403 $\epsilon^{143}\text{Nd}$ (up to -2 at the time of deposition) and extremely radiogenic $\epsilon^{176}\text{Hf}$ (up to
404 +11). This composition reflects the presence of old chert clasts. Indeed, cherts from
405 Buck Reef have very high $^{176}\text{Lu}/^{177}\text{Hf}$ (0.12-1.33) and extremely low Hf/Sm ratios
406 (mean value 0.03, Garçon et al., 2017). Taken together, these two features may
407 explain the radiogenic Hf signature and the unusually low Hf/Sm ratios of the Komati
408 komatiites (Figures 1B and 4) if sediments similar to Buck Reef cherts were
409 incorporated into the mantle source of the komatiites (cf. model of Blichert-Toft et al.,
410 2015). Note that Buck Reef cherts are almost devoid of crustal detritus (i.e. no
411 terrigenous input), and hence represent an extreme pure endmember of what could be
412 an Archean seawater precipitate (Ledevin et al., 2019). The trace element patterns of
413 cherts, in particular Buck Reef cherts, are very different from other types of
414 sedimentary rocks because they have extremely low concentrations of REE and Hf
415 (Figure 5). Because of the elemental mass balance, once these sediments are mixed
416 with other types of sediments, the low Hf/Sm signature of cherts is rapidly
417 overprinted by the more typical Hf/Sm ratios of crustal detritus-rich sediments.
418 Assuming that the cores BARB-4 and BARB-5 are representative of sediments
419 deposited on the seafloor, we estimate that Archean sediments recycled into the
420 mantle would be made of about 31% Si-rich sediments, 24% Ca-, Fe-rich sediments,
421 34% crustal detritus-rich sediments and 10% cherts. The trace element pattern of such
422 a mixture is shown in Figure 5. While cherts have a negative Hf anomaly, the mixture
423 pattern displays a positive Hf anomaly and a higher Hf/Sm ratio (0.97) than the
424 komatiites drilled in BARB-1 and BARB-2 (0.39-0.71). Assuming that Nd and Hf are
425 congruently transferred from the surface to the melting region, recycling of this
426 sediment mixture in the mantle cannot produce the trace element characteristics of the
427 studied komatiites. Preferential extraction of rare earth elements such as Sm and Nd
428 over high field strength elements (HFSE) such as Hf from the slab during subduction,
429 as seen for example in calc-alkaline basalts from Newberry volcano (low Hf/Sm
430 ratios, Carlson et al., 2018), would make things even worse since it would increase the
431 Hf/Sm ratio of the recycled material transported into the deep mantle. The latter

432 process is not considered in the modeling presented below. The modelling also does
433 not include crustal detritus-rich sediments and assumes that chert is the only type of
434 sedimentary rocks being recycled into the source of the komatiites.

435

436 Blichert-Toft et al. (2015) attributed the decoupled Hf-Nd isotope signature to the
437 incorporation of chert into the source of some Barberton komatiites. Modeling
438 performed in our study does not support this conclusion. Blichert-Toft et al. (2015)
439 modelled the Nd-Hf isotopic composition of komatiitic source as a mixture between
440 cherts and peridotitic depleted mantle. We obtained divergent results because we
441 include a third component, oceanic crust. If the recycling of sediments into the mantle
442 occurred, it could be driven by plate tectonics and thus sediments would be subducted
443 as a thin layer on top of the oceanic crust. This scenario is highly speculative but
444 several geochemical evidences support initiation of plate tectonics on Earth shortly
445 after the end of the Hadean (e.g. Shirey et al., 2008). We also considered two
446 compositions for the mantle: primitive mantle and mantle depleted in incompatible
447 elements with a composition similar to depleted MORB mantle. The end-member
448 compositions are reported in Table 2 and plotted in Figure 6. We note that a Hf/Sm
449 ratio as low as 0.6 as measured in the studied komatiites requires an unlikely high
450 contribution of chert in the recycling material (crust-chert ratio of 40:60) with a
451 minimum of 30% of recycling into the mantle i.e. melting of a source consisting of
452 70% peridotitic mantle and 30% crust-chert. Moreover a crust-chert ratio of 40:60
453 corresponds to an unrealistic thickness of 15 km of chert accumulated on top of 10 km
454 of oceanic crust. Furthermore, magmas with the composition of komatiites cannot be
455 produced by melting a source that enriched in SiO₂. This extreme scenario gives a
456 maximum deficit of -3 ppm in $\mu^{142}\text{Nd}$, a $\epsilon^{143}\text{Nd}$ of about -0.5 and a positive $\epsilon^{176}\text{Hf}$ of
457 about +2 assuming a depleted composition for the peridotitic mantle component
458 (Figure 6). However, it does not explain the Hf/Sm - $\mu^{142}\text{Nd}$ correlation observed for
459 Barberton komatiites as shown in Figure 4 (see mixing curves in Supplementary
460 Figure 2).

461 These calculations show that the recycling of deep-sea sediments does not satisfy both
462 the isotope constraints and the Hf/Sm ratio of the studied komatiites. Another
463 mechanism of formation must therefore be envisaged to explain the $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$
464 and ^{176}Lu - ^{176}Hf isotopic systematics of the studied komatiites.

465

466

467 **6.2. Deep residual liquid of magma ocean crystallization in the komatiite source**

468 As mentioned above, Sm-Nd and Lu-Hf fractionate in the same sense when melting or
469 crystallization occur in the upper mantle. The two isotopic systems can however be
470 decoupled when deep mantle mineral phases are involved (Figure 7A). Bridgmanite is
471 the only abundant mantle mineral that preferentially concentrates Hf relative to Lu
472 ($D_{\text{Hf}} > D_{\text{Lu}}$). We calculated the bulk partition coefficient for a mixture of
473 bridgmanite/ferropericlasite/Ca-perovskite in the proportions estimated for the lower
474 mantle (Figure 7B). Sm/Nd and Lu/Hf are decoupled when the bridgmanite
475 proportion exceeds 77% because at this point, the bulk partition coefficient for Lu
476 becomes smaller than that of Hf, and Sm/Nd and Lu/Hf ratios are inversely
477 fractionated during melting or crystallization. This signature has been identified from
478 ^{176}Hf - ^{143}Nd isotope measurements of Isua metabasalts from several formations and
479 interpreted to reflect a deep magma ocean event (Rizo et al., 2011 Hoffman et al.,
480 2011).

481

482 The following discussion explores the different steps that are needed in the
483 fractionation history of the source of the Komati komatiites to explain their low
484 Hf/Sm ratios together with their $^{142}\text{Nd}/^{144}\text{Nd}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic
485 compositions (Table 3, Figures 8 and 9). We argue that the crystallization of a deep
486 magma ocean plays a major role in the generation of the observed $\mu^{142}\text{Nd}$ -Hf/Sm
487 correlation (Figure 4) even if melting and fractional crystallization processes that may
488 occur during magma ascent during the last step can slightly modified the REE-Hf
489 signature (Puchtel et al., 2016; Sossi et al., 2016). This model generally follows the
490 different steps proposed by Puchtel et al. (2016) for Schapenburg komatiites.

491

492 **Stage 1. CHUR evolution**

493 During the first stage starting from the formation of the solar system, the primitive
494 mantle has a chondritic composition.

495

496 **Stage 2. Isotopic evolution of solidified magma ocean**

497 Lu/Hf and Sm/Nd fractionated during crystallization of a deep magma ocean as
498 represented in Figure 8. We used a model similar to model 1 of Morino et al. (2018)
499 and the partition coefficients and other parameters are reported in Table 3. We
500 calculated compositions of cumulate and residual melt at each step using a batch
501 crystallization model. We consider a constant mineralogical assemblage over the
502 crystallization interval proceeding from the bottom up. Melting diagrams show a
503 sequence of crystallization at high pressure and for a BSE bulk composition
504 establishing the normative abundances of bridgmanite, ferropericlaase and Ca-
505 perovskite (see the review by Andraut et al., 2017). Our calculations were made for a
506 constant amount of ferropericlaase (16%) and variable proportions of Ca-perovskite (2
507 to 7%) and bridgmanite (77 to 82%). These changes in proportions are first-order
508 simulations of the progress of crystallization with bridgmanite alone in the early
509 stages and higher proportions of Ca-perovskite in the later stages. The negative
510 $\mu^{142}\text{Nd}$ and strongly positive initial $\epsilon^{176}\text{Hf}$ of Barberton komatiites reflects a source
511 with low Sm/Nd and high Lu/Hf ratios (upper left quadrant in Figure 8). This
512 signature corresponds to residual liquids formed by the crystallization of deep
513 cumulates containing a relatively high proportion of Ca-perovskite. The compositions
514 closest to the BSE values are produced in the first steps of the crystallization while the
515 most extreme compositions correspond to 60% crystallization; i.e. solidification of the
516 entire lower mantle.

517

518 If we assume an age for magma ocean crystallization, we can estimate Sm/Nd ratios
519 for the komatiite source using the ^{142}Nd anomalies in Barberton samples.
520 Fractionation ages calculated from combined ^{146}Sm - ^{142}Nd and ^{147}Sm - ^{143}Nd studies on
521 Archean samples are mostly between 4.36 and 4.40 Ga (Boyet et al., 2003; Caro et al.,
522 2003, 2016, Morino et al., 2018). Given that similar age ranges are obtained for
523 samples from the lunar crust and for differentiation of the lunar mantle, this suggests
524 that the terrestrial magma ocean crystallized shortly after the giant Moon-forming
525 impact (Borg et al., 2019). During the second stage (T_1 from 4.36-4.40 Ga), we
526 assume $^{147}\text{Sm}/^{144}\text{Nd}$ ratios between 0.175 to 0.190 and obtain a deficit of 5 ppm (+/-
527 3) for $\mu^{142}\text{Nd}$.

528

529 The amount of bridgmanite needed to fractionate Sm/Nd ratios in this range has a
530 strong effect on the Lu/Hf ratios, as shown in Figure 8. Lu/Hf ratios are strongly
531 fractionated in residual liquids that form from a source with a high proportion of
532 bridgmanite; the Hf/Sm ratio decreases rapidly as the proportions of bridgmanite
533 increases. We consider it unlikely that liquid is trapped at the beginning of the
534 crystallization when the crystal fraction and the viscosity are both low (Solomatov,
535 2007). Our preferred model assumes an assemblage of 76% bridgmanite, 16%
536 ferropericlase and 5% of Ca-perovskite. After 30% of crystallization, the residual
537 liquid has the composition shown with the symbol 2 in Figure 8 and a Hf/Sm ratio
538 equal to 0.57 (Table 3) that is very similar to the mean Hf/Sm ratio of analyzed
539 samples (0.58 ± 0.07 excluding BARB1 GC34/A). In our model, the crystallization of
540 bridgmanite/Ca-perovskite in the magma ocean lowers the Hf/Sm ratio of the source.
541 We show in the following section that this ratio also varies slightly during melting or
542 crystallization in the upper mantle.

543

544 **Stage 3. Depletion event in the upper mantle**

545 Considerable uncertainty surrounds the ^{147}Sm - ^{143}Nd isotopic signature of the
546 komatiitic source at 3.48 Ga because whole-rock measurements scatter around
547 chondritic compositions while two out of three clinopyroxene separates have a
548 negative initial $\epsilon^{143}\text{Nd}$ of about -2 (Figure 1). Values of $\epsilon^{176}\text{Hf}$ of clinopyroxenes and
549 whole rocks, also calculated for the source at 3.48 Ga, are more coherent and yield an
550 initial $\epsilon^{176}\text{Hf}$ of about +2 (Blichert-Toft et al., 2015). To explain the decoupled
551 signature of the short-lived Sm-Nd systematics and the long-lived ^{176}Lu - ^{176}Hf
552 systematics of the samples from the Komati Formation, we invoke a depletion event
553 that occurred sometime after the extinction of ^{146}Sm . A multistage evolution is even
554 more pronounced in the Schapenburg komatiites which have distinctly positive $\epsilon^{143}\text{Nd}$
555 (+2.4) and $\epsilon^{176}\text{Hf}$ (+5.6) at 3.55 Ga (Puchtel et al., 2016), yet negative $\mu^{142}\text{Nd}$ (-5.5).

556

557 We invoke a low-degree (<1%) melting event after the extinction of ^{146}Sm (4 Ga).
558 This melting event would have depleted the mantle in incompatible elements to reach
559 a depletion degree similar that measured in modern N-MORB (i.e. less than 1% of
560 partial melting after Salters and Stracke, 2004). The mineralogy of the source is
561 estimated from melting models proposed by Salters and Stracke (2004) at 3 GPa

562 (garnet in the source). The composition of the solid residues left after extraction of a
563 0.5% partial melt is indicated by the symbol 3 in Figure 8. The initial $\epsilon^{143}\text{Nd}$ value in
564 this model is always negative (Figure 9) which is consistent with the negative value
565 measured in the Barberton clinopyroxene separate but inconsistent with the near-zero
566 values obtained from the whole rock samples. A small increase of the degree of
567 partial melting (1%) gives initial $\epsilon^{143}\text{Nd}$ and $\epsilon^{176}\text{Hf}$ equal to 0 and 2.2, respectively.
568 The source of Schapenburg komatiite may have experienced a higher degree of partial
569 melt extraction (5% for Schapenburg komatiites) producing highly radiogenic values
570 at 3.55 Ga (Figure 1). The Hf/Sm ratio of the mantle source is not significantly
571 modified during this melting event (see Table 3).

572

573 **Stage 4. Melting to produce the komatiite magmas**

574 After the depletion event, the komatiites formed at 3.48 Ga by decompression melting
575 during which majorite was left in the residue. As shown in Figure 8 the Sm/Nd and
576 Lu/Hf ratios of Komati and Schapenburg komatiites are perfectly reproduced
577 considering 30% partial melting of a source comprising 55% olivine and 45%
578 majorite, which corresponds to the mineralogy of deepest part of the upper mantle
579 (18-22 GPa, Morino et al., 2018). The model well reproduces the negative $\mu^{142}\text{Nd}$ and
580 the positive initial $\epsilon^{176}\text{Hf}$ for komatiites at 3.48 Ga (Figure 9). We obtain a slightly
581 negative $\epsilon^{143}\text{Nd}$ value at 3.48 Ga, which is intermediate between with the negative
582 initial $\epsilon^{143}\text{Nd}$ recorded by the clinopyroxene separates and the near zero value of the
583 whole rocks. Ratios calculated at each step are reported in Table 3. The final Hf/Sm
584 value is slightly lower than those measured in komatiites (0.51 instead of 0.58) but
585 remains in good agreement with the measured ratios when considering model
586 uncertainties (see below and Figure 10).

587

588 Because we do not know the exact timing of the different events and the compositions
589 of the different reservoirs involved in the isotopic model described above, we
590 performed a Monte-Carlo simulation ($N = 10,000$) assuming variable input
591 parameters at each stage (Figure 10) to test the robustness and sensitivity of the
592 model. In Stage 1, we took into account the uncertainty on the initial Sm-Nd and Lu-
593 Hf isotopic composition of the Bulk Silicate Earth (uncertainty on the $^{176}\text{Lu}/^{177}\text{Hf}$ and
594 $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the CHUR from Bouvier et al., 2008). In Stage 2, we assumed

595 that the magma ocean crystallized between 4.36 and 4.40 Ga as discussed above. As
596 we do not precisely know how much of the mantle crystallized, we let the percentage
597 of crystallization vary between 20 and 50% with a range of composition for the
598 cumulate as shown in Figure 9 (bridgmanite/ferropericlaase/Ca-perovskite from
599 77/16/7 to 82/16/2). In Stage 3, we tested the effects of changing the depletion age
600 between 4.1 and 3.9 Ga and a melting fraction between 0.2 and 1.2% for the mantle
601 depletion event. Finally, in Stage 4, we let the melt fraction vary between 30 and 40%
602 to form the komatiite at 3.48 Ga. Using these ranges of parameters for each stage
603 rather than a fixed value show that the results of the komatiite model are consistent
604 with the measured values.

605 The Monte-Carlo simulation perfectly reproduces the range of $^{147}\text{Sm}/^{144}\text{Nd}$,
606 $^{176}\text{Lu}/^{177}\text{Hf}$, and Hf/Sm ratios measured in the studied komatiites (Figure 9). The
607 modelled initial Nd and Hf isotopic composition are within the range of those
608 measured in the komatiites but are under constrained given the wide range of input
609 parameters we used for each stage in the Monte-Carlo simulation (Figure 10). More
610 importantly, we performed several other Monte-Carlo simulations (not shown here)
611 involving melting events only in the upper mantle (i.e. replacing the magma ocean
612 crystallization stage by an early melting event in the upper mantle) and none of them
613 was successful in reproducing the decoupled Nd-Hf isotopic signature of the studied
614 komatiites. Finally, we note that the results of the model are highly sensitive to the
615 partition coefficients used for the melting and crystallization event at each stage. We
616 thus tried to carefully select the most appropriate partition coefficients (mineral
617 assemblages, pressure and temperature similar to those expected for the modeled
618 processes). The sources of the model parameters, including partition coefficients, are
619 reported in Table 3.

620

621 The correlation observed between $\mu^{142}\text{Nd}$ and Hf/Sm in komatiites suggests that the
622 fractionation of Hf from Sm occurred during an early event. Only the crystallization
623 of lower mantle mineral phases fractionates enough the high field strength elements
624 from the rare earth elements. Modeling of the magma ocean crystallization shows that
625 Hf/Sm fractionation remains relatively weak in the residual liquid in comparison to
626 the cumulate (see trace element patterns in supplementary Figure 3), hence it is
627 expected that the trace element pattern of the studied komatiites should not record a

628 strong magma ocean signature. Anomalies in HFSE can be quantified using the Zr
629 anomaly $Zr/Zr^* = Zr_N / (Sm_N + Nd_N) / 2$ with N =normalized to CI (Barrat et al., 2012).
630 The Zr anomaly calculated in the residual melt (0.78 in stage 2) is lower than that
631 measured in Schapenburg and Komati komatiites (0.53 to 0.61), suggesting that the
632 komatiites may have indeed preserved the remnant signature of the magma ocean
633 crystallization event.

634

635 In contrast, the Weltevreden komatiites source does not retain a record of the deep
636 magma ocean crystallization event. Zirconium anomalies are weaker in the samples
637 (0.82 to 0.93) in good agreement with their higher Hf/Sm ratios and the absence of a
638 resolved ^{142}Nd anomaly. The trace elements in these komatiites record a strong
639 depletion event that occurred sometime before or during the melting that produced the
640 komatiite magma. This event decreases only slightly the Hf/Sm ratio.

641

642 Schapenburg komatiites have higher ϵHf and $\epsilon^{143}\text{Nd}$ at the age of crystallization
643 relative to Barberton komatiites. Puchtel et al. (2016) propose that the source was
644 depleted by 5% partial melting in Stage 3. In this case, the depletion event completely
645 erases any magma ocean crystallization signature recorded by the long-lived isotopes.
646 This emphasizes the value of measuring the short-lived ^{146}Sm - ^{142}Nd system when
647 reconstructing events in the Hadean and Archean mantle.

648

649

650 **7. Conclusions**

651

652 Measurements of ^{146}Sm - ^{142}Nd systematics in komatiites and sediments sampled
653 during the ICDP drilling project (BARB1-2-3-4-5) give strong constraints on the
654 evolution of the mantle source through time. The resolved negative $\mu^{142}\text{Nd}$ measured
655 in komatiites prove that the source was fractionated early in Earth history to form a
656 reservoir with a subchondritic Sm/Nd ratio. Deficits in ^{142}Nd are correlated with low
657 Hf/Sm ratios suggesting that fractionation between rare earth elements and high field
658 strength elements occurred during this early differentiation event. These komatiites
659 have strongly radiogenic initial $\epsilon^{176}\text{Hf}$, but near-chondritic initial $\epsilon^{143}\text{Nd}$ indicated
660 decoupling of Sm-Nd and Lu-Hf systematics. As previously proposed for

661 Schapenburg komatiites, which share similar geochemical characteristics (deficit in
662 ^{142}Nd , radiogenic $\varepsilon^{176}\text{Hf}$), the mantle source recorded the crystallization of a deep
663 magma ocean. We calculate that the komatiite mantle source represents the residual
664 liquid for a bridgmanite/ferropericlase/Ca-perovskite mineralogy in proportion
665 79/16/5 after 50% crystallization of the lower mantle. Melting under these conditions
666 decouples Lu-Hf from Sm-Nd, and lowers the Hf/Sm ratio. Parent/daughter ratios
667 were fractionated again during a depletion event that occurred after the extinction of
668 ^{146}Sm . With this model we explain the positive $\varepsilon^{176}\text{Hf}$ and chondritic to slightly
669 subchondritic $\varepsilon^{143}\text{Nd}$, negative $\mu^{142}\text{Nd}$ and low Hf/Sm ratios measured in the
670 komatiitic samples. Recycling of chert cannot explain both the Hf and Nd isotopic
671 systematics of Barberton komatiites. None of the sediments measured in the
672 Barberton area have significantly negative ^{142}Nd and the recycling of these sediments
673 does not change the Hf/Sm ratio of the mantle source.

674

675

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677

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690

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869 TABLE CAPTION

870 **Table 1.** Nd isotopic composition measured in komatiites and sediments drilled at
871 BARB 1-5.

872

873 **Table 2.** Composition of the different end-members considered in the mixing model
874 calculation. The composition of the Primitive Mantle is from Palme and O'Neill
875 (2014). This mantle has chondritic ratios for refractory lithophile elements (Sm, Nd,
876 Lu, Hf) and then has epsilon values at zero. The Depleted MORB Mantle composition
877 is from Salters and Stracke (2004). Hf and Nd isotopic compositions have been
878 calculated to account for an $\epsilon^{143}\text{Nd}$ value of +2 at 3.48 Ga (mean value measured in
879 Archean samples, see Boyet and Carlson 2005). The Hf isotopic composition is then
880 estimated using the Hf-Nd mantle array of Chauvel et al. (2008). This equation
881 defined from modern samples is also valid for Archean samples (Vervoort and
882 Blichert-Toft, 1999). A mafic rock from the Ujaraaluk unit from the Nuvvuagittuq
883 Greenston Belt (sample PC-162 belonging to the enriched low-Ti group) is taken as
884 an early crust analogue characterized by negative $\mu^{142}\text{Nd}$ (O'Neil et al., 2011). Hf and
885 Nd isotopic compositions have been calculated considering the crust formed 4.3 Ga
886 from a chondritic composition (O'Neil et al., 2008). Then the isotopic composition
887 evolved until 3.45 Ga with parent/daughter ratios equal to those measured in the
888 sample PC-162. Concentrations and parent/daughter ratios for chert correspond to the
889 mean value of the 3 chert samples measured in Garçon et al. (2017). Hf-Nd isotopic
890 compositions are calculated assuming an initial chondritic ratio and 0.8 Ga of
891 evolution using the measured parent/daughter ratios. Cherts have extremely high
892 Lu/Hf ratios and then develop with time highly radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. It is
893 assumed that archean sediments on the oceanic seafloor have a residence time much
894 higher than today (up to 200 Ma).

895

896 **Table 3.** Description of the 4-stage model explaining the $^{142,143}\text{Nd}$ and ^{176}Hf isotope
897 signature of the komatiite source at 3.48 Ga and measured Sm/Nd, Lu/Hf and Hf/Sm
898 ratios. For each step are reported 1) the timing, 2) partition coefficients and
899 mineralogy of the source, 3) crystallization and melting rates.

900 Concentrations for the primitive mantle are from Palme and O'Neill (2014). Partition
901 coefficients are from: Ca-perovskite and bridgmanite (Corgne et al., 2005),

902 ferropericlasite (Walter et al., 2004), olivine, orthopyroxene, clinopyroxene and garnet
903 (compilation from Salters and Stracke 2004), majorite (compilation from Morino et
904 al., 2018).

905

906

907

908 **FIGURE CAPTION**

909 **Figure 1.** Initial $\epsilon^{143}\text{Nd}$ (**A**) and $\epsilon^{176}\text{Hf}$ (**B**) for Schapenburg (3.55 Ga), Komati (3.48
910 Ga, ICDP samples are shown with red circles and outcrop samples with white
911 triangles), and Weltevreden (3.33 Ga) komatiites. Data from Blichert-Toft et al.
912 (2015) and Puchtel et al (2013, 2016). ICDP samples analyzed in this study are shown
913 by symbols with red borders. Few samples with extremes values plotting outside of
914 the scale are not represented. Cpx and Amph stand for clinopyroxene and amphibole
915 separates respectively.

916

917 **Figure 2.** $\mu^{142}\text{Nd}$ ($^{142}\text{Nd}/^{144}\text{Nd}$ ratio normalized to terrestrial standard $\times 10^6$) measured
918 in komatiite and sediment samples from the IDCP BARB 2-5 drilled cores. Most of
919 samples were measured several times and the average value for each sample is
920 represented by the symbol with larger border. Error bars are 2SE for individual
921 measurement and 2SD for the mean value. The reference basalt BHVO-2 was
922 measured 4 times yielding a mean value of -1.3 ± 3.9 . Literature data on komatiites
923 (Caro et al., 2006; Puchtel et al., 2013, 2014) and meta-tholeiite of the Komati
924 Formation and two meta-komatiites from the Dwalile Greenstone Remnant
925 (Schneider et al., 2018) are reported in the upper part of the diagram. The two grey
926 fields correspond to average 2SD (dark) and 2SE (light) values calculated from
927 repeated measurements of the JNdi-1 standard reported in Table 1.

928

929 **Figure 3.** Sm-Nd (**A**) and Lu-Hf (**B**) isochron diagrams for drill core komatiites
930 (BARB 1 and BARB 2) analyzed in this study. Data are from Blichert-Toft et al.
931 (2015).

932

933 **Figure 4.** $\mu^{142}\text{Nd}$ vs Hf/Sm in komatiites from Barberton (ICDP this study and
934 Komati from Puchtel et al., 2013), Schapenburg (Puchtel et al., 2016) and

935 Weltevreden (Puchtel et al., 2013).). The two grey fields correspond to average 2SD
936 (dark) and 2SE (light) values calculated from repeated measurements of the JNdi-1
937 standard reported in Table 1.

938

939 **Figure 5.** REE-Hf element patterns normalized to chondrites CI (Barrat et al., 2012)
940 for sediments drilled in the Barberton area. Sediments have been analyzed in Garçon
941 et al. (2017). The 4 groups are defined on the basis of major and trace elements. The
942 red line entitled mixing represents a potential pile of sediments subducted during the
943 Archean. Proportions are defined from the BARB 3-4-5 drilled core lithologies: 31%
944 Si-rich sediments, 24% Ca-,Fe-rich sediments, 34% crustal detritus-rich sediments
945 and 10% cherts. The composition of ICDP komatiites analyzed in this study are
946 represented by the yellow field (Coetzee, 2014)

947

948 **Figure 6.** Evolution of the modeled $\mu^{142}\text{Nd}$ (A), Hf/Sm (B), $\varepsilon^{143}\text{Nd}_{3.48\text{Ga}}$ (C), and
949 $\varepsilon^{176}\text{Hf}_{3.48\text{Ga}}$ (D) with respect to the sedimentary proportions determined using the
950 mixing models. Values considered for the different end-members are reported in
951 Table 2. Blue and black lines represent calculated mixing considering a primitive
952 mantle compositions and a depleted mantle composition, respectively. This model
953 assumes the recycling of a mafic crust with sediments at its top (pile of cherts). The
954 crust/chert ratio gradually decreases from the plain line to the increasingly fine dotted
955 lines (90:10, 70:30, 50:50, 40:60). These ratios mimic a difference in thickness and/or
956 productivity during partial melting. The red line in the 4 panels shows the mean value
957 measured in the studied komatiites. Initial $\varepsilon^{143}\text{Nd}$ and $\varepsilon^{176}\text{Hf}$ values are from Blichert-
958 Toft et al., 2015. Initial $\varepsilon^{176}\text{Hf}$ values are positive for both clinopyroxenes and their
959 host rocks (mean value = +3).

960

961 **Figure 7. A)** Mineral-melt partition coefficients for upper (clinopyroxene,
962 orthopyroxene, olivine, majorite, garnet) and lower mantle phases (ferropericlase, Ca-
963 perovskite, bridgmanite). Partition coefficients are from: Ca-perovskite and
964 bridgmanite (Corgne et al., 2005), ferropericlase (Walter et al., 2004), olivine,
965 orthopyroxene, clinopyroxene and garnet (compilation from Salters and Stracke
966 2004), majorite (compilation from Morino et al., 2018). Values for olivine and its
967 polymorphs are not shown because the partition coefficients for these minerals are

968 extremely low ($<10^{-3}$), thus these phases do not contribute to the total budget of Sm,
969 Nd, Lu, and Hf. **B)** Bulk partition coefficients for lower mantle mineralogy with
970 bridgmanite/ferropericlase/Ca-perovskite proportions varying from 75/16/9 to
971 82/16/2. Sm/Nd and Lu/Hf fractionate in opposite directions when the bridgmanite
972 proportion in the lower mantle is higher than 77% (dashed lines; or equivalent to a
973 bridgmanite proportion higher than 92% in a bridgmanite/Ca -perovskite two
974 component mixing).

975

976 **Figure 8.** Present day $^{176}\text{Lu}/^{177}\text{Hf}$ vs $^{147}\text{Sm}/^{144}\text{Nd}$ ratios calculated in the mantle
977 source at the different stages (1 to 4) compared to data measured in komatiites from
978 the Komati Formation (this study, Blichert-Toft et al., 2015; Puchtel et al., 2013),
979 Schapenburg (Puchtel et al., 2016) and Weltevreden (Puchtel et al., 2013). ICDP
980 samples analyzed in this study for ^{146}Sm - ^{142}Nd systematics are red circles with thick
981 borders. The different stages are indicated by numbers in black circles: Stage 1: 4.567
982 Ga to 4.537 Ga - CHUR evolution; Stage 2: 4.537 Ga to 4.027 Ga - Isotopic evolution
983 of the solidified magma ocean; Stage 3: 4.027 Ga to 3.48 Ga - depletion in upper
984 mantle; Stage 4: 3.48 Ga - komatiite formation. See Table 3 for details. The
985 compositions residual liquids and cumulates formed during the crystallization of a
986 magma ocean are also plotted in the figure. Lu/Hf and Sm/Nd are decoupled (upper
987 left quadrant) when the bridgmanite proportion in a two-component mixture
988 (bridgmanite/Ca-perovskite) exceeds 92% (proportions are indicated at the ends of the
989 lines). Compositions are represented for 10, 20, 30, 40, 50 and 60% of crystallization
990 (60% corresponds to the entire lower mantle). The OIB-MORB correlation illustrates
991 the positive trend commonly observed in ocean-island and mid-ocean ridge basalts
992 (mantle array from Chauvel et al., 2008).

993

994 **Figure 9.** Isotopic evolution of $\epsilon^{143}\text{Nd}$, $\epsilon^{176}\text{Hf}$, and $\mu^{142}\text{Nd}$ (right Y-axis) through
995 time, from the start of solar system formation to the age of crystallization of
996 Barberton komatiites. These 3 steps are described in detail in Table 3. Stars and
997 circles represent the initial composition of ICDP drill core komatiites for $\epsilon^{143}\text{Nd}$ and
998 $\epsilon^{176}\text{Hf}$, respectively (red symbols correspond to the initial defined from the
999 isochrons). Measured $\mu^{142}\text{Nd}$ for the same samples are represented by the blue
1000 squares. Constants used in the calculation: $T_{1/2}^{146}\text{Sm}=103$ Ma (Friedman et al., 1966),

1001 $\lambda^{147}\text{Sm} = 6.54 \times 10^{-12} \text{ y}^{-1}$, $\lambda^{176}\text{Lu} = 1.865 \times 10^{-11} \text{ y}^{-1}$ (Scherer et al., 2001), CHUR
1002 parent/daughter ratios from Bouvier et al. (2008). The starting initial $^{142}\text{Nd}/^{144}\text{Nd}$ of
1003 the primitive mantle is considered equal to that of modern terrestrial samples (Bouvier
1004 and Boyet, 2016; Burkardt et al., 2016).

1005

1006 **Figure 10.** Results of Monte-Carlo simulations to test the sensitivity of the model
1007 (N=10 000). The range of input parameters tested at each of the four stages is
1008 indicated in the bottom left corner. Red circles and green squares are komatiite data
1009 from Barberton (same symbols as in Figure 8). ICDP samples analyzed in this study
1010 for ^{146}Sm - ^{142}Nd systematics are red circles with thick borders. **A)** Present-day
1011 $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ modeled at each stage. CHUR compositions are from
1012 Bouvier et al. (2008). **B)** Histogram showing modeled Hf/Sm ratios at each stage.
1013 CHUR composition is similar to the primitive mantle composition defined by Palme
1014 and O'Neill (2014). Komatiite data were arbitrarily plotted at a data frequency of
1015 2000. **c)** Modeled Nd and Hf isotopic compositions at T₁ for Stage 1, T₂ for Stage 2,
1016 and T₃ for Stage 3. Epsilon values are calculated relative to the CHUR composition of
1017 Bouvier et al. (2008).

1018

	Primitive Mantle	Depleted MORB Mantle	Crust	Chert
$\mu^{142}\text{Nd}$	0	0	-8	0
$\varepsilon^{143}\text{Nd}_{,3.48\text{Ga}}$	0	2	-3.5	-1
$\varepsilon^{176}\text{Hf}_{,3.48\text{Ga}}$	0	4.5	-1.9	163
Sm	0.4347	0.27	1.6	0.763
Nd	1.341	0.713	5.9	2.593
Lu	0.07083	0.063	0.3	0.147
Hf	0.3014	0.199	1.4	0.024
Hf/Sm	0.693	0.74	0.88	0.03

Table 2.

Composition of the different end-members considered in the mixing model calculation. The composition of the Primitive Mantle is from Palme and O'Neill (2014). This mantle has chondritic ratios for refractory lithophile elements (Sm, Nd, Lu, Hf) and then has epsilon values at zero. The Depleted MORB Mantle composition is from Salters and Stracke (2004). Hf and Nd isotopic compositions have been calculated to account for an $\varepsilon^{143}\text{Nd}$ value of +2 at 3.48 Ga (mean value measured in Archean samples, see Boyet and Carlson 2005). The Hf isotopic composition is then estimated using the Hf-Nd mantle array of Chauvel et al. (2009). This equation defined from modern samples is also valid for Archean samples (Vervoort and Blichert-Toft, 1999). A mafic rock from the Ujaraaluk unit from the Nuvvuagittuq Greenstone Belt (sample PC-162 belonging to the enriched low-Ti group) is taken as an early crust analogue (O'Neil et al., 2011). Hf and Nd isotopic compositions were calculated considering the crust formed 4.3 Ga from a chondritic composition (O'Neil et al., 2008). Then the isotopic composition evolved until 3.45 Ga with parent/daughter ratios equal to those measured in the sample PC-162. Concentrations and parent/daughter ratios for chert correspond to the mean value of the 3 chert samples measured in Garçon et al. (2017). Hf-Nd isotopic compositions are calculated assuming an initial chondritic ratio and 0.8 Ga of evolution using the measured parent/daughter ratios. Cherts have extremely high Lu/Hf ratios and then develop with time highly radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. Archean sediments on the oceanic seafloor are assumed to have a residence time much higher than today (up to 200 Ma).

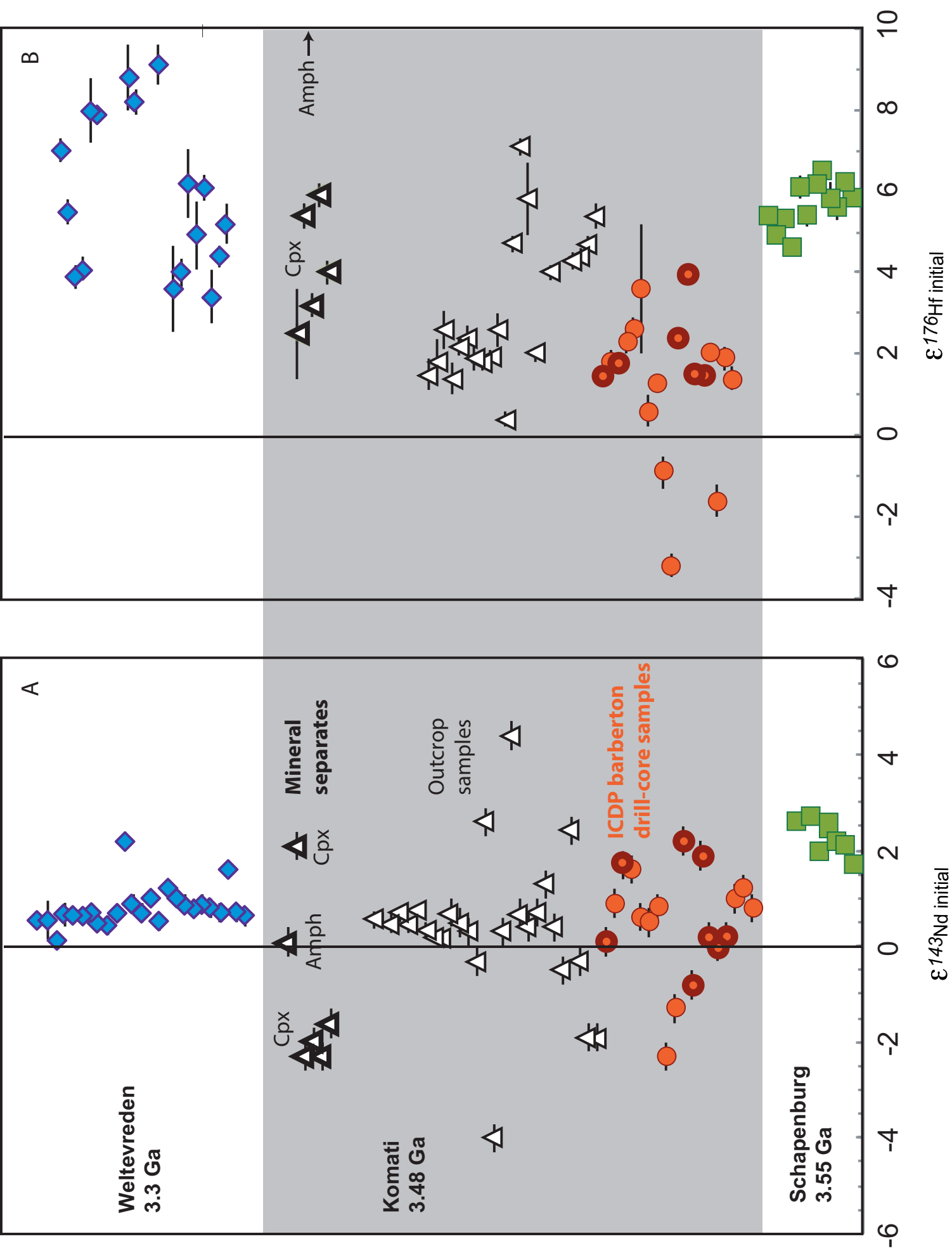


Figure 1 . Boyet et al.

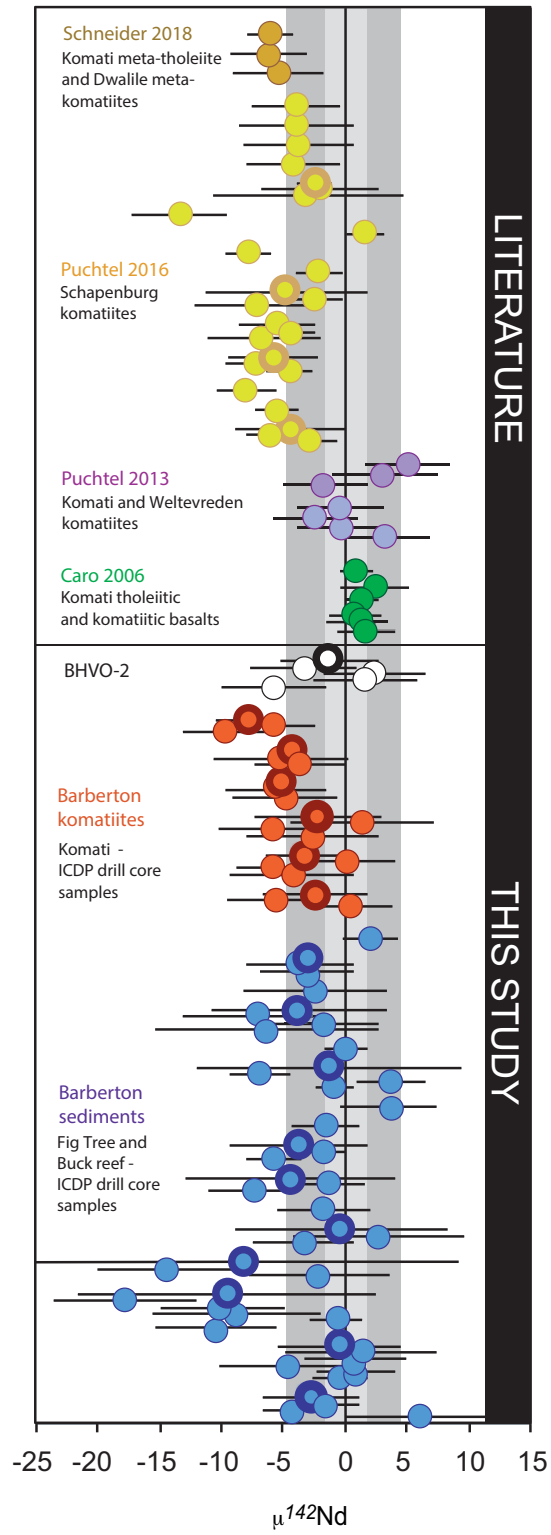


Figure 2. Boyet et al.

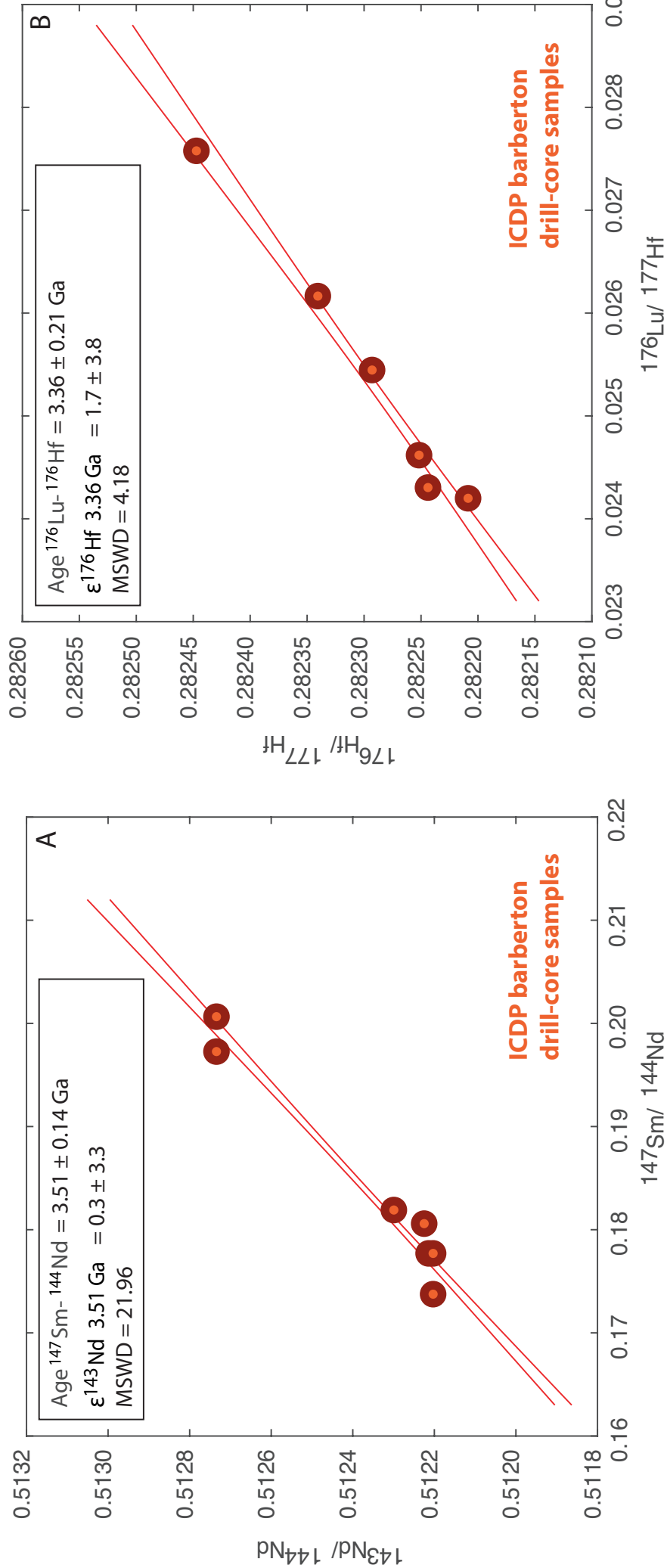


Figure 3. Boyet et al.

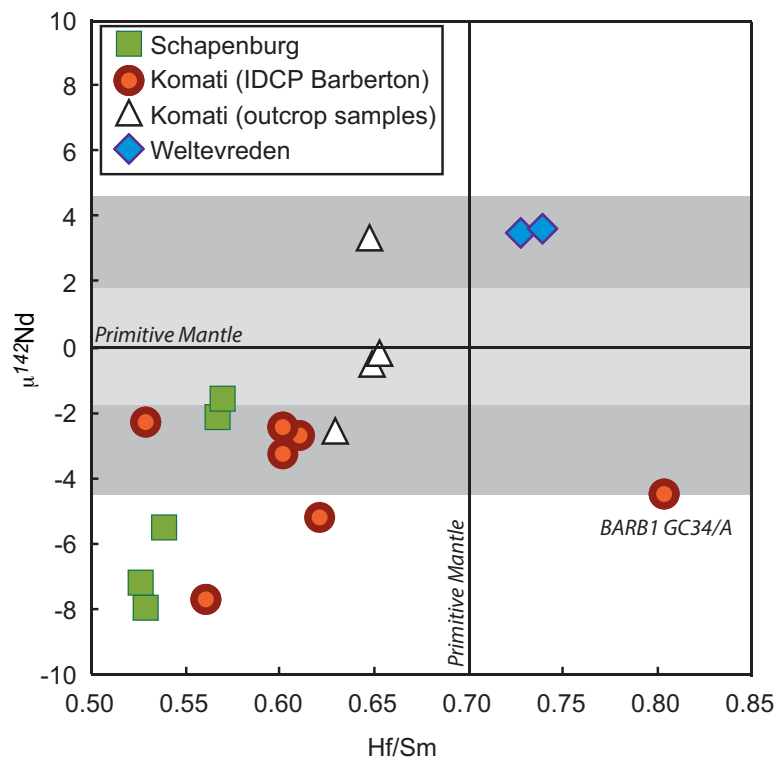


Figure 4. Boyet et al.

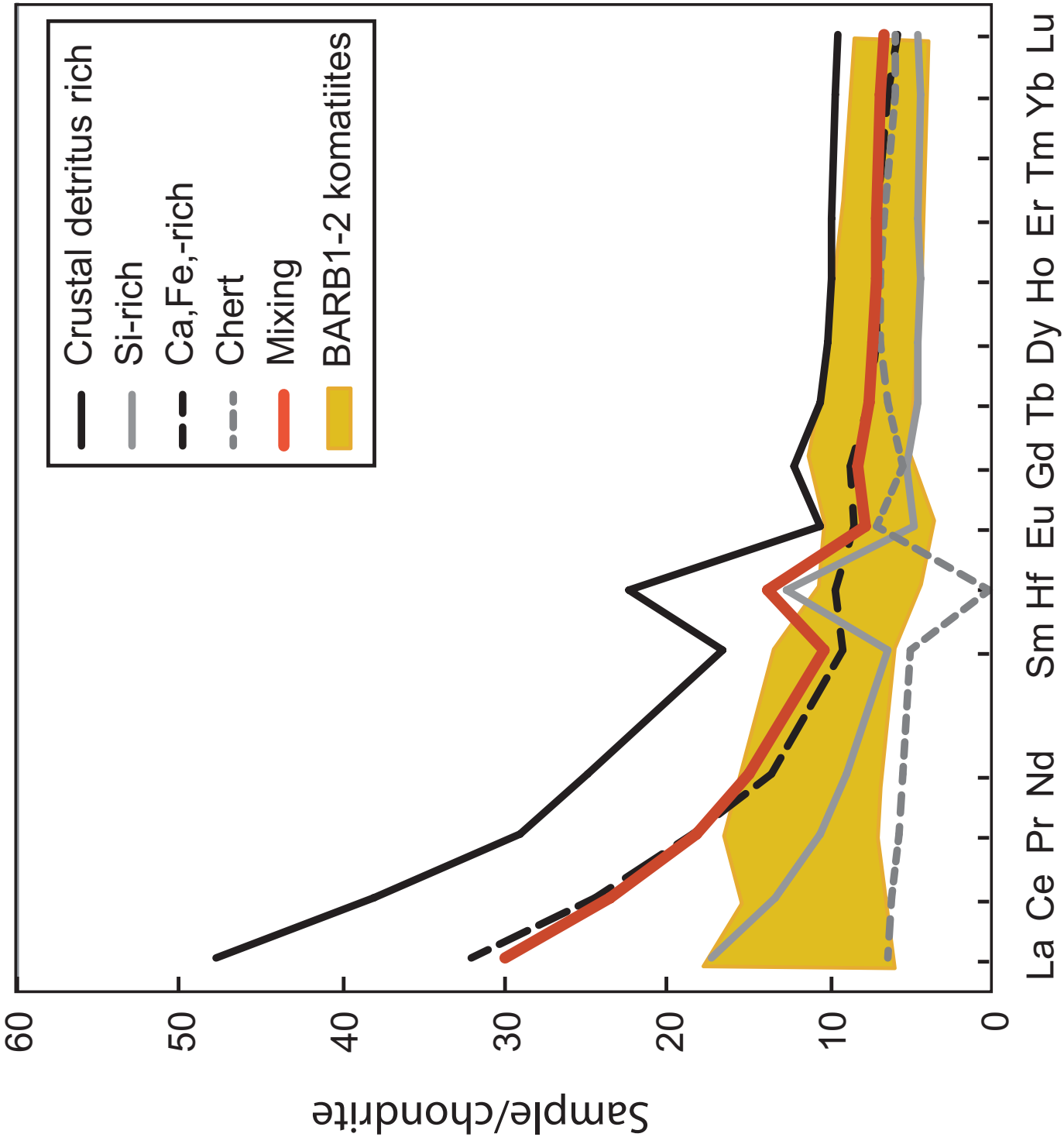


Figure 5. Boyet et al.

Figure 6

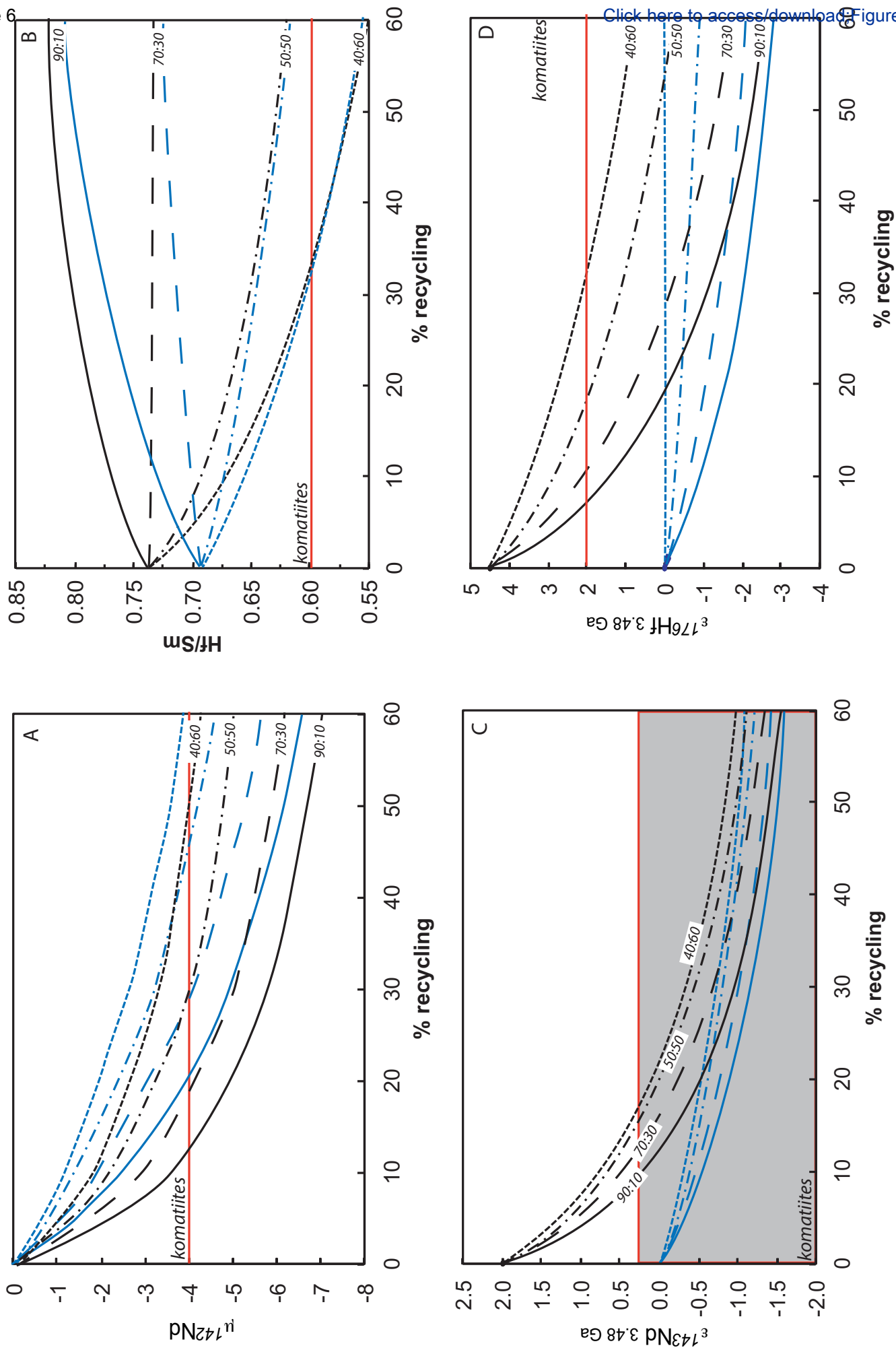


Figure 6. Boyet et al.

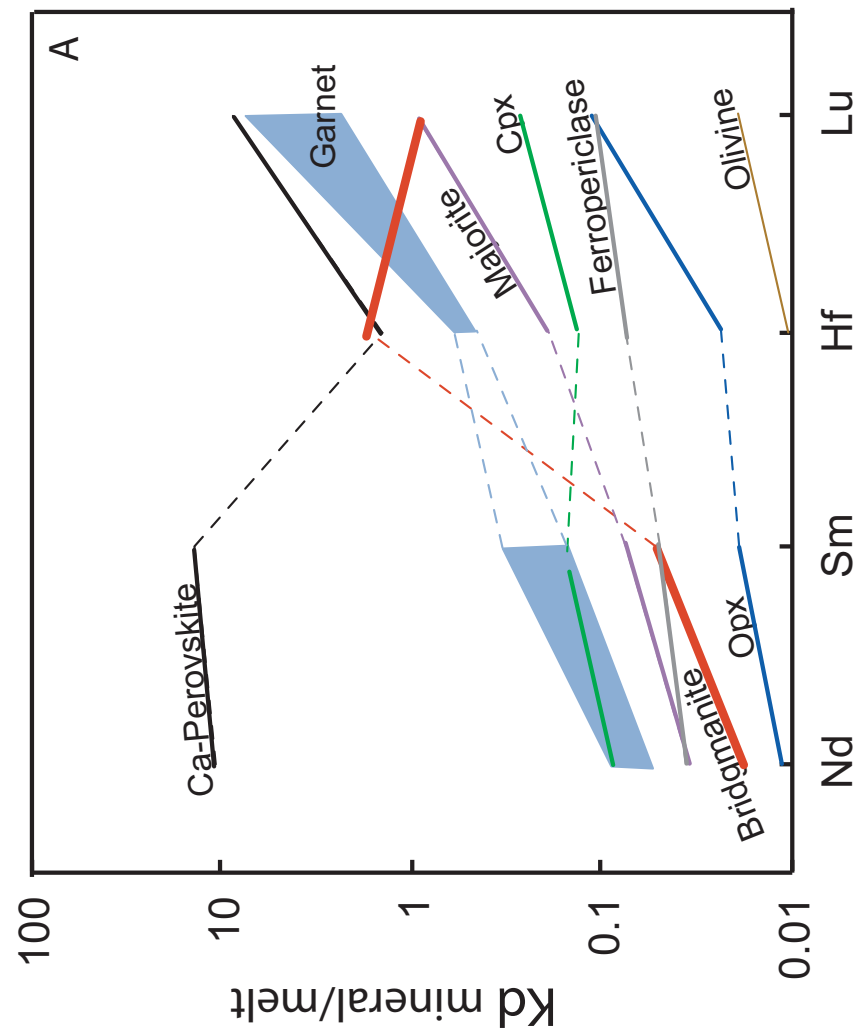
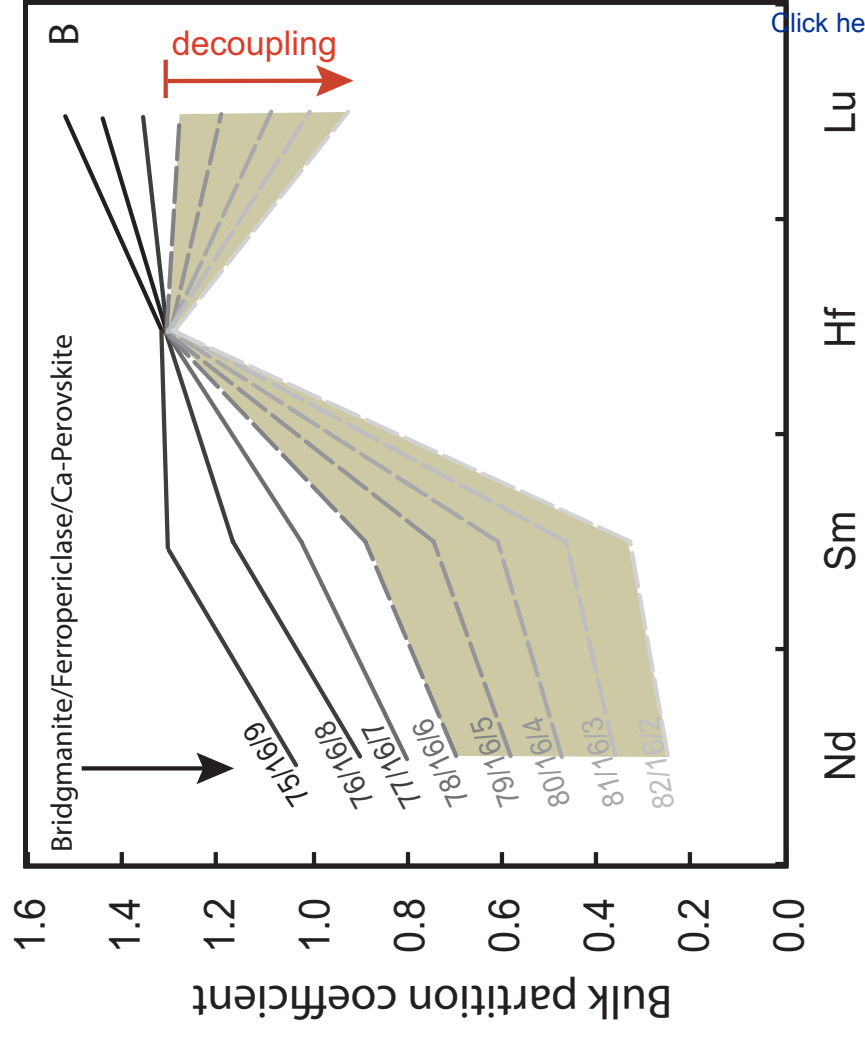


Figure 7. Boyet et al.

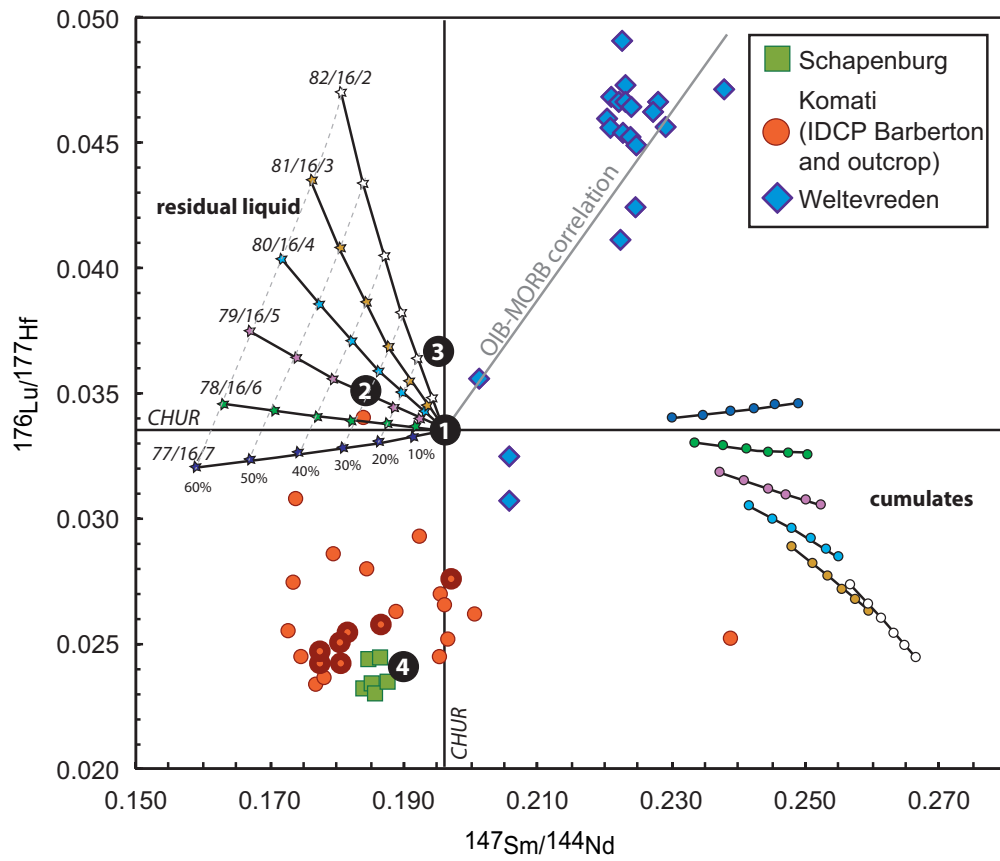


Figure 8. Boyet et al.

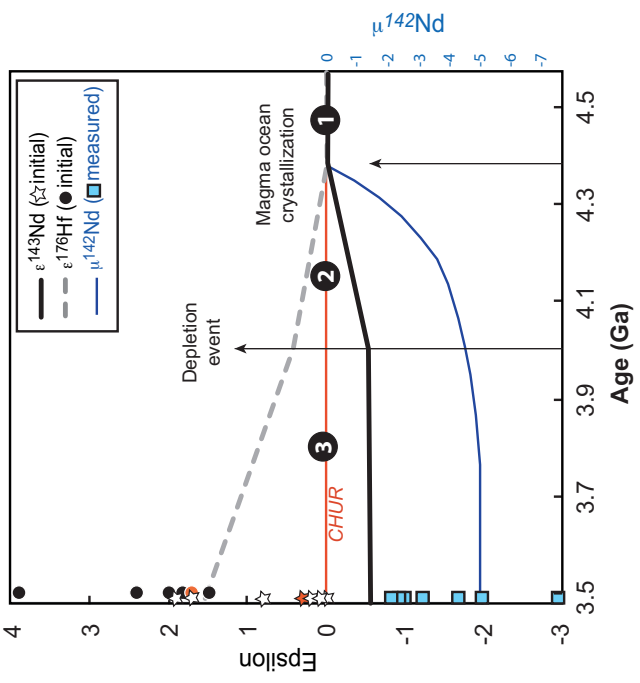


Figure 9. Boyet et al.