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# Early differentiation of the bulk silicate Earth as recorded by the oldest mantle reservoir

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26 **ABSTRACT**

27       An emerging challenge for understanding the Earth system is to determine the  
28 relative roles of early planetary processes versus progressive differentiation in shaping  
29 the Earth's chemical architecture. An enduring tenet of modern chemical  
30 geodynamics is that the Earth started as a well-mixed and homogeneous body which  
31 evolved progressively over the geologic time to several chemically distinct domains.  
32 As a consequence, the observable chemical heterogeneity in mantle-derived rocks has  
33 generally been attributed to the Earth's dynamic evolution over the past 4.5 Ga.  
34 However, the identification of chemical heterogeneity formed during the period 4.53–  
35 4.45 Ga in the ca. 60 Ma Baffin Bay high-magnesium lavas provides strong evidence  
36 that chemical effects of early differentiation can persist in mantle reservoirs to the  
37 present day. Here, we demonstrate that such an ancient mantle reservoir is likely  
38 composed of enriched and depleted dense melts, and propose a model for early global  
39 differentiation of the bulk silicate Earth that would produce two types of dense melts  
40 with distinctive chemical compositions in the deep Earth. These dense melts  
41 ultimately became parts of the thermo-chemical piles near the core-mantle boundary  
42 that have been protected from complete entrainment by subsequent mantle convection  
43 currents. We argue that although such dense melts likely exhibit some 'primordial'  
44 geochemical signatures, they are not reprehensive of the bulk silicate Earth. Our work  
45 provides a strong case for the mantle chemical heterogeneity being formed by a major  
46 differentiation event shortly after planet accretion rather than through the subsequent  
47 geodynamic evolution.

## 48 INTRODUCTION

49 The Earth's mantle is chemically heterogeneous at all scales (Hofmann, 1997;  
50 Zindler and Hart, 1986). Knowledge about the chemical composition and  
51 differentiation of the primordial silicate Earth is crucial for understanding how the  
52 Earth's mantle works (e.g., Caro, 2011; Hofmann, 1997; Zindler and Hart, 1986).  
53 However, chemical signatures related to the Earth's early differentiation are believed  
54 to have largely been scrambled or diluted by whole mantle convection, tectonic-plate  
55 recycling and continuous exchanges between the mantle and crust over the past 4.5  
56 Ga (e.g., Allègre, 1982; Caro, 2011). As a result, the isotopic and chemical  
57 heterogeneities observed in modern mantle-derived rocks are generally believed to  
58 reflect later production and recycling of oceanic and continental crust through  
59 geological time, and thus bear no direct signature of the primordial silicate Earth (e.g.,  
60 Allègre, 1982; Hofmann, 1997; Zindler and Hart, 1986). This led to the widely held  
61 believe that the Earth started as a well-mixed homogeneous body that evolved  
62 progressively over geologic time to several chemically distinct domains (Allègre,  
63 1982; Hofmann, 1997; Zindler and Hart, 1986). However, we demonstrated here that  
64 the very-early-formed chemical heterogeneity as recorded by the oldest mantle  
65 reservoir can persist in mantle reservoirs to the present day.

66 The ca. 60 Ma old Baffin Bay picrites between Baffin Island and West  
67 Greenland (BIWG) are among the earliest manifestations of the ancestral Iceland  
68 mantle plume. The high  $^3\text{He}/^4\text{He}$  end-member of the mantle composition range (up

69 to 50  $R_A$ , where  $R_A$  is the atmospheric value of  $1.39 \times 10^{-6}$  (Starkey et al., 2009) in  
70 the picrites may signify an undegassed primitive mantle source or isolated primordial  
71 He-rich reservoir that is a residue of ancient mantle depletion (Heber et al., 2007).  
72 The recent landmark discovery of a primitive Pb isotopic composition confirmed that  
73 the BIWG lavas were derived from a deep-Earth reservoir preserved at the  
74 core-mantle boundary (CMB) that has remained isolated since the earliest days of  
75 planetary accretion some 4.5 Ga (Jackson et al., 2010). Jackson et al. (2010) proposed  
76 that the composition of such an ancient reservoir is representative of the bulk silicate  
77 Earth (BSE) (Andreasen et al., 2008) ‘parental to all mantle reservoirs’.

## 78 **DISCUSSION**

79 A previous back-calculation based on the two highest  $^3\text{He}/^4\text{He}$  samples (DUR8  
80 and BI/PI/25) (Jackson et al., 2010) suggested that the oldest mantle reservoir  
81 represents a residue of an ancient global depletion event. If this is true, the estimated  
82 Nb/La ratio for the oldest mantle reservoir should be similar to typical depleted  
83 mantle reservoirs. However, such a back-calculation resulted in an extremely high  
84 Nb/La ratio of 1.41 that is much higher than any known depleted reservoir, such as  
85 modern depleted mid-ocean-ridge basalt (MORB) mantle reservoirs (Nb/La = 0.64–  
86 0.97; Workman and Hart, 2005) and early depleted reservoirs (Nb/La = 0.74–0.79;  
87 Carlson and Boyet, 2008). Furthermore, uncontaminated BIWG picrites (Starkey et al.,  
88 2009) and their olivine-hosted melt inclusions (Starkey et al., 2012) exhibit a large  
89 range of isotopic and chemical compositions, overlapping that of both typical depleted

90 and enriched mantle reservoirs. There has been no evidence suggesting the existence  
91 of either depleted melt inclusions in the enriched picrites, or enriched inclusions in the  
92 depleted picrites (Starkey et al., 2012), arguing strongly against the derivation of the  
93 picrites from a single depleted reservoir. This emphasizes the needs for a better  
94 understanding of the nature and origin of the oldest mantle reservoirs, and the  
95 chemical heterogeneity of the BIWG picrites holds the key for unrevealing early  
96 global differentiation of the BSE (e.g., Bennett et al., 2007; Caro, 2011; Lee et al.,  
97 2010; Nomura et al., 2011). Before discussing the characteristics of the BIWG source,  
98 we first use a set of criteria (Figs. 1–2) to first strip-off the highly evolved BIWG  
99 samples, and then reconstruct the primary melt compositions (Appendix Table S1).  
100 The uncontaminated BIWG picrites show a fairly narrow  $^{206}\text{Pb}/^{204}\text{Pb}$  range that plots  
101 within the geochrons of 4.53 to 4.40 Ga, whereas the contaminated lavas show a  
102 larger  $^{206}\text{Pb}/^{204}\text{Pb}$  range plotting outside this geochron band (Fig. 2h). This confirms  
103 the effectiveness of the criteria used for stripping-off the effects of  
104 assimilation-fractional crystallization. The estimated primary melt compositions and  
105 melting pressures suggest melt fractions of ~7 to 22%, that correlate with Sm/Nd,  
106 Nb/La, Zr/Sm, Zr/Nb and La/Sm ratios (Fig. 3). Thus, refractory lithophile element  
107 ratios of the less-evolved BIWG picrites and partial melting conditions can be used to  
108 examine the nature and origin of such an ancient mantle reservoir.

109 The refractory lithophile element ratios and isotopic results of the less-evolved  
110 BIWG picrites suggest that their source likely contains two extreme end-member  
111 components (Fig. 4 and Appendix Fig. R2). This is consistent with the end-members

112 defined by olivine-hosted melt inclusions from uncontaminated BWG picrites (Fig.  
113 4a–c). The compositions of the two end-member sources were estimated based on  
114 forward partial melting modelling (Fig. 4). Melt fractions for the enriched and  
115 depleted end-member melts are constrained by the correlation of refractory lithophile  
116 element ratios with melt fractions (Fig. 3). The best estimate for the enriched  
117 end-member source is  $\text{Sm}/\text{Nd} = 0.33$  (corresponding to  $^{147}\text{Sm}/^{144}\text{Nd} = 0.1977$ ),  $\text{La}/\text{Sm}$   
118  $= 1.7$ ,  $\text{Nb}/\text{La} = 1.4$ ,  $\text{Zr}/\text{Sm} = 29.2$ ,  $\text{Zr}/\text{Nb} = 12.2$ , and  $\epsilon\text{Nd}_{60} = +2$  to  $+4$ . The estimated  
119 depleted end-member source, on the other hand, has  $\text{Sm}/\text{Nd} = 0.38$  ( $^{147}\text{Sm}/^{144}\text{Nd} =$   
120  $0.217$ ),  $\text{La}/\text{Sm} = 0.77$ ,  $\text{Nb}/\text{La} = 0.62$ ,  $\text{Zr}/\text{Sm} = 22.1$ ,  $\text{Zr}/\text{Nb} = 50.0$ , and  $\epsilon\text{Nd}_{60} = +8$  to  
121  $+11$ . The corresponding parent/daughter ratios of Rb-Sr, Lu-Hf and Re-Os for the two  
122 end-member sources are shown in Fig. 4f–h. Because the BIWG source likely formed  
123 at 4.5 Ga (Jackson et al., 2010), the above two end-members therefore likely bear  
124 important information regarding early global differentiation of the BSE (e.g., Caro,  
125 2011).

126 The depleted end-member source likely represents a residual of the global  
127 depletion event early in the Earth's history (Jackson et al., 2010). This end-member  
128 source is highly depleted relative to chondritic BSE, with refractory lithophile element  
129 ratios similar to that of modern depleted MORB mantle and early depleted reservoirs,  
130 and Nd-Sr-Hf isotope comparable to early depleted reservoirs (Fig. 4). The  
131 differentiation of the early silicate Earth was expected to produce such an early  
132 depleted reservoir with super-chondritic Sm/Nd and Lu/Hf, and sub-chondritic Rb/Sr  
133 ratios (Caro and Bourdon, 2010 and references therein), which is similar to that

134 observed in the depleted end-member source (Figs. 4d–f). Evidence for the existence  
135 of such an early depleted reservoir is mainly from superchondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios  
136 (e.g., Caro, 2011) and coupled  $^{182}\text{W}$ – $^{142}\text{Nd}$  anomalies (Moynier et al., 2010) in most  
137 terrestrial samples.

138 However, it has been unclear whether a complementary early-formed enriched  
139 component exists in modern silicate domains and, if any, how it affects modern  
140 mantle reservoirs (e.g., Andreasen et al., 2008; Caro, 2011). The enriched  
141 end-member source calculated here is characterized by a higher superchondritic  
142 Nb/La ratio (1.4) and broadly chondritic Sm/Nd, La/Sm and Zr/Nb ratios and Nd  
143 isotopes (Fig. 4b–d). The following argument suggests that the decoupling of Nb/La  
144 ratios from Sm/Nd ratios and associated Nd isotopes is a lower mantle signature. Bulk  
145 solid-melt Sm/Nd partition coefficients ( $^{\text{bulk}}D_{\text{Sm/Nd}}$ ) at upper mantle pressures are  
146 about 2, and decrease to unity at lower mantle pressures (Appendix Table S3 and Fig.  
147 R3). Furthermore, experimental partition coefficients for lower mantle minerals show  
148 that rare earth elements are strongly compatible in Ca-perovskite (Corgne et al., 2005).  
149 By contrast, Nb, Ta, Pb, Rb and Ba are incompatible in Ca-perovskite. As a  
150 consequence, melt segregated from a basal magma ocean (Nomura et al., 2011) will  
151 be depleted in rare earth elements, U and Th, but enriched in Rb, Ba, and Nb, Ta, and  
152 Sr (Jackson et al., 2010) (Fig. 5a). Therefore, freezing of a magma ocean with a  
153 nonchondritic BSE composition (Sm/Nd = 0.343, Nb/La = 0.89; Fig. 5a) initiated at  
154 the base of mantle (Caro et al., 2005 and references therein) would have resulted in an  
155 incompatible element-enriched residual melt with Nb/La, Zr/Nb, La/Sm, Zr/Sm and



156 Sm/Nd ratios and Nd-Sr-Os isotopes, as observed in the BIWG enriched end-member  
157 (Figs. 4 and 5a). In contrast, differentiation of a chondritic BSE (McDonough and Sun,  
158 1995) cannot produce the enriched end-member source (Fig. 2d and f). Together with  
159 the homogeneous super-chondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios in the BIWG picrites (de Leeuw  
160 et al., 2010), we propose that the enriched end-member source originated from a  
161 nonchondritic BSE in the lower mantle.

162 Because both the depleted and enriched BIWG end-member sources possess  
163 primordial (high)  $^3\text{He}/^4\text{He}$  signatures (Starkey et al., 2012), the above two  
164 end-member sources were most likely generated in an undegassed deep Earth. It has  
165 been argued that differentiation of early silicate Earth in deep Earth can generate  
166 undegassed dense melts concentrating at the CMB (e.g., Lee et al., 2010; Nomura et  
167 al., 2011) and ultimately result in the primordial time-integrated high  $^3\text{He}/^4\text{He}$  of ca.  
168  $60 R_A$  at 60 Ma (Lee et al., 2010) (Fig. 5b). The large range in the estimated Th, U  
169 and He contents implies that the oldest mantle reservoir should evolve to have  
170  $^3\text{He}/^4\text{He} = 33\text{--}54 R_A$  after ca. 4.4 Ga of isolation from whole-mantle convection (Fig.  
171 5b). This coincides well with observed values in the uncontaminated BIGW picrites  
172 (Fig. 3B). Although the early-formed dense melts exhibit some ‘primordial’ isotopic  
173 signatures, providing an elegant argument for the survival of a primitive geochemical  
174 component in the mantle, we argue that they did not preserve the true primordial bulk  
175 silicate Earth composition in terms of major element and key trace element  
176 compositions.

## 177 CONCLUSION

178 Understanding the way of early silicate Earth differentiation requires knowledge of  
179 the density contrast between solid and melt fractions (e.g., Lee et al., 2010; Nomura et  
180 al., 2011). Positive and negative melt buoyancies yield drastically different  
181 geodynamical models. The prevailing view of differentiation of Earth's silicate  
182 mantle is driven by extraction of low-density melts. As the mantle upwells and  
183 decompresses across its solidus, it partially melts. These low-density melts rise to the  
184 surface and form the continental and oceanic crusts, driving the differentiation of the  
185 silicate part of the Earth. Lee et al. (2010) proposed a fresh perspective on the way of  
186 early Earth silicate Earth differentiation if liquids sink instead of rise. Under certain  
187 high-pressure conditions in upper mantle, it has been suggested that peridotite partial  
188 melts may be more dense than solid peridotite because such liquids are Fe-rich and  
189 more compressible than solids (e.g., Lee et al., 2010; Miller et al., 1991; Stolper et al.,  
190 1981; Suzuki et al., 1998). Recent experimental determined iron partitioning over the  
191 entire mantle pressure range suggested that liquid formed at  $\geq 1,800$  km becomes  
192 denser than coexisting solid in the lower mantle (Nomura et al., 2011). It should be  
193 pointed out that the behaviour of solid–liquid iron partitioning in Earth's deep mantle  
194 is still poor constrained and highly debated (e.g., Andrault et al., 2012).

195 We use Figure 6 to illustrate how global differentiation of the early silicate Earth  
196 during 4.55–4.40 Ga may have produced two types (depleted and enriched) of dense  
197 melts in an undegassed deep Earth. If crystallization of a magma ocean began at the

198 base of the Earth's mantle and progressed upward (Caro et al., 2005 and references  
199 therein), the global differentiation of the BSE would have occurred in two  
200 independent layers at  $>1,800$  km and  $\leq 1,800$  km depths (Nomura et al., 2011) (Fig.  
201 6a). With progressive crystallization, the density contrast (Nomura et al., 2011) would  
202 produce an enriched denser liquid phase at the core-mantle boundary, enriching in  
203 incompatible trace elements (Rb, Ba, Nb, Pb, and Sr) including volatile species  
204 (Labrosse et al., 2007). In contrast, within the upper layer ( $\leq 1,800$  km), as the  
205 crystallization proceeded, the residual liquid would rise buoyantly until a small  
206 fraction ( $\leq 1\%$ ) of melt ultimately formed a protocrust at the Earth surface, resulting in  
207 depleting 60% of the silicate Earth. This is consistent with the 60% depletion  
208 constraint by the Nd budget of the crust (Caro et al., 2005 and references therein). The  
209 depleted dense melt may have been generated by high degree partial melting of  
210 peridotite at about 300-410 km depths (Lee et al., 2010) shortly after magma ocean  
211 crystallization (Fig. 6a). The above two types of dense melts would result in materials  
212 constituting the present-day thermo-chemical piles hosted within the two large  
213 low-shear-wave-velocity provinces above the CMB (e.g., Jackson and Carlson, 2011;  
214 Nomura et al., 2011), that have been protected from complete entrainment by  
215 subsequent mantle convection currents (e.g., Caro, 2011; Nomura et al., 2011).

216 Because the homogeneous superchondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  signatures in the BIWG  
217 picrites (de Leeuw et al., 2010) were mainly formed within the Earth's first 30 Ma  
218 (Caro et al., 2008), both the enriched and the depleted end-members likely formed at  
219 4.53–4.45 Ga, as independently constrained by the primitive Pb isotopes (Fig. 1h).

220 This coincides with a mean early mantle differentiation age of  $4.51 \pm 0.02$  Ga  
221 (Bennett et al., 2007). The identification of such very-early-formed chemical  
222 heterogeneity in modern mantle-derived rocks therefore provides strong evidence that  
223 the BSE was affected by non-uniformitarian processes early on in Earth history,  
224 resulting in extremely local chemical differentiation (e.g., Bennett et al., 2007).  
225 Furthermore, such chemical effects can persist in mantle reservoirs to the present day,  
226 which is attributed to a combination of compositionally induced high density and low  
227 viscosity (e.g., Caro, 2011; Nomura et al., 2011). This provides a strong case against  
228 the popular chemical geodynamic model that the observable isotopic and elemental  
229 heterogeneity in mantle-derived rocks mainly reflects the presence of several  
230 end-member mantle reservoirs formed through the Earth's younger geodynamic  
231 processes (e.g., Hofmann, 1997; Zindler and Hart, 1986). Thus, an emerging  
232 challenge for the understanding the Earth system is to determine the relative roles of  
233 early planetary processes versus progressive differentiation in shaping the Earth's  
234 chemical architecture.

235 How such a dense chemical layer can be sampled and brought to the surface is an  
236 important question. Geological evidence related to supercontinent reconstructions  
237 (e.g., Li and Zhong, 2009) shows that both the location and formation of superplumes  
238 were dominantly controlled by the first order geometry of global subduction zones.  
239 Recent studies proposed that sinking subducted slabs could not only push the dense  
240 chemical layer upward, but also push the thermal boundary layer to form  
241 thermal-chemical domes (Steinberger and Torsvik, 2012), enhancing or triggering

242 thermal instability (Fig. 6b). The physical properties of mantle plumes also imply that  
243 materials from the dense chemical layer near the CMB should only be a minor  
244 component of mantle plumes and thus can only be identified in the earliest phase of  
245 high temperature melts (picrites and komatiites) (e.g., Campbell and O'Neill, 2012).

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253

254 Figure Caption

255 Fig. 1. Variation of selected oxides, trace element ratios, and isotopes as a function of  
256 MgO concentration in the BIWG lavas (Dale et al., 2009; Jackson et al., 2010; Larsen  
257 and Pedersen, 2009; Lightfoot et al., 1997; Robillard et al., 1992; Schaefer et al., 2000;  
258 Starkey et al., 2009). Black dashed lines in (a-f) represent the BIWG lavas evolution  
259 path. The solid black lines with arrows indicate the effect of fractional crystallization  
260 of single minerals on magmatic evolution (Wang et al., 2012). These figures show  
261 that after stripping-off the effect of crustal contamination, the samples with MgO > 12  
262 wt.% are only affected by olivine fractional crystallization or accumulation. Due to  
263 the extremely high incompatibility in olivine, the incompatible trace element ratios of  
264 the samples with MgO > 12 wt.% reflect the contribution of source region and/or  
265 crustal contamination.

266 Fig. 2. Evaluating the effects of crustal contamination on BIWG magma compositions.  
267 This figure shows that the effects of assimilation-fractional crystallization (AFC) on  
268 the samples with SiO<sub>2</sub> ≤ 50 wt.%, MgO > 12 wt.%, and εNd(t) > +2 are insignificant if  
269 any. Black curves indicate evolution of <sup>207</sup>Pb/<sup>204</sup>Pb versus <sup>206</sup>Pb/<sup>204</sup>Pb starting from  
270 the initial Pb-isotope composition of Canyon Diablo (Paul et al., 2002). Also shown  
271 are 4.568 Ga, 4.53 Ga, and 4.45 Ga geochrons (Jackson et al., 2010). Pb\* =  
272 2Pb<sub>N</sub>/(Ce<sub>N</sub> + Pr<sub>N</sub>), subscript N indicates the CI-chondrite (McDonough and Sun, 1995)  
273 normalized values.

274 Fig. 3. Plots of incompatible trace element ratios versus calculated melt fraction  
275 number (**F**, %). The melt fraction number is calculated by function A1 and A2 in the  
276 appendix of Putirka et al. (2007). The calculated melt fraction broadly correlates with  
277 the incompatible trace element ratios from the uncontaminated picrites. This implies  
278 that the enriched and depleted end-members were likely generated at different melting  
279 degree. Such new information combined with the melt inclusion data (Starkey et al.,  
280 2012) and petrological evidence (e.g., Francis, 1985; Herzberg and O'Hara, 2002;  
281 Kent et al., 2004) suggests that both the mantle source and degree of partial melting  
282 for the enriched- and depleted-type of picrites are different.

283 Fig. 4. (**a–c**): Correlations of selected refractory lithophile element ratios with Sm/Nd.  
284 A chondritic BSE (McDonough and Sun, 1995), average compositions of  
285 normal-MORB (N-MORB), ocean island basalt (OIB) (Sun and McDonough, 1989),  
286 depleted MORB mantle (DMM) (Workman and Hart, 2005) the range of early  
287 depleted reservoirs (EDR, black rectangles in **a** and **c**) (Carlson and Boyet, 2008),  
288 nonmodal batch partial melting (solid lines with cross), binary mixing (green dashed  
289 lines), super-chondritic Earth model (light pink colour area) and chondritic BSE (Caro  
290 and Bourdon, 2010) are shown. EMI and DMI represent the enriched and depleted  
291 types of melt inclusions from high  $^3\text{He}/^4\text{He}$  BIWG picrites (Starkey et al., 2012).  
292 Numbers in italic mark partial melt fractions (%). (**d–f**): Evolution of Nd-Sr-Hf-Os  
293 isotopes in the oldest mantle reservoir. The grey fields represent the isotopic evolution  
294 of the enriched end-member with Nb/La = 1.3–1.5 that originated from a chondritic  
295 BSE (McDonough and Sun, 1995). The  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios for both the enriched and

296 depleted end-members are estimated according to end-member Sm/Nd ratios. The  
 297 Rb-Sr and Re-Os system for the enriched end-member is calculated using  $(^{87}\text{Rb}/^{86}\text{Sr})_E$   
 298  $= K_E(^{87}\text{Rb}/^{86}\text{Sr})_{\text{CN}}$  and  $(^{187}\text{Re}/^{188}\text{Os})_E = K_E(^{187}\text{Re}/^{188}\text{Os})_{\text{CN}}$ , where  $K_E =$   
 299  $[(\text{Nb}/\text{La})_E/(\text{Nb}/\text{La})_{\text{CN}} + (\text{Sm}/\text{Nd})_E/(\text{Sm}/\text{Nd})_{\text{CN}}]/2$ , with subscripts E and CN refer to the  
 300 enriched end-member and the chondritic BSE, respectively. The same functions are  
 301 used for calculating the isotopic systems of the depleted end-member. All isotopic  
 302 evolution paths start at 4.4 Ga. The data sources for the BIWG picrites are the same as  
 303 in Fig. 1. The nonmodal batch melting was conducted at the garnet stability field  
 304 according to  $C_L = C_0/[D_0 + F(1-P)]$ , where  $D_0$  is the initial bulk distribution coefficient,  
 305 and  $P$  is the bulk distribution coefficient determined by the melting model.  $F$  is the  
 306 weight fraction of melt formed.  $C_0$  and  $C_L$  are the concentrations of an element in the  
 307 source and melt, respectively. The mineral/melt partition coefficient datasets for  
 308 olivine, clinopyroxene, and orthopyroxene are from (Kelemen et al., 2004), and  
 309 the garnet/melt partition coefficient datasets are from (van Westrenen et al., 2000).  
 310 The mineral model and melt reaction are from (Salters and Stracke, 2004).

311

312 Fig. 5. (a): CI chondrite normalized (McDonough and Sun, 1995)  
 313 trace-element-source budget of the early-formed silicate Earth. The nonchondritic  
 314 BSE composition is based on the collision erosion model (O'Neill and Palme, 2008).  
 315 The depleted mantle-1 and -2 were derived from the above nonchondritic BSE by  
 316 respective extraction of 0.002 and 0.01 of basaltic melts to form protocrust, based on



317 mantle-crust partition coefficients (Workman and Hart, 2005) and the method  
318 proposed by (Hofmann, 1988). The depleted end-member source is produced by 22%  
319 partial melt of a depleted mantle-1 at 300-410 km. The enriched end-member source  
320 is melt segregation from a basal magma ocean at  $\geq 1,800$  km (see text). The  
321 back-calculated BIWG source (Jackson et al., 2010), estimates 1 and 2 for EDR  
322 (Carlson and Boyet, 2008), enriched and depleted MORB mantles (Workman and  
323 Hart, 2005), and chondritic BSE (McDonough and Sun, 1995) are also shown. **(b)**:  
324 Evolution of  $^3\text{He}/^4\text{He}$  in the Earth's silicate reservoirs. Evolution of  $^3\text{He}/^4\text{He}$  for the  
325 early formed dense chemical layer (blue colour area) is based on the method of (Class  
326 and Goldstein, 2005) with the following constraints: (1) an initial  $^3\text{He}/^4\text{He} = 120 R_A$ ;  
327 (2)  $[^3\text{He}]$  ranging from  $2.0 \times 10^{11}$  atomsg $^{-1}$  [25% higher than the estimate for  
328 undegassed primitive mantle; Class and Goldstein, 2005) to  $0.8 \times 10^{10}$  atomsg $^{-1}$  (10%  
329 of the modern OIB source; Class and Goldstein, 2005) due to extraction of protocrust];  
330 (3) U = 0.038 to 0.0028 ppm; Th = 0.0735 to 0.010 ppm. Evolution of deep mantle  
331 (thick red line) and shallow mantle (grey band) are devolved from Lee et al (Lee et al.,  
332 2010). The  $^3\text{He}/^4\text{He}$  lower than  $37R_A$  (open circles) were likely affected by  
333 post-eruption  $^4\text{He}$  accumulation and concomitant reduction of  $^3\text{He}/^4\text{He}$  (Appendix Fig.  
334 R4).

335 Fig. 6. **(a)**: Freezing of a magma ocean with nonchondritic BSE composition (Fig. 5a)  
336 would have produced enriched dense melts below 1,800 km depth that accumulated at  
337 the CMB, and 60% depletion of the BSE occurred at above 1,800 km depths due to  
338 positive buoyance of the residual melt (e.g., Nomura et al., 2011). Shortly after

339 magma ocean crystallization, hot and deep melting of the upper mantle could have  
340 generated depleted dense melts at 410–300 km depth (e.g., Lee et al., 2010). The two  
341 types of dense liquids sunk and accumulated at the CMB to form a dense chemical  
342 layer. **(b)**: Late Archean to present-day mantle: melting is restricted to shallow depths.  
343 The dense chemical layer is likely hosted by large low-shear-wave velocity provinces  
344 (LLSVPs) and ultralow-velocity zones (ULVZs) (e.g., Nomura et al., 2011) and  
345 appears to have persisted for much of Earth’s history unless pushed by  
346 deep-subducted slabs to rise up.

347

348 REFERENCES CITED

- 349 Allègre, C.J., 1982. Chemical geodynamics. *Tectonophysics* 81, 109-132.
- 350 Andraut, D., Petitgirard, S., Lo Nigro, G., Devidal, J.-L., Veronesi, G., Garbarino, G.,  
351 Mezouar, M., 2012. Solid-liquid iron partitioning in Earth's deep mantle. *Nature*  
352 487, 354-357.
- 353 Andreasen, R., Sharma, M., Subbarao, K.V., Viladkar, S.G., 2008. Where on Earth is  
354 the enriched Hadean reservoir? *Earth Planet. Sci. Lett.* 266, 14-28.
- 355 Bennett, V.C., Brandon, A.D., Nutman, A.P., 2007. Coupled  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  Isotopic  
356 Evidence for Hadean Mantle Dynamics. *Science* 318, 1907-1910.
- 357 Campbell, I.H., O'Neill, S.C.H., 2012. Evidence against a chondritic Earth. *Nature*  
358 483, 553-558.
- 359 Carlson, R.W., Boyet, M., 2008. Composition of the Earth's interior: the importance  
360 of early events. *Phil. Trans. R. Soc. A* 366, 4077-4103.
- 361 Caro, G., 2011. Early Silicate Earth Differentiation. *Annu. Rev. Earth Planet. Sci.* 39,  
362 31-58.
- 363 Caro, G., Bourdon, B., 2010. Non-chondritic Sm/Nd ratio in the terrestrial planets:  
364 Consequences for the geochemical evolution of the mantle-crust system. *Geochim.*  
365 *Cosmochim. Acta* 74, 3333-3349.
- 366 Caro, G., Bourdon, B., Halliday, A.N., Quitte, G., 2008. Super-chondritic Sm/Nd  
367 ratios in Mars, the Earth and the Moon. *Nature* 452, 336-339.
- 368 Caro, G., Bourdon, B., Wood, B.J., Corgne, A., 2005. Trace-element fractionation in  
369 Hadean mantle generated by melt segregation from a magma ocean. *Nature* 436,  
370 246-249.

371 Class, C., Goldstein, S.L., 2005. Evolution of helium isotopes in the Earth's mantle.  
372 Nature 436, 1107-1112.

373 Corgne, A., Liebske, C., Wood, B.J., Rubie, D.C., Frost, D.J., 2005. Silicate  
374 perovskite-melt partitioning of trace elements and geochemical signature of a deep  
375 perovskitic reservoir. *Geochim. Cosmochim. Acta* 69, 485-496.

376 Dale, C.W., Pearson, D.G., Starkey, N.A., Stuart, F.M., Ellam, R.M., Larsen, L.M.,  
377 Fitton, J.G., Macpherson, C.G., 2009. Osmium isotopes in Baffin Island and West  
378 Greenland picrites: Implications for the  $^{187}\text{Os}/^{188}\text{Os}$  composition of the convecting  
379 mantle and the nature of high  $^3\text{He}/^4\text{He}$  mantle. *Earth Planet. Sci. Lett.* 278,  
380 267-277.

381 de Leeuw, G.A.M., Carlson, R.W., Ellam, R.M., Stuart, F.M., 2010. Baffin Island  
382 picrites contain normal terrestrial Nd-142/Nd-144: Implications for the source of  
383 high He-3/He-4 in deep Earth. *Geochim. Cosmochim. Acta* 74, A219-A219.

384 Francis, D., 1985. The Baffin Bay lavas and the value of picrites as analogues of  
385 primary magmas. *Contrib. Mineral. Petrol.* 89, 144-154.

386 Heber, V.S., Brooker, R.A., Kelley, S.P., Wood, B.J., 2007. Crystal-melt partitioning  
387 of noble gases (helium, neon, argon, krypton, and xenon) for olivine and  
388 clinopyroxene. *Geochim. Cosmochim. Acta* 71, 1041-1061.

389 Herzberg, C., O'Hara, M.J., 2002. Plume-associated Ultramafic magmas of  
390 Phanerozoic age. *J. Paleontol.* 43, 1857-1883.

391 Hofmann, A.W., 1988. Chemical differentiation of the Earth: the relationship between  
392 mantle, continental crust, and oceanic crust. *Earth Planet. Sci. Lett.* 90, 297-314.

393 Hofmann, A.W., 1997. Mantle geochemistry: the message from oceanic volcanism.  
394 Nature 385, 219-229.

395 Jackson, M.G., Carlson, R.W., 2011. An ancient recipe for flood-basalt genesis.  
396 Nature 476, 316-319.

397 Jackson, M.G., Carlson, R.W., Kurz, M.D., Kempton, P.D., Francis, D., Blusztajn, J.,  
398 2010. Evidence for the survival of the oldest terrestrial mantle reservoir. Nature  
399 466, 853-856.

400 Kelemen, P.B., Yogodzinski, G.M., Scholl, D.W., 2004. Alongstrike variation in lavas  
401 of the Aleutian island arc: implications for the genesis of high Mg# andesite and  
402 the continental crust,. AGU Monograph.

403 Kent, A.J.R., Stolper, E.M., Francis, D., Woodhead, J., Frei, R., Eiler, J., 2004. Mantle  
404 heterogeneity during the formation of the North Atlantic Igneous Province:  
405 Constraints from trace element and Sr-Nd-Os-O isotope systematics of Baffin  
406 Island picrites. *Geochem. Geophys. Geosyst.* 5, Q11004.

407 Labrosse, S., Hernlund, J.W., Coltice, N., 2007. A crystallizing dense magma ocean at  
408 the base of the Earth's mantle. *Nature* 450, 866-869.

409 Larsen, L.M., Pedersen, A.K., 2009. Petrology of the Paleocene Picrites and Flood  
410 Basalts on Disko and Nuussuaq, West Greenland. *J. Petrol.* 50, 1667-1711.

411 Lee, C.-T.A., Luffi, P., Hoink, T., Li, J., Dasgupta, R., Hernlund, J., 2010.  
412 Upside-down differentiation and generation of a 'primordial' lower mantle. *Nature*  
413 463, 930-933.

414 Li, Z.-X., Zhong, S., 2009. Supercontinent-superplume coupling, true polar wander

415 and plume mobility: Plate dominance in whole-mantle tectonics. *Phys. Earth*  
416 *Planet Interiors* 176, 143-156.

417 Lightfoot, P.C., Hawkesworth, C.J., Olshefsky, K., Green, T., Doherty, W., Keays,  
418 R.R., 1997. Geochemistry of Tertiary tholeiites and picrites from Qeqertarsuaq  
419 (Disko Island) and Nuussuaq, West Greenland with implications for the mineral  
420 potential of comagmatic intrusions. *Contrib. Mineral. Petrol.* 128, 139-163.

421 McDonough, W.F., Sun, S.s., 1995. The composition of the Earth. *Chem. Geol.* 120,  
422 223-253.

423 Miller, G.H., Stolper, E.M., Ahrens, T.J., 1991. The equation of state of a molten  
424 komatiite. 2. Application to komatiite petrogenesis and the Hadean mantle. *J.*  
425 *Geophys. Res.* 96, 11849-11864.

426 Moynier, F., Yin, Q.-Z., Irisawa, K., Boyet, M., Jacobsen, B., Rosing, M.T., 2010.  
427 Coupled  $^{182}\text{W}$ - $^{142}\text{Nd}$  constraint for early Earth differentiation. *PNAS* 107,  
428 10810-10814.

429 Nomura, R., Ozawa, H., Tateno, S., Hirose, K., Hernlund, J., Muto, S., Ishii, H.,  
430 Hiraoka, N., 2011. Spin crossover and iron-rich silicate melt in the Earth's deep  
431 mantle. *Nature* 473, 199-202.

432 O'Neill, H.S.C., Palme, H., 2008. Collisional Erosion and the Non-Chondritic  
433 Composition of the Terrestrial Planets. *Phil. Trans. R. Soc. A* 366, 4205-4238.

434 Paul, D., White, W.M., Turcotte, D.L., 2002. Modelling the isotopic evolution of the  
435 Earth. *Phil. Trans. R. Soc. Lond. A* 360, 2433-2474.

436 Putirka, K.D., Perfit, M., Ryerson, F.J., Jackson, M.G., 2007. Ambient and excess

437 mantle temperatures, olivine thermometry, and active vs. passive upwelling. *Chem.*  
438 *Geol.* 241, 177-206.

439 Robillard, I., Francis, D., Ludden, J.N., 1992. The relationship between E- and N-type  
440 magmas in the Baffin Bay Lavas. *Contrib. Mineral. Petrol.* 112, 230-241.

441 Salters, V.J.M., Stracke, A., 2004. Composition of the depleted mantle. *Geochem.*  
442 *Geophys. Geosyst.* 5, Q05B07.

443 Schaefer, B.F., Parkinson, I.J., Hawkesworth, C.J., 2000. Deep mantle plume osmium  
444 isotope signature from West Greenland Tertiary picrites. *Earth Planet. Sci. Lett.*  
445 175, 105-118.

446 Starkey, N., Stuart, F., Ellam, R., Fitton, J., Basu, S., Larsen, L., 2009. Helium  
447 isotopes in early Iceland plume picrites: Constraints on the composition of high  
448  $^3\text{He}/^4\text{He}$  mantle. *Earth Planet. Sci. Lett.* 277, 91-100.

449 Starkey, N.A., Fitton, J.G., Stuart, F.M., Larsen, L.M., 2012. Melt inclusions in  
450 olivines from early Iceland plume picrites support high  $^3\text{He}/^4\text{He}$  in both enriched  
451 and depleted mantle. *Chem. Geol.* 306–307, 54-62.

452 Steinberger, B., Torsvik, T.H., 2012. A geodynamic model of plumes from the margins  
453 of Large Low Shear Velocity Provinces. *Geochem. Geophys. Geosyst.* 13,  
454 Q01W09.

455 Stolper, E., Walker, D., Hager, B.H., Hays, J.F., 1981. Melt segregation from partially  
456 molten source regions: the importance of melt density and source region size. *J.*  
457 *Geophys. Res.* 86, 6261-6271.

458 Sun, S.-s., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic

459 basalts: implications for mantle composition and processes., in: Saunders, A.D.,  
460 Norry, M.J. (Eds.), *Magmatism in the Ocean Basins*. Geol. Soc. London, Spec.  
461 Publ., pp. 313-345.

462 Suzuki, A., Ohtani, E., Kato, T., 1998. Density and thermal expansion of a peridotite  
463 melt at high pressure. *Phys. Earth Planet. Inter.* 107, 53-61.

464 van Westrenen, W., Blundy, J.D., Wood, B.J., 2000. Effect of Fe (super 2+) on  
465 garnet-melt trace element partitioning: experiments in FCMAS and quantification  
466 of crystal-chemical controls in natural systems. *Lithos* 53, 189-201.

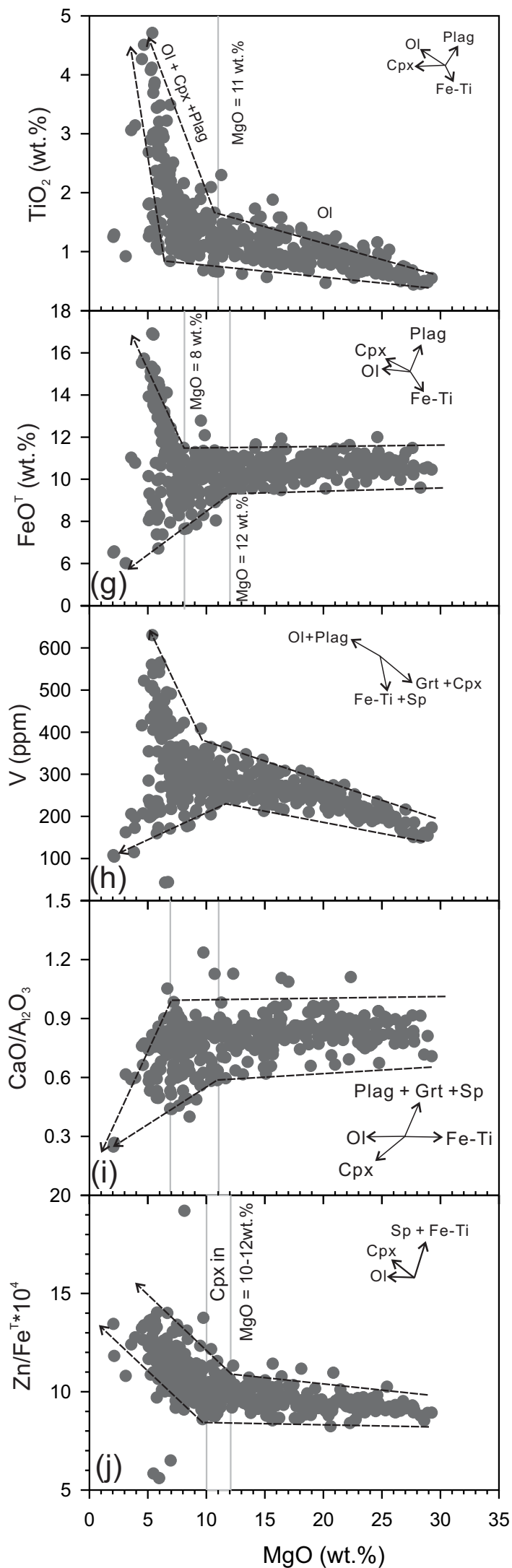
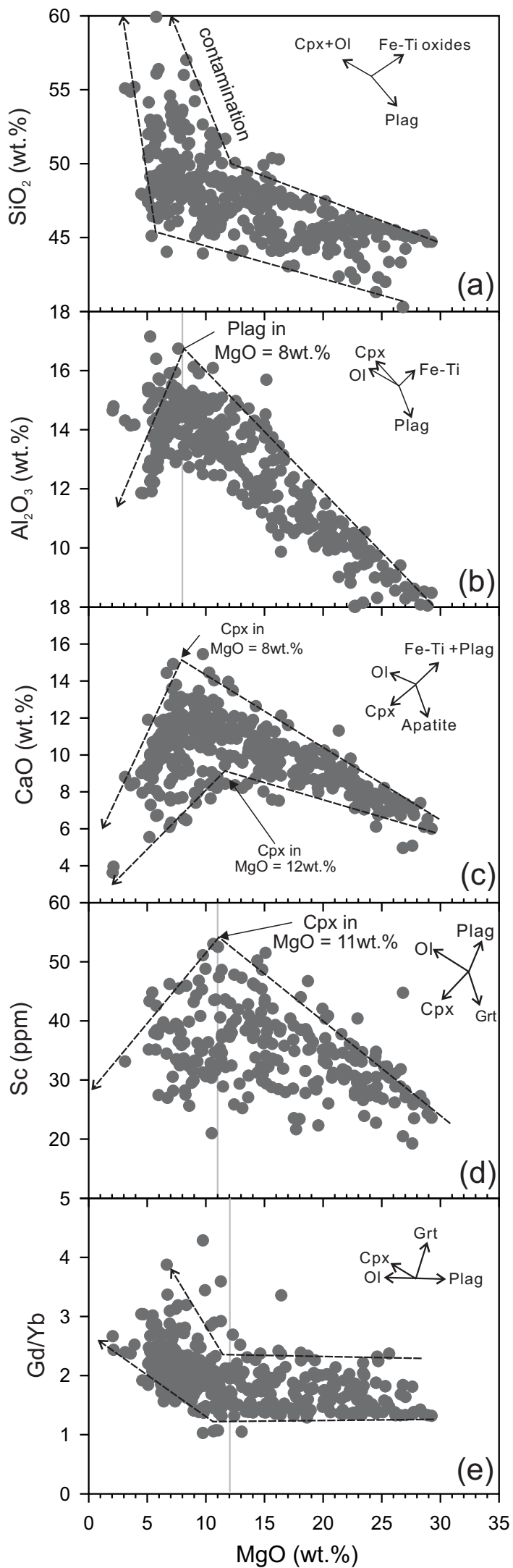
467 Wang, X.-C., Li, Z.-X., Li, X.-H., Li, J., Liu, Y., Long, W.-G., Zhou, J.-B., Wang, F.,  
468 2012. Temperature, Pressure, and Composition of the Mantle Source Region of  
469 Late Cenozoic Basalts in Hainan Island, SE Asia: a Consequence of a Young  
470 Thermal Mantle Plume close to Subduction Zones? *J. Petrol.* 53, 177-233.

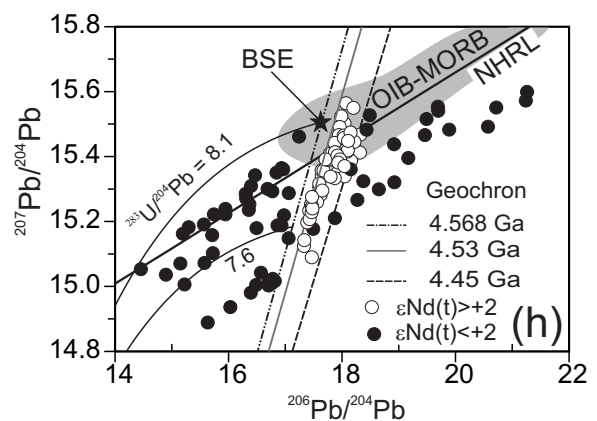
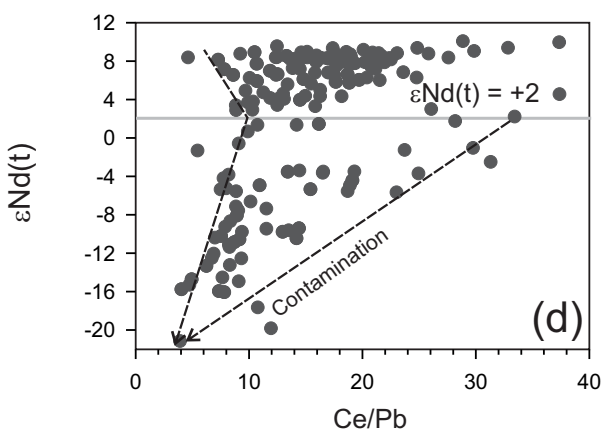
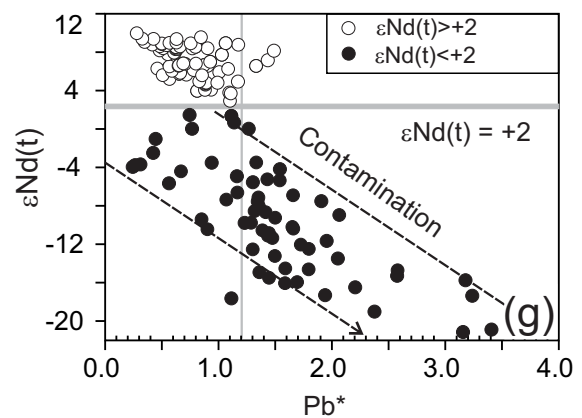
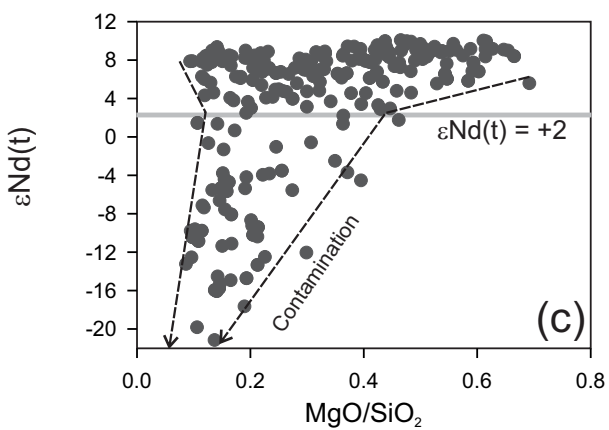
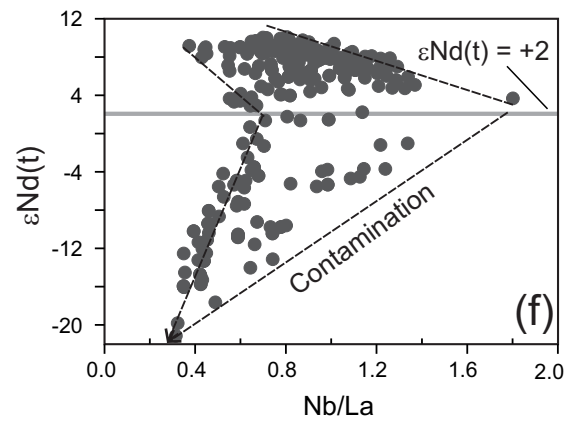
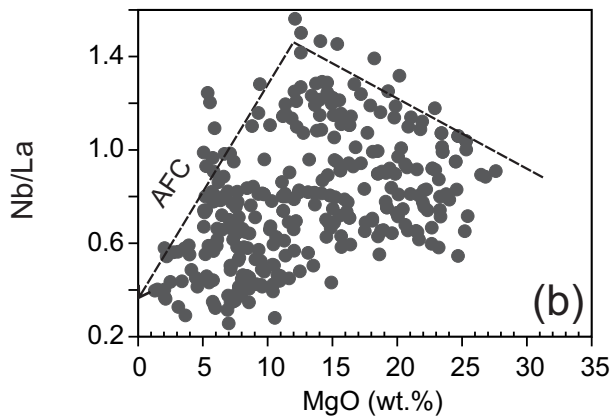
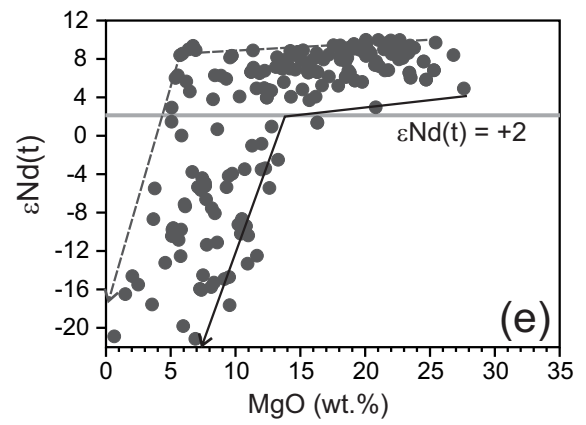
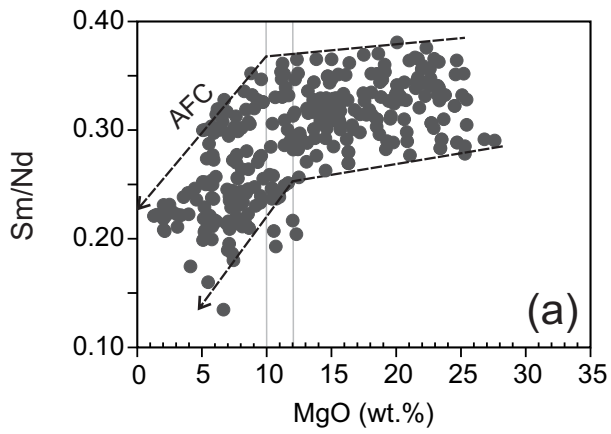
471 Workman, R.K., Hart, S.R., 2005. Major and trace element composition of the  
472 depleted MORB mantle (DMM). *Earth Planet. Sci. Lett.* 231, 53-72.

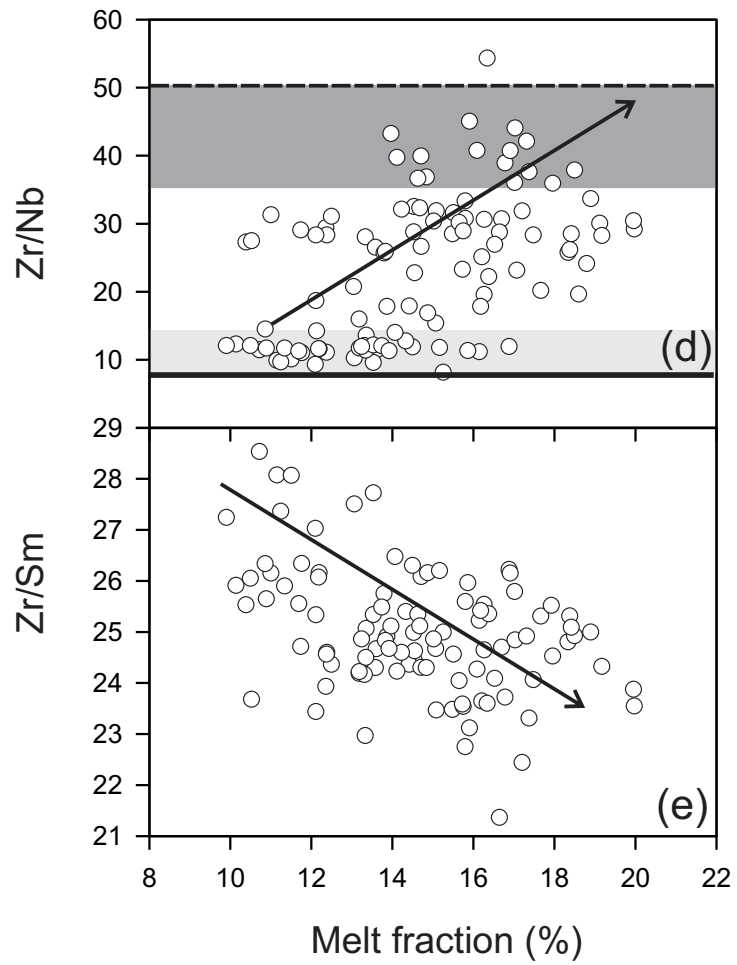
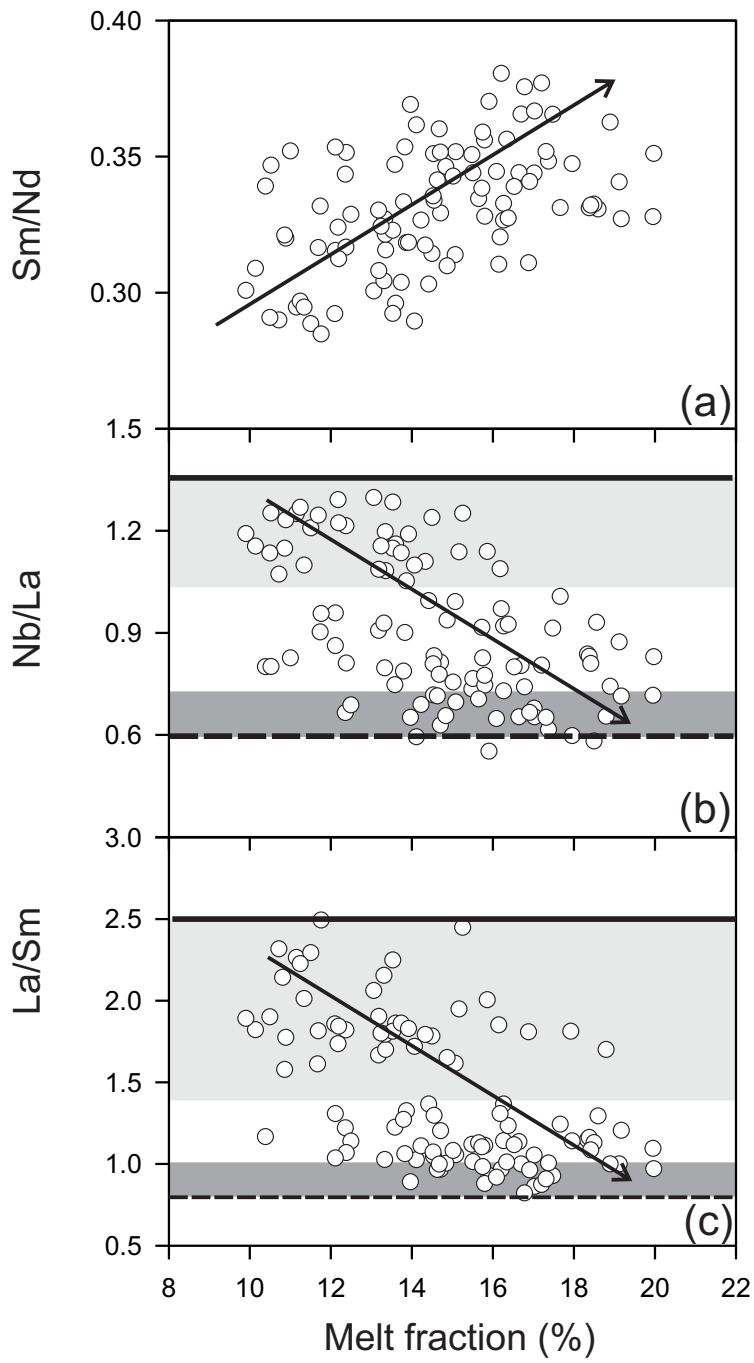
473 Zindler, A., Hart, S., 1986. Chemical geodynamics. *Annu. Rev. Earth Planet. Sci.* 14,  
474 493-571.

475

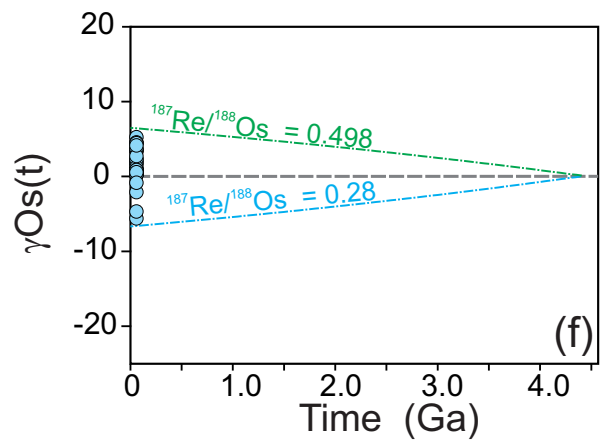
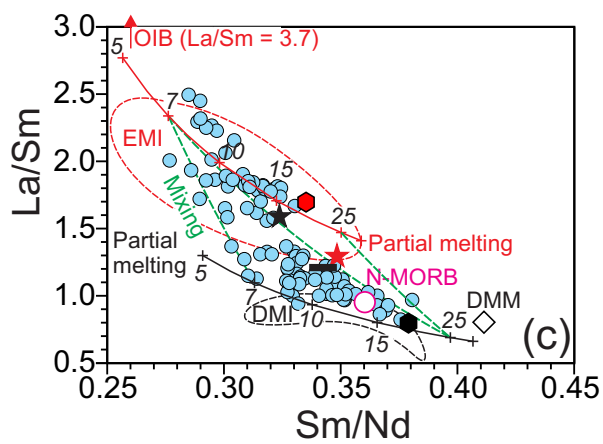
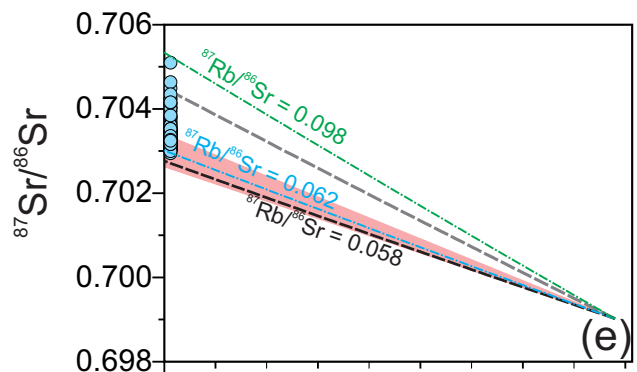
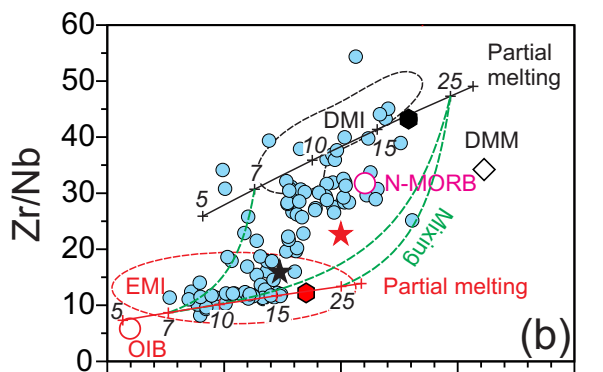
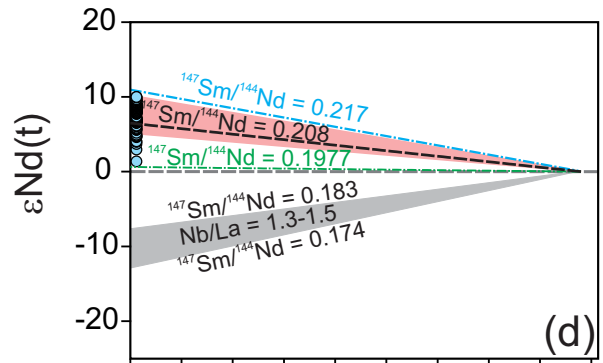
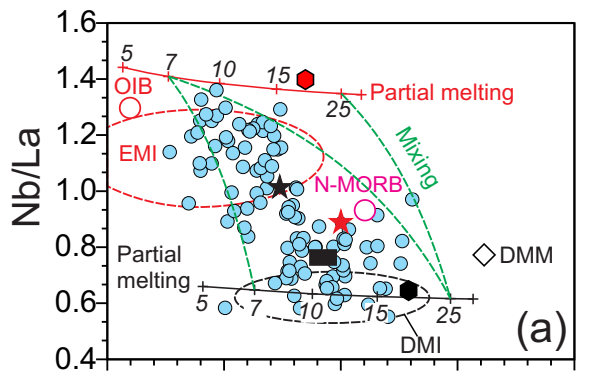








- Range of depleted type of melt inclusion
- Range of enriched type of melt inclusion
- Depleted end-member ratio
- Enriched end-member ratio



- Uncontaminated BIWG picrites
- ★ Chondritic BSE
- ★ Nonchondritic BSE (this study)
- ◆ Enriched end-member source
- ◆ Depleted end-member source
- ▬ Range of EDR

- Depleted end-member source
- Enriched end-member source
- CHUR
- Nonchondritic BSE (this study)

