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1 Formation of the Ce-Nd mantle array: crustal extraction vs. recycling by
2 subduction

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14
15 ABSTRACT

16 We present new measurements of $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios in terrestrial and extra-
17 terrestrial samples. The mean value obtained from nine chondrites defines the $^{138}\text{Ce}/^{142}\text{Ce}$ ratio of the
18 chondritic uniform reservoir (CHUR) as 0.02256577 ± 66 (2sd). MORBs and OIBs define the mantle
19 array in the ϵNd vs. ϵCe diagram to be $\epsilon\text{Nd} = -7.3 (\pm 0.5) \times \epsilon\text{Ce} + 0.4 (\pm 0.3)$. From MORB
20 measurements, we derive the isotopic composition of the depleted MORB mantle (DMM) to be $\epsilon\text{Ce} = -$
21 1.1 ± 0.6 (2sd). Both CHUR and a modelled early-depleted mantle reservoir plot on the mantle array.
22 Thus, the precise determination of the mantle array does not further constrain the La/Ce and Sm/Nd
23 ratios of the bulk silicate Earth (BSE; i.e., primitive mantle). The composition of 1.8 Ga upper
24 continental crust obtained from aeolian sediments is $\epsilon\text{Ce} = 1.8 \pm 0.3$ (2sd; $\epsilon\text{Nd} = -11.2$), and that of its
25 2.2 Ga equivalent is $\epsilon\text{Ce} = 2.3 \pm 0.3$ (2sd; $\epsilon\text{Nd} = -17$). Binary mixing models between depleted (DMM)
26 and enriched (upper crust or mafic crust composition) components do not reproduce the linear Ce-Nd
27 mantle array but plots close to the island arc basalt data. When the bulk Ce isotopic composition of the

28 continental crust is calculated from the range of accepted Nd isotope values and a mass-balance budget
29 of the BSE, the mixing curves are closer to the mantle array. However the calculated Ce isotopic
30 composition for the bulk crust is always less radiogenic than measurements. Adjusting the Ce-Nd
31 isotopic composition or the Ce/Nd ratio of the end-members to fully linearise the mixing curve leads to
32 unrealistic values never measured in terrestrial samples. We propose a recycling model to reconstruct
33 the mantle array with the participation of both oceanic crust and sediments in the mantle through time.
34 Cerium is a redox sensitive element, making the La-Ce and Sm-Nd systematics an ideal combination to
35 investigate sediment recycling through time. In this recycling model, the most extreme EM-like
36 signatures require the involvement of oceanic sediments that formed under reduced conditions before
37 the Great Oxygenation Event at 2.4 Ga, and which are devoid of Ce elemental anomalies.

38

39 Keywords: $^{138}\text{Ce}/^{142}\text{Ce}$; rare earth elements; chondritic bulk silicate Earth; silicate reservoirs; mantle
40 array; ocean island basalts.

41

42

43 **1. Introduction**

44

45 Long-lived isotope systematics are remarkable tracers of the long-term evolution of the different
46 terrestrial reservoirs. Radiometric systems based on refractory lithophile elements are the most likely to
47 provide robust information on the bulk silicate Earth (BSE) because they were not lost during Earth's
48 accretion or segregated into the core during its differentiation. Indeed, rare earth elements (REEs) have
49 high condensation temperatures and remain strictly lithophile at the conditions of Earth's core formation
50 (Bouhifd et al., 2015). The REE concentrations of the primitive mantle (PM) are assumed to be
51 equivalent to those of the BSE, and their ratios should be chondritic if chondrites are the Earth's main
52 building blocks. Boyet and Carlson (2005) identified a systematic offset between the $^{142}\text{Nd}/^{144}\text{Nd}$ ratios
53 of modern terrestrial rocks and chondrites resulting in an active debate on the refractory lithophile
54 element composition of the PM (see Caro et al., 2008; Jackson and Jellinek, 2013; O'Neill and Palme,

55 2008). ^{142}Nd is a radiogenic isotope partly produced by the decay of ^{146}Sm ($T_{1/2}=103$ Ma). Variations in
56 the ^{142}Nd abundances exist among Solar System materials and they reflect isotopic heterogeneities
57 within the protoplanetary disk (Bouvier and Boyet, 2016; Burkhardt et al., 2016). Determining terrestrial
58 variations relative to chondrites thus requires precise knowledge of the nature of Earth's building blocks.
59 Isotopic similarities between terrestrial samples and enstatite chondrites (ECs) suggest this group of
60 chondrites to be the main terrestrial component (Dauphas, 2017; Javoy, 1995). The mean EC $^{142}\text{Nd}/^{144}\text{Nd}$
61 value is nevertheless lower than that of the BSE without distinguishable variations in their non-
62 radiogenic Nd isotopic compositions from Earth (Burkhardt et al., 2016; Boyet et al., 2018). Variations
63 in $^{142}\text{Nd}/^{144}\text{Nd}$ values between different EC subgroups show further that the EL3 subgroup matches the
64 terrestrial value (Boyet et al., 2018). These results remove the need of an early fractionation of the
65 Sm/Nd ratio of the Earth if the Earth was purely made of EL3 materials. The EL3 chondrites are
66 nevertheless problematic in regards to the elemental composition (e.g. Mg/Si) of the bulk Earth.
67 This study presents measurements of two long-lived isotopic systems in which both the parent and
68 daughter elements are REEs. ^{138}La decays into ^{138}Ce by beta emission ($t_{1/2,\beta} = 295.5$ Gyr: Tanimizu,
69 2000) and into ^{138}Ba by electron capture, whereas ^{147}Sm decays into ^{143}Nd by alpha emission ($t_{1/2,\alpha} = 106$
70 Gyr: Begemann et al., 2001). Variations of $^{138}\text{Ce}/^{142}\text{Ce}$ ratios are expected to be small due to the long
71 half-life and low abundance (0.09% of total La) of ^{138}La . The latest generation of thermal ionisation
72 mass spectrometers (TIMS) can achieve long-term analytical errors below 30 ppm on $^{138}\text{Ce}/^{142}\text{Ce}$
73 (Bonnand et al., 2019), allowing characterisation of Ce isotopic variations in terrestrial and
74 extraterrestrial materials. Here we present analyses of 11 chondrites (ordinary, enstatite, and
75 carbonaceous) that we use to estimate the Ce isotopic composition of the chondritic uniform reservoir
76 (CHUR). We also redefine the Ce-Nd mantle array based on previous and new measurements including
77 seven mid-ocean ridge basalts (MORBs) and 51 ocean island basalts (OIBs). Lastly, we report the first
78 Ce-Nd isotopic compositions of loess samples as a proxy for the upper continental crust (UCC).
79
80 Dickin (1987) first used the Ce-Nd isotopic correlation defined by OIBs to estimate the Ce isotopic
81 composition of the BSE. His regression intercepts the CHUR Nd isotopic composition at a BSE Ce
82 isotopic composition that is 60 ppm less radiogenic than the CHUR value defined by Shimizu et al.

83 (1984). However, new results from chondrites and mantle-derived samples lead to a different
84 observation. The mantle array passes directly through the CHUR composition in the Ce-Nd isotopic
85 diagram (Willig and Stracke, 2019). Our new results first confirm this trend. Moreover we show that a
86 modelled reservoir depleted in incompatible elements (and characterised by a depleted REE pattern; see
87 early-depleted reservoir in Boyet and Carlson, 2005) that would be formed early in the Solar System's
88 history also plots on the mantle array.

89

90 The mantle array must reflect the formation of the major silicate reservoirs and their interactions during
91 Earth's history. Important questions have been addressed by coupling Lu-Hf and Sm-Nd isotope
92 systematics; for example, arc lavas do not follow the Hf-Nd mantle array, which reflects the elevated
93 $^{176}\text{Hf}/^{177}\text{Hf}$ signature measured in most oceanic sediments (Carpentier et al., 2009). Also, the presence
94 of pelagic sediments in the source of the Hawaiian hotspot was first identified from Hf-Nd isotopic
95 measurements (Blichert-Toft et al., 1999). Cerium is a redox sensitive element, making the La-Ce and
96 Sm-Nd systematics an ideal combination to investigate sediment recycling through time. Indeed, most
97 documented modern forearc sediments are depleted in Ce relative to neighbouring elements (Plank,
98 2014). Before the Great Oxygenation Event (GOE), however, all REEs should have behaved similarly
99 and no Ce fractionation is expected to have occurred during that time. Coupling Ce and Nd isotopic
100 measurements will thus provide additional constraints on the nature of sediments recycled into the deep
101 mantle and sampled via hotspot volcanism. Chauvel et al. (2008) explained the Hf-Nd mantle array by
102 the recycling of oceanic crust and sediments into the mantle. Here, we present similar models in Ce-Nd
103 isotope diagrams for the first time.

104

105

106 **2. Sample selection**

107

108 We measured the Ce and Nd isotopic compositions of four ordinary chondrites, six enstatite chondrites,
109 one carbonaceous chondrite, seven MORBs, 51 OIBs, one intraplate continental volcanism occurrence
110 (Ethiopia), and six loess samples. To include all mantle end-members, we selected rocks with extreme

111 Nd-Sr-Pb-He compositions. OIB samples were selected from 13 locations covering the Atlantic
112 (Iceland, São Miguel (Azores archipelago), Cape Verde, Saint Helena, Tristan Da Cunha), Pacific
113 (Hawaii, MacDonald seamount, Rurutu and Tubuai Islands (Austral archipelago), Fangataufa (Tuamotu
114 archipelago), Tahaa Island (Society archipelago)), and Indian Oceans (Heard, Kerguelen, Reunion and
115 Saint-Paul Island (French Southern and Antarctic Lands)). MORB samples are unaltered glasses
116 collected on the Pacific ridge (Bellot et al., 2015) and the Southwest Indian Ridge. The Pacific MORBs
117 have similar REE patterns and do not show the Dupal anomaly (Sr and Pb isotopic anomalies in MORBs
118 and OIBs erupted around 30° S). We used loesses from western Europe (wind-transported periglacial
119 deposits), China and Tajikistan (sediments originating in northwestern Mongolia and the Karakum
120 (Turkmenistan) and Kyzylkum deserts (Kazakhstan and Uzbekistan), respectively), and the Sahara
121 Desert (dusts blown to Southern France; Chauvel et al., 2014 and references therein; Supplementary
122 data 1, Figs S1-4).

123

124

125 **3. Analytical procedures**

126 3.1. Dissolution and chromatography protocols

127

128 All samples were entirely processed at the Laboratoire Magmas et Volcans (LMV, Clermont-Ferrand,
129 France), except three chondrites (NWA 8007, NWA 10854, and Adrar Bous) that were dissolved at the
130 University of Western Ontario (UWO). Mantle-derived and loess samples were dissolved using the
131 following protocol. We used 50 to 300 mg of sample depending on the REE concentration and the
132 quantity of powder available. Powders were digested in a 3:1 mixture of HF (65%) and HNO₃ (48%)
133 that was maintained at 75 °C on a hot plate for 48 h. Once dried, the samples were dissolved a second
134 time in 6 M HCl. The dissolution protocol was slightly different for chondrites. Oudiyat Sbaa, Yilmia,
135 Pillistfer, Agen, Sahara 97158, and Saint-Séverin were dissolved in a 10:1 mixture of HF (65%) and
136 HNO₃ (48%) in PFA-Savillex beakers placed on a hot plate at 110 °C for seven days. Fluorides were
137 broken down in a second step using concentrated HClO₄. Allende, Sahara 97072, Adrar Bous, NWA

138 8007, and NWA 10854 were dissolved in Parr bombs using the same acid mixtures (48 hours at 180 °C
139 in HF-HNO₃, or seven days at 150 °C, followed by HClO₄ treatment). Once dried, all chondrite samples
140 were dissolved in 6 M HCl for two to five days on a hot plate at 110 °C.

141
142 All sample solutions were then separated into two aliquots for trace element and isotopic dilution (5–
143 10%) and Ce-Nd isotopic analyses (90–95%). Ce and Nd were chemically separated following the
144 procedure reported in detail by [Bonnand et al., 2019](#); modified from [Tazoe et al., 2007](#) and [Bellot et al.,](#)
145 [2015](#) and summarised here. REEs (including Ba) were first separated from the matrix using AG50W-
146 X8 resin. An additional step using AG1-X8 resin (200–400 mesh) was performed on the meteorites to
147 remove Fe. Then, Ce was separated from the trivalent REEs using an oxidation technique (NaBrO₃) on
148 Ln-Spec resin, and purified in a final step using AG50W-X8 resin to remove any residual Ba. The
149 remaining REE fraction was processed using Ln-Spec resin (25–50 mesh) and Nd was collected in 0.25
150 M HCl. Total procedural blanks for Ce and Nd were 0.4 ± 1.7 ng (2sd, $n = 12$) and 0.02 ± 0.05 ng (2sd,
151 $n = 7$), respectively, and were always negligible relative to the quantities collected from the samples.

152

153 3.2. Trace element concentrations and Ce and Nd isotopic measurements

154

155 We determined trace element abundances for all samples except NWA 8007, NWA 10854, and Adrar
156 Bous by inductively coupled plasma mass spectrometry (ICP-MS) using the Agilent 7500 quadrupole
157 instrument in normal mode (no collision cell) at LMV. These 3 meteorites were analysed using a Thermo
158 iCAP quadrupole ICP-MS in collision cell mode with He flux at UWO. Concentrations were calculated
159 using an external calibration (CMS reference material standard, Inorganic Ventures). We analysed
160 certified rock standard BHVO-2 (or BCR-2 at UWO) together with our samples to assess the accuracy
161 of our analytical protocol.

162

163 We performed Ce isotopic analyses in static mode with double Re filaments on a ThermoScientific™
164 Triton Plus TIMS at LMV. Ce isotopes were measured as CeO⁺ oxides using the procedure described
165 in [Bonnand et al. \(2019\)](#). A typical run comprised 27 blocks with 20 cycles of 8 s integration time each,

166 and a baseline measurement (deflected ion beams) of 60 s. Matrix rotation of the amplifiers was not
167 active because the 10^{11} , 10^{12} , and 10^{13} Ω resistors were used simultaneously. All corrections (oxygen,
168 mass discrimination using $^{136}\text{Ce}/^{142}\text{Ce} = 0.01688$, and tailing effect) were performed offline. All reported
169 uncertainties are 2 standard deviations. During the course of the study, the value of the tailing correction
170 was $\Delta\epsilon\text{Ce} = 0.77 \pm 0.18$ ($n = 151$). Repeated measurements of our Ce_{LMV} synthetic reference material
171 gave $^{138}\text{Ce}/^{142}\text{Ce} = 0.02257063 \pm 54$ (24 ppm; $n = 31$). $^{138}\text{Ce}/^{142}\text{Ce}$ ratios measured for rock reference
172 standards BCR-2 and BHVO-2 were equal to 0.02256684 ± 48 (21 ppm; $n = 9$) and 0.02256453 ± 99
173 (44 ppm; $n = 7$), respectively (see [Supplementary data 2](#) for details on the total reproducibility of
174 measurements). The mean $^{134}\text{Ba}^{16}\text{O}$ signal was 0.000003 ± 0.000010 V ($n = 139$), and the maximum
175 reached 1×10^{-5} V, which has no significant effect on the $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{136}\text{Ce}/^{142}\text{Ce}$ ratios. Ce isotopic
176 compositions of loess samples were measured on the same TIMS but using the two-line acquisition
177 method of 360 cycles ([Bellot et al., 2015](#)).

178

179 We performed Nd isotopic analyses in static mode with double Re filaments using a ThermoScientific™
180 Triton TIMS at LMV. A typical run comprised 18 blocks of 10 cycles, allowing a full rotation of the
181 amplifier system. Mass discrimination was corrected using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Repeated
182 measurements of the JNdi-1 standard and the two rock reference standards BCR-2 and BHVO-2 gave
183 $^{143}\text{Nd}/^{144}\text{Nd} = 0.512099 \pm 4$ (7 ppm; $n = 16$), 0.512623 ± 8 (17 ppm; $n = 3$) and 0.512973 ± 3 (6 ppm; n
184 = 3), respectively. The Sm contribution measured at mass 147 was negligible in all analyses.

185

186

187 **4. Results**

188

189 Measured Ce and Nd isotopic compositions are reported in [Table 1 and 2](#), and details for individual runs
190 (number of cycles, mean intensity, tailing value) are given in [Supplementary data 2](#).

191

192 4.1. Chondrites

193

194 Chondrites define a small range of $^{138}\text{Ce}/^{142}\text{Ce}$ ratios between 0.02256522 and 0.02256633, excluding
195 the two EL6 samples (Yilmia and Pillistfer) that show lower values (0.02256251 and 0.02256272,
196 respectively). Enstatite, ordinary, and carbonaceous chondrites have indistinguishable average values
197 within errors (Fig. 1A). The two EL6 samples plot on the 4.568 Ga isochron in the $^{138}\text{Ce}/^{142}\text{Ce}$ vs. La/Ce
198 diagram (Fig. 1B) suggesting that their La/Ce ratios were modified early in the history of the Solar
199 System, in agreement with previous conclusions (Barrat et al., 2014; Boyet et al., 2018). Consequently,
200 we define the Ce isotopic composition of CHUR as the mean value of the other nine (i.e., unmodified)
201 chondrite samples: $^{138}\text{Ce}/^{142}\text{Ce}_{\text{CHUR}} = 0.02256577 \pm 66$ (29 ppm).

202

203 To compare our CHUR value with the most recent estimates of Bellot et al. (2015) and Willig and
204 Stracke (2019), we have normalised these previous data using a common reference material
205 ($^{138}\text{Ce}/^{142}\text{Ce}_{\text{CeLMV}}/^{138}\text{Ce}/^{142}\text{Ce}_{\text{CeAMES}} = 0.02257053/0.02257426$, Bonnard et al., 2019). The normalised
206 CHUR value of Willig and Stracke (2019) is thus $^{138}\text{Ce}/^{142}\text{Ce} = 0.02256644 \pm 53$ (using $^{136}\text{Ce}/^{142}\text{Ce} =$
207 0.01688), consistent with our estimate within errors. In contrast, the normalised CHUR value of Bellot
208 et al. (2015) is significantly distinct from our value (Fig 1A). Combining the normalised data of Willig
209 and Stracke (2019) with our measurements to calculate a mean chondritic $^{138}\text{Ce}/^{142}\text{Ce}$ ratio increases the
210 uncertainty from 29 to 39 ppm because their chondrite measurements were systematically 30 ppm more
211 radiogenic than ours. This deviation exists also for MORB and OIB data and it is highlighted when data
212 are reported in a $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{138}\text{Ce}/^{142}\text{Ce}$ isotope diagram. Thus, to compare these different datasets,
213 we henceforth strictly use the epsilon notation (Fig. 1B). In the future, to achieve better interlaboratory
214 reliability, chondrites should be measured under similar analytical conditions (see Supplementary Fig.
215 S5).

216

217 4.2. Ce-Nd isotopic compositions of terrestrial samples

218

219 The Ce and Nd isotopic compositions of terrestrial samples measured in this study are reported in a ϵNd
220 vs. ϵCe diagram (Fig. 2) and compared with recent MORB and OIB data from the literature. MORB
221 samples have the least radiogenic Ce ratios and the most radiogenic Nd ratios, with ϵCe and ϵNd values
222 ranging from -1.19 to -0.71 and from 8.85 to 10.42 , respectively. Pacific MORBs have slightly lower
223 Ce isotopic ratios than Indian ones. OIB samples define larger compositional ranges with ϵCe and ϵNd
224 values ranging from -1.44 to 0.43 and from -2.49 to 10.42 , respectively. Enriched mantle (EM1 and
225 EM2)-like OIBs (Heard, Gough, Kerguelen, Tristan Da Cunha, São Miguel, and Tahaa) have the highest
226 Ce isotopic ratios. Samples from Iceland and two samples from Hawaii plot in the MORB field. Other
227 OIBs, including those with HIMU affinity (Saint-Helena), have compositions intermediate between
228 Iceland samples and those with EM affinities, forming a continuum between these two end-members.
229 The seven samples from Ethiopia have subchondritic ϵCe values and plot along the OIB trend. The
230 entire range of MORB ϵCe values is relatively large (1 unit) compared to OIBs (1.5 units) considering
231 the dispersion of ϵNd values (3 units for MORBs and 12 units for OIBs).

232

233 Loess samples have ϵCe and ϵNd values ranging from 1.6 to 2.0 and from -13.52 to -9.73 , respectively,
234 with average values of $\epsilon\text{Ce} = 1.8 \pm 0.3$ and $\epsilon\text{Nd} = -11.2 \pm 3.0$. Our samples represent a sub-sampling of
235 those analysed by Chauvel et al. (2014), who determined a mean ϵNd value of -10.3 ± 2.3 , consistent
236 with our results.

237

238 5. Discussion

239 5.1. Definition of the Ce-Nd mantle array

240

241 Dickin (1987) was the first to present coupled Ce and Nd isotopic measurements of OIB samples and
242 define the Ce-Nd mantle array. Recently, Willig and Stracke (2019) published new high-precision
243 measurements of MORBs and OIBs and refined the ϵCe - ϵNd correlation. We extended their results by
244 analysing 66 new mantle-derived samples. The regression line calculated from all samples presented in
245 Figure 2 ($n = 134$) gives the following equation for the mantle array: $\epsilon\text{Nd} = -7.3 (\pm 0.5) \times \epsilon\text{Ce} + 0.4 (\pm$

246 0.3), using Isoplot[®] and considering errors of 0.25 for ϵCe and 0.10 for ϵNd . In agreement with Willig
247 and Stracke (2019), the mantle array intercepts the chondritic composition. However, we will show in
248 the following section that a chondritic intercept for the mantle array does not prove that these mantle-
249 derived samples come from a source with a chondritic light REE (LREE) pattern.

250

251 5.2. Chondritic vs. non-chondritic REE composition of the primitive mantle

252

253 A non-chondritic REE composition of the primitive mantle was initially proposed to explain the
254 radiogenic ϵNd values measured in Eoarchean samples (e.g., Chase and Patchett, 1988). High-precision
255 isotopic measurements of the short-lived ^{146}Sm - ^{142}Nd systematics in both terrestrial samples and
256 chondrites have strongly revived the debate on the nature of the REE composition of the PM (Boyet and
257 Carlson, 2005). Most $^{142}\text{Nd}/^{144}\text{Nd}$ variations measured in the different chondrite groups are now
258 attributed to initial isotopic heterogeneities of nucleosynthetic origin within the solar nebula during
259 planetary accretion (Bouvier and Boyet, 2016; Burkhardt et al., 2016; Carlson et al., 2007). However,
260 in terms of non-radiogenic Nd isotope compositions, enstatite chondrites are the closest to the Earth and,
261 on average, are depleted in ^{142}Nd by 10 ppm relative to terrestrial samples (Boyet et al., 2018; Dauphas,
262 2017) with the exception of the EL3 sub-group. Carbonaceous chondrites may have been involved
263 during the last stage of Earth's accretion, and, because they are depleted in ^{142}Nd by 32 ppm relative to
264 terrestrial samples, they may have further contributed to the difference between terrestrial and EC values
265 (Boyet et al., 2018). None of the current meteorite groups available for analysis and mixing models
266 satisfy the isotopic and elemental composition of the Earth, and call for unknown end-members or
267 fractionation processes. Thus, it is still possible that some of the observed difference between terrestrial
268 and chondritic ^{142}Nd abundances was produced by the decay of ^{146}Sm in a superchondritic Sm/Nd
269 reservoir.

270

271 To attempt to constrain the REE composition of the PM, we consider a 10 ppm increase in radiogenic
272 ^{142}Nd that corresponds to the difference between modern terrestrial samples and either EC values having

273 a terrestrial mean $^{142}\text{Nd}/^{144}\text{Nd}$ 10 ppm higher than that of the continental crust, or an Earth made with
274 90% of EL3 chondrites + 10% carbonaceous chondrites (Boyet et al., 2018). This excess ^{142}Nd would
275 have been produced in a high-Sm/Nd reservoir. Assuming this reservoir formed 4.568 Ga, this
276 corresponds to a 3.6% increase of the BSE Sm/Nd ratio relative to the chondritic value. Modelled Sm/Nd
277 ratios in early-differentiated reservoirs have been discussed in a large number of publications (e.g. Boyet
278 and Carlson, 2005; Caro et al., 2008) and can go up to 5% higher if this early-differentiated reservoir
279 formed 4.5 Ga. Here we use the terms “early depleted reservoir” (EDR) and “early enriched reservoir”
280 (EER) as defined by Boyet and Carlson (2005): the EDR has a chondrite-normalised REE pattern that
281 is depleted in LREEs relative to heavy REEs and thus a superchondritic Sm/Nd ratio, whereas the
282 complementary EER has a subchondritic Sm/Nd ratio. The EER may exist in the lower mantle (Boyet
283 and Carlson, 2005) or may correspond to embryonic crust lost by collisional erosion during Earth’s
284 accretion (O’Neill and Palme, 2008).

285

286 We calculate the REE composition of the EDR by the method developed by Jackson and Jellinek (2013),
287 which is based on three different isotopic systematics (^{146}Sm - ^{142}Nd , ^{147}Sm - ^{143}Nd , and ^{176}Lu - ^{176}Hf) and
288 invariant elemental ratios (e.g., Sm/Hf). CHUR REE elemental ratios needed for this calculation were
289 obtained from a large and recent database of ordinary, enstatite, and carbonaceous chondrites (Barrat et
290 al., 2012, 2014; Boyet et al., 2018; Braukmüller et al., 2018; Dauphas and Pourmand, 2015; Pourmand
291 et al., 2012). We selected the least thermally metamorphosed fall samples (types 1–4, $n = 42$), and
292 outliers (Orgueil and Kelly) were removed. The mean La/Ce ratio thus calculated for CHUR is $0.387 \pm$
293 0.022 ($n = 39$), similar to the value we obtained from our smaller sample set ($\text{La}/\text{Ce}_{\text{CHUR}} = 0.390 \pm$
294 0.022). The CHUR Sm/Nd ratio determined from the same database of chondrite samples is $0.324 \pm$
295 0.014 , consistent with the value proposed by Bouvier et al. (2008). Lastly, we used the Lu/Hf ratio of
296 CHUR (0.236) calculated from the average $^{176}\text{Lu}/^{177}\text{Hf}$ value determined by Bouvier et al. (2008).

297

298 The calculated REE pattern for an EDR is presented in Figure 3. For a 3.6% increase of the Sm/Nd ratio
299 of the BSE, the modelled EDR has $\epsilon\text{Ce} = -0.4$ and $\epsilon\text{Nd} = 4.1$. This reservoir plots very close to the
300 mantle array in the ϵNd vs. ϵCe diagram, and shows Ce-Nd isotopic compositions similar to those

301 measured in several OIBs (Fig. 4). A large-scale silicate differentiation event early in the Solar System's
302 evolution does not produce any offset in the Ce-Nd isotopic composition of the EDR relative to the
303 mantle array. Thus, defining the Ce-Nd mantle array does not resolve the long-standing debate over the
304 chondritic vs. EDR-like REE composition of the PM.

305

306 5.3. Crustal extraction mass-balance calculations

307

308 Mantle melting and subsequent extraction of the crust has contributed to the depletion of the mantle in
309 incompatible elements. Crustal growth models are widely discussed and several authors have proposed
310 rapid continental growth early in Earth's history despite the scarce geological record of the Earth's first
311 billion years (Belousova et al., 2010; Dhuime et al., 2012). Geochemical signatures in mantle-derived
312 samples linked to this process are particularly difficult to decipher because surface material is
313 continuously reintegrated into the mantle via subduction. In this section, to investigate the production
314 of the various mantle reservoirs, we attempt to recreate the Ce-Nd mantle array via mass-balance mixing
315 calculations between the depleted MORB mantle (DMM) and continental crust (CC). We first simplify
316 our approach by assuming that the CC was extracted from the PM in a single differentiation step (i.e.,
317 $DMM + CC = BSE$). Since we have not resolved the chondritic vs. EDR-like composition of the PM,
318 we explore both bulk compositions and compare their modelled Ce-Nd mixing curves to the mantle
319 array. Distinct scenarios proposed that oceanic crust formation was the dominant process of mantle
320 depletion with continents formed later by reworking in subduction zones (e.g., Jones et al., 2019).
321 Furthermore, isotopic studies of rocks from the Nuvvuagittuq Supracrustal Belt and the neighbouring
322 Hudson Bay terrane show that the Archean felsic crust formed by reworking of Hadean mafic crust
323 (O'Neil et al., 2019; O'Neil and Carlson, 2017). From these observations, we choose to calculate the
324 Ce-Nd isotopic composition of such an enriched reservoir and compare it to the global dataset to evaluate
325 the effect of primitive mafic crustal extraction on the mantle.

326

327 5.3.1. End-members

328 *Depleted MORB Mantle*

329 The DMM end-member isotopic composition is commonly calculated from MORB samples. Our
330 measurements and literature data are plotted in the ϵNd vs. ϵCe diagram (Fig. 2). The average of 48
331 MORB measurements gives $\epsilon\text{Ce}_{\text{DMM}} = -1.1 \pm 0.6$ and $\epsilon\text{Nd}_{\text{DMM}} = 9.7 \pm 2.3$. This mean Nd isotopic
332 composition is consistent with previously proposed values of 9.2 and 9.8 based on a more complete
333 dataset (Salters and Stracke, 2004, and Workman and Hart, 2005, respectively). Restricting the MORB
334 samples to those that do not show the Dupal anomaly (i.e., North Atlantic and Pacific MORBs) gives
335 an identical result ($\epsilon\text{Ce} = -1.2 \pm 0.6$, $n = 33$).

336

337 *Continental Crust*

338 The CC is a low-mass reservoir containing 20–70% of the PM's incompatible element budget. The
339 difficulty in constraining the CC composition stems from its nature. With a mean age of 1.8–2.4 Ga
340 (Chauvel et al., 2014; Taylor and McLennan, 1995) and an average thickness of about 40 km, it is much
341 older and thicker than the present-day oceanic crust. The major- and trace-element compositions of the
342 upper, middle, and lower crust are based on numerous rock samples from which global compositions
343 were obtained (Rudnick and Gao, 2003, and references therein), though the isotopic composition of the
344 bulk CC is largely under-constrained; very few data are available for Ce, and ϵNd values generally vary
345 between -21 and -10 . Based on loess measurements, Chauvel et al. (2014) proposed a model age of 1.8
346 Ga for the UCC and a ϵNd value of -10 . On the other hand, Goldstein and Jacobsen (1988) considered
347 suspended materials in rivers ($\epsilon\text{Nd} = -11$, $T_{\text{DM}} = 1.6$ Ga) but corrected their mean value for the
348 preferential erosion of young terranes ($\epsilon\text{Nd} = -17$ recalculated at 2.1 Ga). Similarly, Hawkesworth et al.
349 (2017) discussed the erosional bias based on the proportions of young and old source rocks and proposed
350 a bulk CC ϵNd value of -12 . Other studies consider that the upper and bulk crusts have distinct isotope
351 signature; Allègre and Lewin (1989) calculated a ϵNd value of -21 from DMM-bulk CC mass-balance
352 equations, whereas Jacobsen and Wasserburg (1980) obtained a slightly higher value with a similar
353 approach ($\epsilon\text{Nd} = -14$).

354

355 To date, CC rocks analysed for Ce and Nd isotopes are mainly ~ 2 Ga granites and gneisses (see
356 Supplementary Fig. S6 for details). Combining all published Ce-Nd measurements gives average values

357 of $\epsilon_{\text{Ce}} = 2.8$ and $\epsilon_{\text{Nd}} = -19$ (Fig. 4). This is slightly different from the sole published estimate for the
358 CC ($\epsilon_{\text{Ce}} = 1.3$ and $\epsilon_{\text{Nd}} = -14$; Tanaka et al., 1987), which was calculated by regression from five crustal
359 rock measurements ($\epsilon_{\text{Ce}} = -0.112 \times \epsilon_{\text{Nd}}$) anchored to the mean ϵ_{Nd} value of aeolian sediments and
360 particulates in rivers ($\epsilon_{\text{Nd}} = -11.4$; Goldstein et al., 1984). Our loess average is $\epsilon_{\text{Ce}} = 1.8$ and $\epsilon_{\text{Nd}} = -$
361 11.2, relatively close to Tanaka et al.'s (1987) value.

362

363 *Mafic crust*

364 Results obtained on the ^{146}Sm - ^{142}Nd short-lived systematics suggest that the oldest mafic crust preserved
365 at the Earth's surface is the ~ 4.3 Ga Nuvvuagittuq Supracrustal Belt in northern Quebec (O'Neil et al.,
366 2008). Even if this age is debated, the neighbouring Hudson Bay terrane shows that the Archean felsic
367 crust formed by reworking of an Hadean mafic crust (O'Neil et al., 2019; O'Neil and Carlson, 2017).
368 We chose sample PC-162 ($\text{La}/\text{Ce} = 0.49$ and $\text{Sm}/\text{Nd} = 0.27$) as representative of the Archean mafic crust
369 to model its Ce and Nd isotopic compositions. This and other samples from the enriched low-Ti group
370 (O'Neil et al., 2011) are enriched in LREEs by 10 to 80 times the chondritic reference, whereas rocks
371 from the depleted low-Ti and high-Ti units show lower LREE enrichments (< 20 times). Furthermore,
372 PC-162 is one of the most REE-depleted samples among those of the enriched low-Ti group that do not
373 show any evidence of metamorphic disturbance (O'Neil et al., 2012), and thus its REE contents
374 correspond to a reasonable crustal extraction rate: that is, more enriched compositions reflect increased
375 depletion of the mantle during extraction of the crust. The Ce-Nd isotopic compositions of the modelled
376 mafic end-member are reported in Figure 4; they are identical ($\epsilon_{\text{Ce}} = 3.8$ and $\epsilon_{\text{Nd}} = -17.3$) for a crust
377 formed at 4.3 Ga, irrespective of the PM considered (CHUR or EDR). The EER calculated by Carlson
378 and Boyet (2008) has similar La/Ce and Sm/Nd ratios of 0.47 and 0.28, respectively, producing present-
379 day isotopic compositions of $\epsilon_{\text{Ce}} = 3$ and $\epsilon_{\text{Nd}} = -13.5$ if this reservoir formed 4.3 Ga. Both these models
380 plot to the right of the mantle array (Fig. 4).

381

382 5.3.2. Model parameters and mixing hyperbolas

383

384 Our mass-balance models consider DMM-CC complementarity for chondritic and early-depleted PM
385 compositions. We aim to determine the ϵ_{Ce} value of the CC using four-successive calculation steps
386 (Supplementary material). 1) We calculate the mass fraction of Nd in the CC relative to the total amount
387 in the crust and DMM (the sialic index; e.g., Allègre and Lewin, 1989) based on the DMM, CHUR/EDR
388 (Table 3), and CC ϵ_{Nd} values. As the range of published CC isotopic values is large, we do not set a
389 precise ϵ_{Nd} value in the mass-balance model, but consider all possibilities between $\epsilon_{\text{Nd}} = -10$ and -21 .
390 2) We calculate the mass fraction of CC using the Nd contents of the BSE (as determined in section 5.2
391 with REE patterns anchored to a Lu content of 68 ppb; McDonough and Sun, 1995) and CC (Rudnick
392 and Gao, 2003). The Ce/Nd ratio is set to 1.28 for a chondritic BSE and to 1.22 for the EDR model
393 (Table 3). Importantly, the Lu value chosen to anchor the REE pattern of the BSE has no consequence
394 on the final ϵ_{Ce} value. 3) The Ce sialic index is calculated using the Ce contents of the BSE (see step 2)
395 and CC (Rudnick and Gao, 2003). 4) The ϵ_{Ce} value of the CC is calculated from the Ce sialic index and
396 the ϵ_{Ce} values of the DMM and CHUR/EDR (Table 3): ϵ_{CeCC} varies from 0.2 to 1 in the chondritic case
397 and from 0.4 to 1.2 in the EDR case. All CCs are represented as orange or green lines at the lower end
398 of the mixing curves in Figure 4 (chondritic or EDR model, respectively) and all calculated DMM-CC
399 mixing hyperbolas are plotted in the form of a coloured field. Their curvature is a function of the Ce/Nd
400 ratios of both end-members.

401

402 In the upper left of the ϵ_{Nd} vs. ϵ_{Ce} diagram, the DMM-CC mixing hyperbolas overlap and pass through
403 both the CHUR and EDR compositions. However, they do not fully overlap the data points defining the
404 mantle array. The Ce-Nd isotopic compositions calculated for the CC are always less radiogenic in
405 cerium than the mean values estimated from measurements, which might question the relevance of the
406 published data used to estimate the isotopic composition of the bulk CC. Most of the samples are upper
407 crust (e.g., loess) samples. If the observed difference reflects heterogeneities within the crustal reservoir,
408 the lower and middle crust should be characterised by negative ϵ_{Ce} values to adjust the mass balance
409 budget within the continental crust (Willig and Stracke, 2019). However, Vervoort et al. (2000)
410 suggested that lower crustal xenoliths have $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ values close to the mantle array.

411

412 The mass fraction of depleted mantle relative to the whole mantle can be calculated in the case of the
413 mass balance calculations for the entire range of $\epsilon\text{Nd}_{\text{CC}}$ considered. It varies from 14 to 33% and from
414 28 to 64% ($\pm 20\%$) for the CHUR and EDR bulk compositions, respectively (Fig. 5). As mentioned in
415 section 5.3.1, a more depleted initial composition implies that a larger volume of the mantle was depleted
416 by crustal extraction (Boyet and Carlson, 2006). For comparison, Allègre and Lewin (1989) calculated
417 the mass fraction of depleted mantle to be comprised between 32 and 40% using a chondritic BSE.

418

419 The mixing curve joining the DMM and a 4.3 Ga early mafic crust is also reported in Figure 4. The
420 Ce/Nd ratio of this mafic crust is 1.9, only slightly different from the mean value of 2.15 determined for
421 the CC by Rudnick and Gao (2003). Thus, the DMM-mafic crust mixing hyperbola has a curvature close
422 to that of the DMM-CC mixing curve. Again, such a mixing scenario seems unlikely to reproduce the
423 mantle array.

424

425 5.3.3. What parameters can bring the DMM-CC mixing model closer to the mantle array?

426

427 To superimpose the DMM-CC mixing curve on the mantle array, Willig and Stracke (2019) proposed
428 using a more depleted isotopic composition for the DMM end-member (see their Figure 5). However,
429 for a likely CC Nd isotopic composition, such a DMM-CC hyperbola requires DMM Ce-Nd isotopic
430 ratios very different from those measured in MORB samples. For example, to fully reproduce the mantle
431 array, the ϵCe and ϵNd values of the DMM should be approximately -10 and $+40$, respectively, if we
432 set the ϵNd value of the bulk CC to -17 (in the case of a chondritic BSE). Such compositions have never
433 been measured in MORBs or peridotites.

434

435 Several authors have proposed loess samples to be a good approximation of the upper crust because
436 these clastic rocks sample large surface areas and have relatively uniform Nd and Hf isotopic
437 compositions (e.g., Chauvel et al., 2014). Because the lower crust appears to have Hf-Nd isotopic ratios
438 similar to those of the upper crust (Vervoort et al., 2000), we also calculated the ϵCe - ϵNd mixing
439 hyperbola between the DMM end-member and a loess-like component. Its curvature is a function of the

440 Ce/Nd ratios of both end-members. The mean Ce/Nd value calculated from our loess samples ($2.38 \pm$
441 0.30) is similar within errors to the value of 2.33 determined for the upper crust by [Rudnick and Gao](#)
442 [\(2003\)](#) and to that of the global subducting sediment reservoir that represents the bulk composition of
443 trench sediments ([Plank, 2014](#)). However, this result is more than twice the Ce/Nd ratios of 1.08 and
444 0.95 determined for the DMM by [Salters and Stracke \(2004\)](#) and [Workman and Hart \(2005\)](#),
445 respectively. Consequently, considering the Ce-Nd isotopic composition of loess as representative of
446 the CC moves the DMM-CC mixing curve further from the mantle array ([Fig. 4](#)).

447

448 The model age of loesses is 1.8 Ga ([Chauvel et al., 2014](#)), which is not widely agreed to be the mean
449 age of the crust. An older equivalent (2.2 Ga) of these samples would have a less radiogenic Ce-Nd
450 isotopic composition that still plots on the mantle array. Superimposing the DMM-loess mixing curve
451 on the mantle array (i.e., to linearise the DMM-loess hyperbola) requires increasing the DMM Ce/Nd
452 ratio towards a value identical to that of loesses. Unlike the CC reservoir, which has been calculated
453 from a large number of measurements, the DMM remains a model based on a series of assumptions,
454 such that its REE pattern can be questioned. Such a reservoir is represented in MORB Ce and Nd isotopic
455 compositions as a strong long-term depleted REE element pattern, and a consistent Ce/Nd_{DMM} ratio
456 requires the DMM to have a positive Ce elemental anomaly. Cerium anomaly generally reflects a
457 specific behaviour of Ce^{4+} relative to REE^{3+} . However, such a Ce anomaly has never been measured in
458 MORBs.

459

460 The DMM-loess mixing curve coincides with the repartition of Island Arc Basalts (IABs) from the
461 Lesser Antilles and the Mariana Islands ([Bellot et al., 2015, 2018](#)). The isotopic compositions of OIBs
462 and IABs differ from those of MORBs due to the introduction of crustal material into their sources.
463 Although the isotopic compositions of arc lavas can be modified by post-melting reactions such as
464 assimilation-fractional crystallisation processes (AFC), this is not the case for the Marianas and Lesser
465 Antilles (e.g., [Labanieh et al., 2010](#)), and their Ce-Nd isotopic compositions are well explained by the
466 incorporation of sediments into the mantle wedge ([Bellot et al., 2015, 2018](#)). We expect a larger
467 incorporation of sediments in arc lavas relative to hotspot lavas since REEs are enriched in slab

468 dehydration fluids, whereas sediments are recycled with oceanic crust into the OIB source and their
469 signatures are consequently diluted. Indeed, OIBs and IABs are clearly distinct in the ϵCe - ϵNd diagram
470 (Fig. 4).

471

472

473 5.4. Effect of recycled surface material on the mantle array

474

475 The EM1, EM2, and HIMU mantle end-members have been defined from the most extreme isotopic
476 compositions measured in OIBs (Zindler and Hart, 1986) and are classically interpreted as representing
477 the recycling of surface materials into the deep mantle. Chauvel et al. (2008) modelled the Hf and Nd
478 isotopic compositions of basaltic crust and sediments recycled at different times during Earth's history
479 and showed that the Hf-Nd mantle array required the incorporation of surface material older than 2 Ga
480 into the OIB source. Here we apply the evolution model to the Ce-Nd systematics (see Supplementary
481 Fig. S7): 1) the isotopic composition of recycled sediments and recycled oceanic crust (ROC) calculated
482 back in time is assumed to be on the evolution line built between their present-day isotopic composition
483 and the CHUR value at 4.568 Ga; 2) the actual isotopic compositions of these two reservoirs are then
484 calculated considering the parent/daughter ratios in their source reservoirs. To this end, we consider the
485 mean $^{143}\text{Nd}/^{144}\text{Nd}$, $^{138}\text{Ce}/^{142}\text{Ce}$, $^{147}\text{Sm}/^{144}\text{Nd}$, and $^{138}\text{La}/^{142}\text{Ce}$ ratios measured in oceanic sediments in
486 front of the Mariana trench (Sites 801 and 802, ODP Leg 129; Bellot et al., 2018) and near the Lesser
487 Antilles arc (DSDP site 144; Bellot et al., 2015) together with those of the MORB samples plotted in
488 Figure 2. Modern oceanic sediments are characterised by negative elemental cerium anomalies,
489 reflecting an oxidised environment. Before the GOE, dated around 2.4 Ga (see Holland, 2002), all REEs
490 in sediments were necessarily trivalent under the anoxic conditions. Thus, we removed the elemental
491 cerium anomaly from all oceanic sediments older than 2.4 Ga.

492

493 Our calculations produce important results. First, the ROC follows a positive slope in the ϵCe - ϵNd
494 diagram, whereas the mantle array defines a negative slope (Fig. 6, see Supplementary Fig. S7 for further
495 details). Thus, the incorporation of ROC into the mantle tends to shift the isotopic composition of OIBs

496 toward slightly less radiogenic Ce isotopic ratios than MORBs. Second, as previously shown by [Chauvel](#)
497 [et al. \(2008\)](#), the mantle array can be reproduced by mixing either a DMM-like or a FOZO-like
498 component (FOZO is assumed to have $\epsilon_{\text{Ce}} = -0.6$ and $\epsilon_{\text{Nd}} = 6.24$; see [Boyet et al., 2019](#)) and recycled
499 surface material (ROC and sediments have the same recycling ages). On the sole basis of Ce and Nd
500 isotopes, it is still unclear whether the different plume sources contain surface material recycled at
501 various time or pre-GOE material in various proportions (the two propositions being not mutually
502 exclusive). Also, the intersections of the recycled crust-sediment mixing curves and the mantle array
503 indicate the proportion of sediments in the recycled material ($m_{\text{sediments}} / (m_{\text{sediments}} + m_{\text{oceanic crust}})$) to be
504 between 6 and 12%; this proportion decreases for younger recycled components. This last result must
505 be considered in parallel with the decreasing rate of crustal destruction until the present value of 3.2–
506 $5.5 \text{ km}^3 \text{ yr}^{-1}$ ([Dhuime et al., 2018, and references therein](#)).

507

508 Sediments formed before and after the GOE evolved to distinct Ce isotopic compositions. For a similar
509 proportion of sediments in the recycled component (i.e., 10% sediment and 90% oceanic crust), the ϵ_{Ce}
510 value of a 2.5 Ga recycled component is inferior by 0.3 ϵ -units when we remove the Ce anomaly. More
511 importantly, in our model, only the recycling of pre-GOE sediments can explain the most enriched
512 isotopic compositions measured in OIBs. Corresponding samples are classified either as EM1 (samples
513 from Tristan Da Cunha, Gough, Heard, and Kerguelen Islands) or EM2 (Tahaa Island in the Society
514 archipelago). The Ce-Nd isotopic composition of Gough Island lavas was explained by the incorporation
515 of subcontinental lithospheric material at shallow depths into the mantle ([Boyet et al., 2019](#)). The lack
516 of correlation between the cerium anomalies and the Ce isotope compositions measured in Gough Island
517 lavas proves that ancient sediments carrier of negative element cerium anomaly were not incorporated
518 in the Gough mantle source. Moreover, mass-independent S isotopic fractionations measured in olivine-
519 hosted sulphides from other EM1 (e.g., Pitcairn) lavas similarly suggest the recycling of surface
520 materials that existed in a reduced atmosphere before the GOE ([Cabral et al., 2013; Delavault et al.,](#)
521 [2016](#)).

522

523

524 6. Conclusions

525

526 We measured the Ce isotopic compositions of 51 OIBs, 1 intraplate continental volcanism occurrence,
527 7 MORBs, 6 loess samples, and 11 chondrites, enhancing the terrestrial and extra-terrestrial Ce isotopic
528 database. We define the $^{138}\text{Ce}/^{142}\text{Ce}$ CHUR reference to be 0.02256577 ± 66 . OIB and MORB samples
529 define the mantle array as $\epsilon\text{Nd} = -7.3 (\pm 0.5) \times \epsilon\text{Ce} + 0.4 (\pm 0.3)$. The mantle array passes through the
530 CHUR value and is not significantly different from a modelled early-depleted reservoir. We conclude
531 that combining Ce and Nd isotopic measurements in mantle-derived samples does not further constrain
532 the composition of the PM.

533

534 Mixing models between the DMM and CC end members, both estimated from sample measurements
535 (upper, or early mafic crusts), cannot reproduce the Ce-Nd mantle array but better fit IAB data. The
536 mantle array is better reproduced by considering bulk CCs consistent with a mass-balance budget of the
537 BSE (Ce isotopic compositions calculated for a range of accepted Nd). But the mixing hyperbolas do
538 not perfectly overlap the OIB samples with subchondritic Ce isotopic composition; and the calculated
539 ϵCe for the bulk crust are significantly different from all crustal rocks measured so far. In all these
540 models, linearising the mixing curves requires unrealistic Ce-Nd isotopic compositions and/or Ce/Nd
541 ratios never measured in rock samples. Alternatively, the recycling of sediments and oceanic crust into
542 hotspot sources, and their mixing with DMM- or FOZO-like material may explain the Ce-Nd mantle
543 array. Our results further show that Ce-Nd isotopic compositions measured in the most enriched EM-
544 like lavas can be reproduced by the incorporation in their source of recycled oceanic sediments that do
545 not have any elemental Ce anomaly. Because Ce is a redox-sensitive trace element that can be used to
546 trace the oxygenation of atmosphere (GOE at 2.4 Ga), our results suggest that some OIBs sample very
547 deep mantle reservoirs that may preserve pre-GOE recycled surface materials, in agreement with
548 observed S isotopic fractions in EM1 lavas. Constraining the long-term history of recycled surface
549 material in the mantle is essential to understand the isotope signature of mantle-derived samples. The
550 La-Ce isotope systematics offers a unique opportunity to detect changes on the chemical composition
551 of oceanic sediments through time.

552

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554

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569

570

571 **Appendix A. Supplementary material**

572

573 Supplementary material related to this article can be found online at XX.

574 Supplementary data 1: Major and trace element contents measured by quadrupole ICP-MS.

575 Supplementary data 2: Ce and Nd isotopic ratios of standard and rock samples and supplementary
576 information.

577 Supplementary material: 1) Sample descriptions from trace element diagrams and Ce anomalies; 2)
578 $^{138}\text{Ce}/^{142}\text{Ce}$ ratios from literature and example of normalisation with MORB; 3) $^{138}\text{Ce}/^{142}\text{Ce}$ ratios of
579 crustal samples from literature; 4) mass-balance calculations; and 5) recycling models.

580

581

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759

760

761 **Table captions**

762

763 Table 1. $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios and La/Ce and Sm/Nd ratios of whole-rock OIBs,
764 MORBs and loesses. The Nd isotopic compositions of loess and Kerguelen samples (*) are from
765 [Chauvel et al. \(2014\)](#) and unpublished data from B. Moine, respectively. Epsilon values are normalised

766 according to the CHUR references defined for Ce in this study as $\epsilon\text{Ce} = \left(\frac{\frac{^{138}\text{Ce}}{^{142}\text{Ce}}_{\text{sample}}}{\frac{^{138}\text{Ce}}{^{142}\text{Ce}}_{\text{CHUR}}} - 1 \right) \times 10,000$

767 and for Nd by [Bouvier et al. \(2008\)](#) as $\epsilon\text{Nd} = \left(\frac{\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{sample}}}{\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{CHUR}}} - 1 \right) \times 10,000$. Errors correspond to

768 internal errors (2se).

769

770 Table 2. $^{138}\text{Ce}/^{142}\text{Ce}$ isotopic ratios and La/Ce whole-rock chondrites. Epsilon values are normalised

771 according to the CHUR references defined for Ce in this study as $\epsilon\text{Ce} = \left(\frac{\frac{^{138}\text{Ce}}{^{142}\text{Ce}}_{\text{sample}}}{\frac{^{138}\text{Ce}}{^{142}\text{Ce}}_{\text{CHUR}}} - 1 \right) \times 10,000$.

772 Errors correspond to internal errors (2se).

773

774 Table 3. Elemental and isotopic compositions of Earth's main silicate reservoirs used in our calculations:

775 BSE, bulk silicate Earth; EDR, early depleted reservoir; DMM, depleted MORB mantle; CC, continental

776 crust; UCC, upper continental crust; and mafic crust. Errors are errors on data averages. No errors are

777 given for model-based isotopic compositions (EDR, aged UCC, and mafic crust). Values in italics refer

778 to literature data: CC Ce and Nd concentrations are from [Rudnick and Gao \(2003\)](#), concentrations for

779 the mafic crust are those measured in PC-162 from [O'Neil et al., \(2011\)](#), and BSE $^{143}\text{Nd}/^{144}\text{Nd}$ ratios

780 are from [Bouvier et al. \(2008\)](#). BSE range of Ce and Nd concentrations are modelled using Lu contents

781 from [Allègre et al. \(2001\)](#), [Lyubetskaya and Korenaga \(2007\)](#), [McDonough and Sun \(1995\)](#), [Palme and](#)

782 [O'Neill \(2014\)](#) and chondritic REE ratios (see [supplementary material S4](#) for more details). Ce/Nd of

783 the BSE is constant and set to 1.28 (1.22 for EDR). DMM isotopic composition is the mean value of

784 data from this study, [Bellot et al., 2015, 2018](#), [Makishima and Masuda, 1994](#) and [Willig and Stracke,](#)

785 [2019](#). UCC (1.8 Ga) Ce and Nd contents and isotopic compositions are the mean values of loess data

786 from this study. UCC (2.2 Ga) isotopic compositions are calculated by aging 1.8 Ga UCC.

787

788 **Figure captions**

789

790 Fig. 1. A) $^{138}\text{Ce}/^{142}\text{Ce}$ ratios measured in enstatite (green squares), ordinary (red diamonds), and

791 carbonaceous (black triangles) chondrites. Literature values are from [Bellot et al. \(2015, 'B et al. 15'\)](#)

792 and [Willig and Stracke \(2019, 'W&S19'\)](#). Data from the literature are normalised to the Ce_{LMV} reference

793 material from this study: $^{138}\text{Ce}/^{142}\text{Ce}_{\text{Ce}_{\text{LMV}}}/^{138}\text{Ce}/^{142}\text{Ce}_{\text{Ce}_{\text{AMES}}} = 0.02257053/0.02257426$ ([Bonnand et al.,](#)

794 [2019](#)). B) ϵCe ratios vs. La/Ce ratios of chondrites from [Willig and Stracke \(2019\)](#) and this study. Data

795 are normalised to the CHUR reference defined in these studies. The dashed line represents the 4.568 Ga
796 CHUR reference isochron.

797

798 Fig. 2. ϵNd vs. ϵCe of mantle-derived samples and loesses from this study (coloured symbols). Nd
799 isotopic compositions of loess and Kerguelen samples are from Chauvel et al. (2014) and B. Moine
800 (unpublished data), and Ce and Nd isotopic compositions of Gough samples are from Boyet et al. (2019).
801 Literature data are in grey (Bellot et al., 2015, 2018; Makishima and Masuda, 1994; Willig and Stracke,
802 2019). Error bars are 2se (internal error). Literature data are reported considering the epsilon values and
803 CHUR references measured in each study to limit any bias introduced by normalisation. The data from
804 Tanaka et al. (1987) are not included because we do not have the corresponding CHUR reference. The
805 mantle array is defined by regression on mantle-derived samples only. Its equation defined from 134
806 data is $\epsilon\text{Nd} = -7.3 (\pm 0.5) \times \epsilon\text{Ce} + 0.4 (\pm 0.3)$ (calculated with Isoplot[®] and considering errors of 0.25
807 and 0.10 for ϵCe and ϵNd , respectively).

808

809 Fig. 3. REE patterns normalised to a chondritic primitive mantle for a chondritic BSE model (orange)
810 and an EDR model with $\text{Sm}/\text{Nd} = \text{Sm}/\text{Nd}_{\text{BSE}} + 3.6\%$ (green). The EDR REE pattern is calculated as
811 follows. 1) The REE patterns are anchored at Lu, the least incompatible REE. 2) The early depleted
812 $\epsilon\text{Nd}_{\text{present}}$ value is calculated using the initial CHUR value (Bouvier et al., 2008) at 4.568 Ga and a Sm/Nd
813 ratio 3.6% above that of the BSE. 3) The early depleted $^{177}\text{Hf}/^{176}\text{Hf}$ ratio is deduced from the Hf-Nd
814 mantle correlation ($\epsilon\text{Hf}_{\text{present}} = 1.59 \times \epsilon\text{Nd}_{\text{present}} + 1.28$; Chauvel et al., 2008). 4) The Lu/Hf ratio is
815 obtained by comparison of the initial $^{177}\text{Hf}/^{176}\text{Hf}_{\text{CHUR}}$ ratio (Bouvier et al., 2008) and the early depleted
816 Hf isotopic composition calculated in step 3. That is, the Hf concentration is obtained from the known
817 Lu concentration set as the anchor point in step 1. 5) The Sm concentration is calculated from the Sm/Hf
818 ratio, which has a constant value of 1.44 in OIBs (Jackson and Jellinek, 2013). 6) The Nd concentration
819 is calculated from the Sm/Nd ratio (known after steps 2 and 5). 7) The La and Ce concentrations are
820 calculated using a binomial fit through the chondrite normalised Sm, Nd, and Lu concentrations (i.e.,
821 the equation of the La–Lu pattern is of the form $y = ax^2 + bx + c$, where x represents the REEs, numbered
822 1–15 for La–Lu).

823

824 Fig. 4. ϵNd vs. ϵCe measured in mantle-derived samples (see Fig. 2, with additional data for IABs from
825 [Bellot et al., 2015, 2018](#) and continental crust samples; see Supplementary Fig. S6). The global linear
826 trend of the mantle array is shown as the black dashed line and intercepts the chondritic composition
827 ($\epsilon\text{Nd} = 0.00$, $\epsilon\text{Ce} = 0.07 \pm 0.05$ (2σ)). Large symbols represent terrestrial reservoirs. Note that mean
828 loess corresponds to a 1.8 Ga UCC (T_{DM}); and we represent a 2.2 Ga UCC as a modelled composition
829 (aged loess). The mean CC value is the mean value of continental samples averaged by location. The
830 continental crust value published in [Tanaka et al. \(1987\)](#) is calculated from 5 measurements. The 4.3 Ga
831 mafic crust composition results from an extraction model from the depleted mantle. The red field
832 represents the DMM-UCC mixing curves. The brown field corresponds to the DMM-4.3 Ga mafic crust
833 mixing curves. The fields correspond to the different curves calculated using DMM Ce and Nd
834 concentrations given by [Salters and Stracke, 2004](#) and [Workman and Hart, 2005](#). The orange field
835 represents all the DMM-CC mixing curves calculated for a chondritic BSE model (bulk crust
836 compositions shown by the bold orange line). The green field represents all the DMM-CC mixing curves
837 calculated for an EDR model (bulk crust compositions shown by the bold green line). See details in the
838 text and calculation parameters in [Table 3](#).

839

840 Fig. 5. Mass fraction of the depleted mantle relative to the primitive mantle ($m_{\text{DM}}/m_{\text{PM}}$, expressed in
841 percent) vs. the ϵNd value of the bulk continental crust. Two cases are represented: DMM-CC mixing
842 for a chondritic BSE (orange) and DMM-CC mixing for an EDR (green). Parameters used in the
843 calculations are discussed in the text and reported in [Table 3](#).

844

845 Fig. 6. ϵNd vs. ϵCe measured in mantle-derived samples compared with reservoir evolution models. The
846 present-day average compositions of the recycled oceanic crust (ROC = MORB; this study) and oceanic
847 sediments ([Bellot et al., 2015, 2018](#)) are shown as large symbols. Solid lines outline the present-day
848 isotopic compositions of these reservoirs if formed at different ages. The yellow line shows the evolution
849 of MORBs using mean La/Ce and Sm/Nd ratios of MORBs and the MORB source. Similarly, the blue
850 and purple lines show the evolution of oceanic sediments with chondrite-normalised REE patterns

851 showing a Ce negative anomaly as observed in modern oceanic sediments ($\text{La/Ce} = 0.57$) or without a
852 Ce anomaly ($\text{La/Ce} = 0.47$), representing oceanic sediments formed in reduced conditions before the
853 GOE (~ 2.4 Ga), respectively. The Ce-Nd isotopic composition of the recycled material is shown by
854 mixing curves between contemporaneous ROC and oceanic sediments (dashed lines).

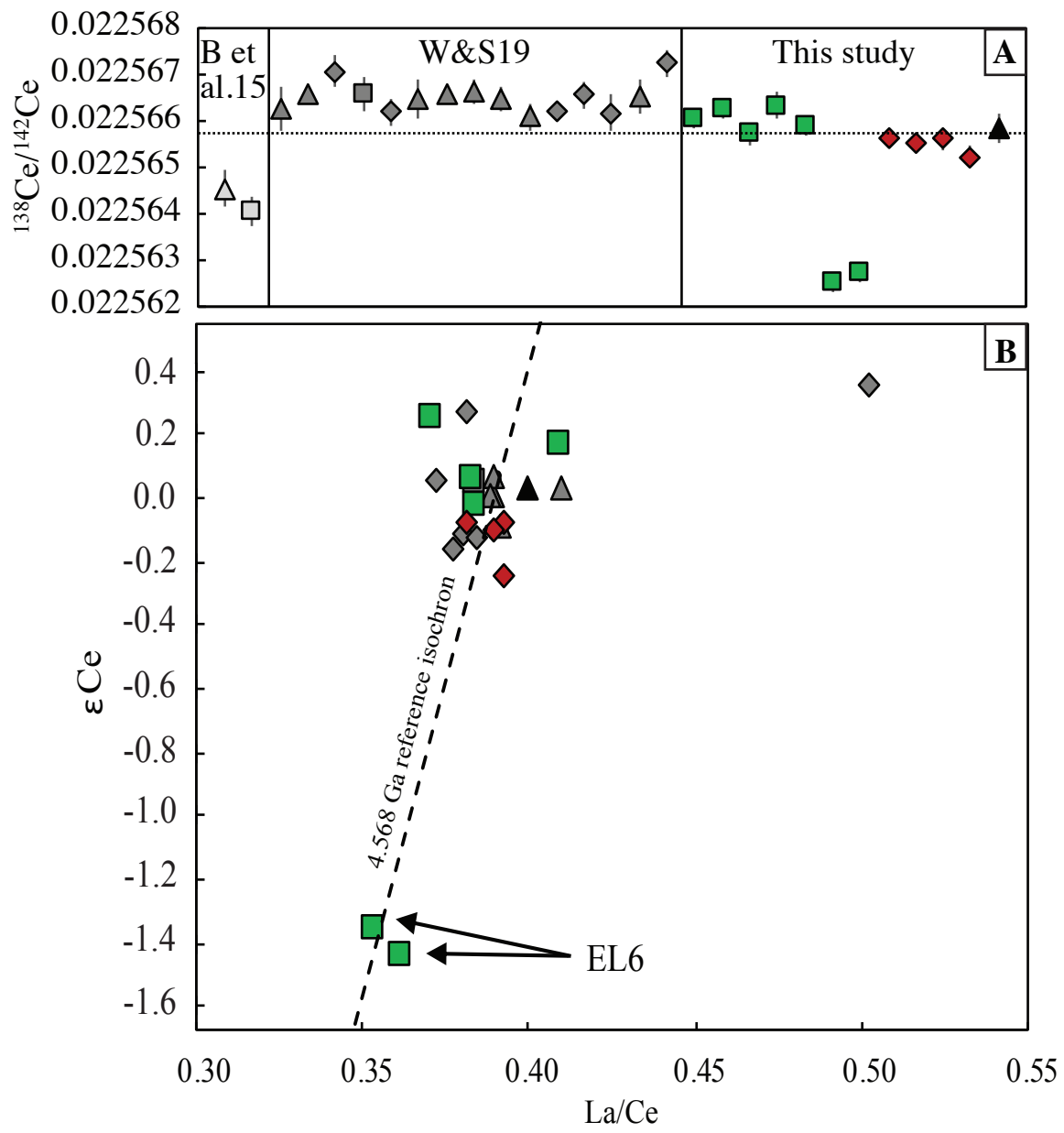


Fig.1

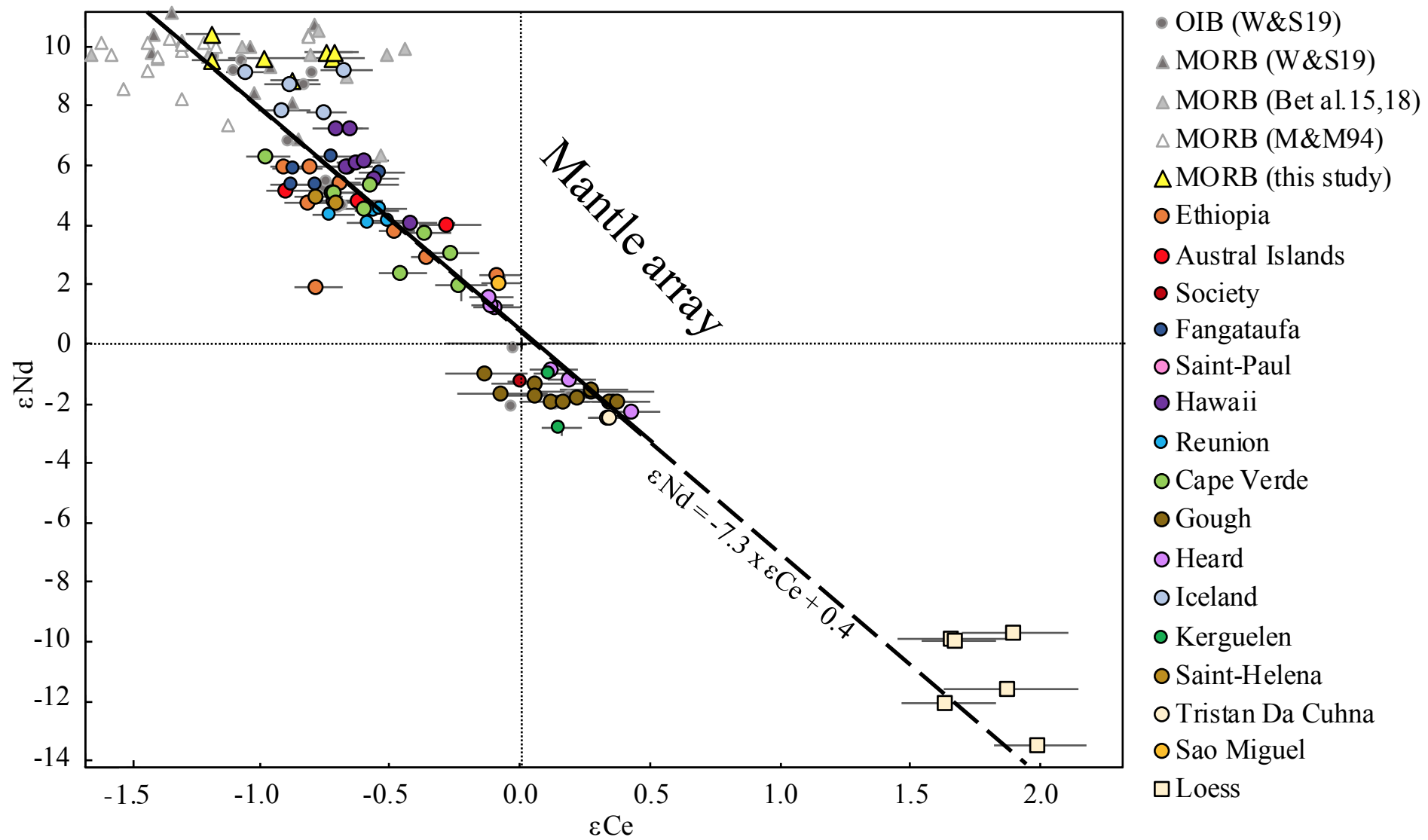


Fig.2

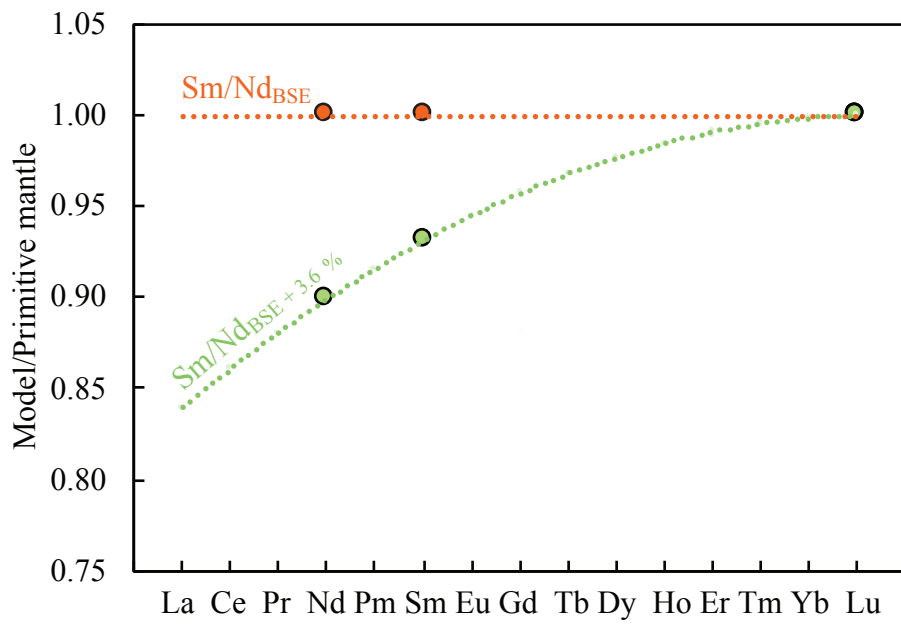


Fig.3

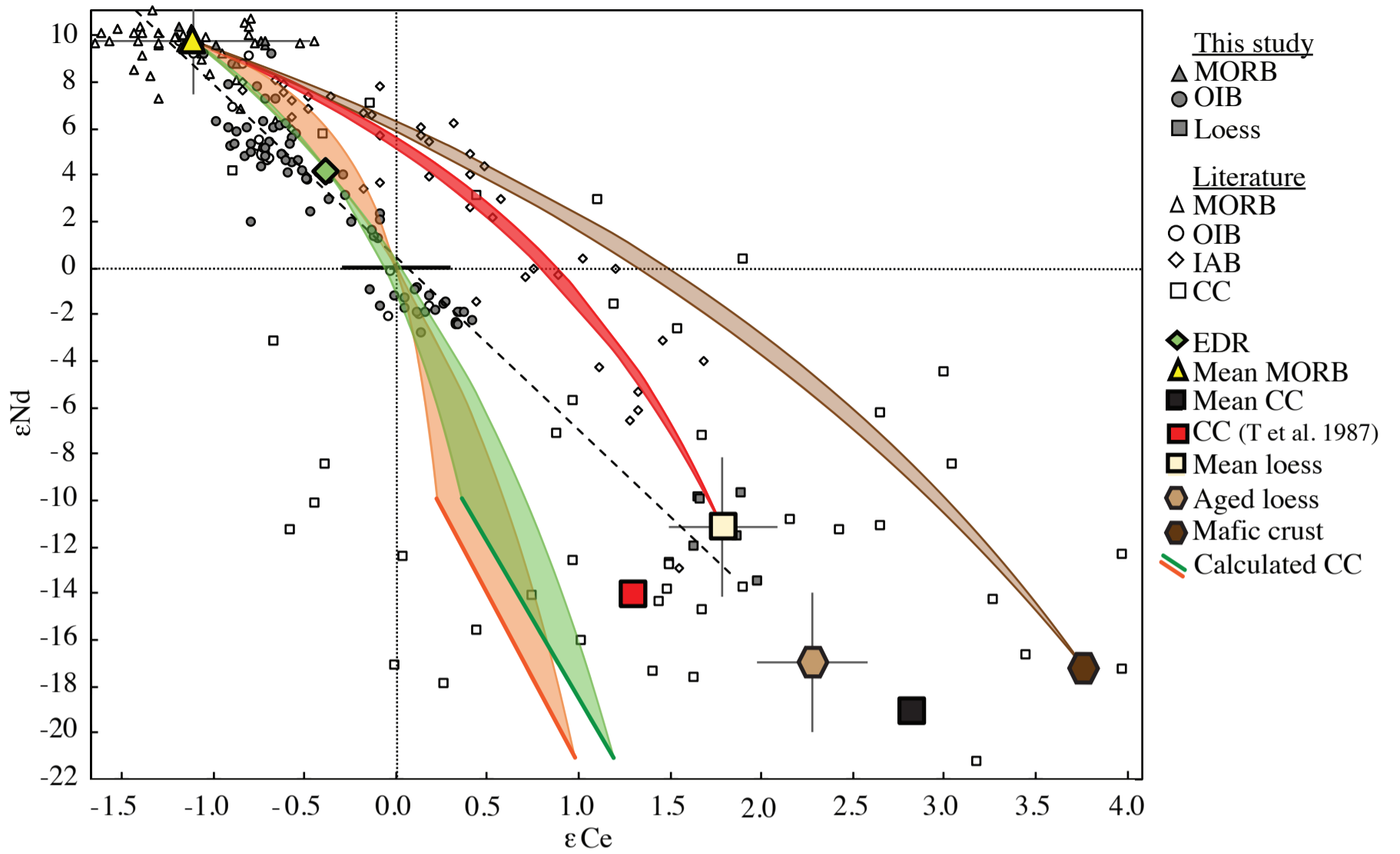


Fig.4

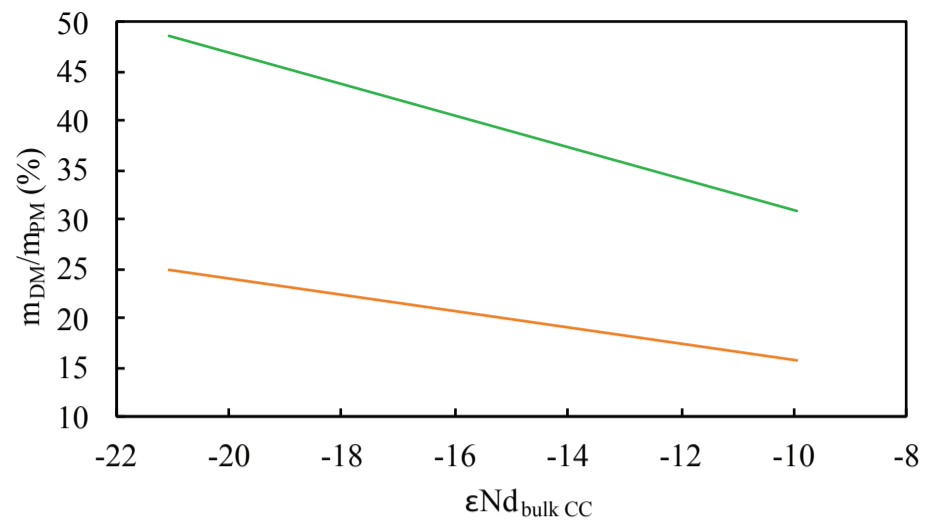


Fig.5

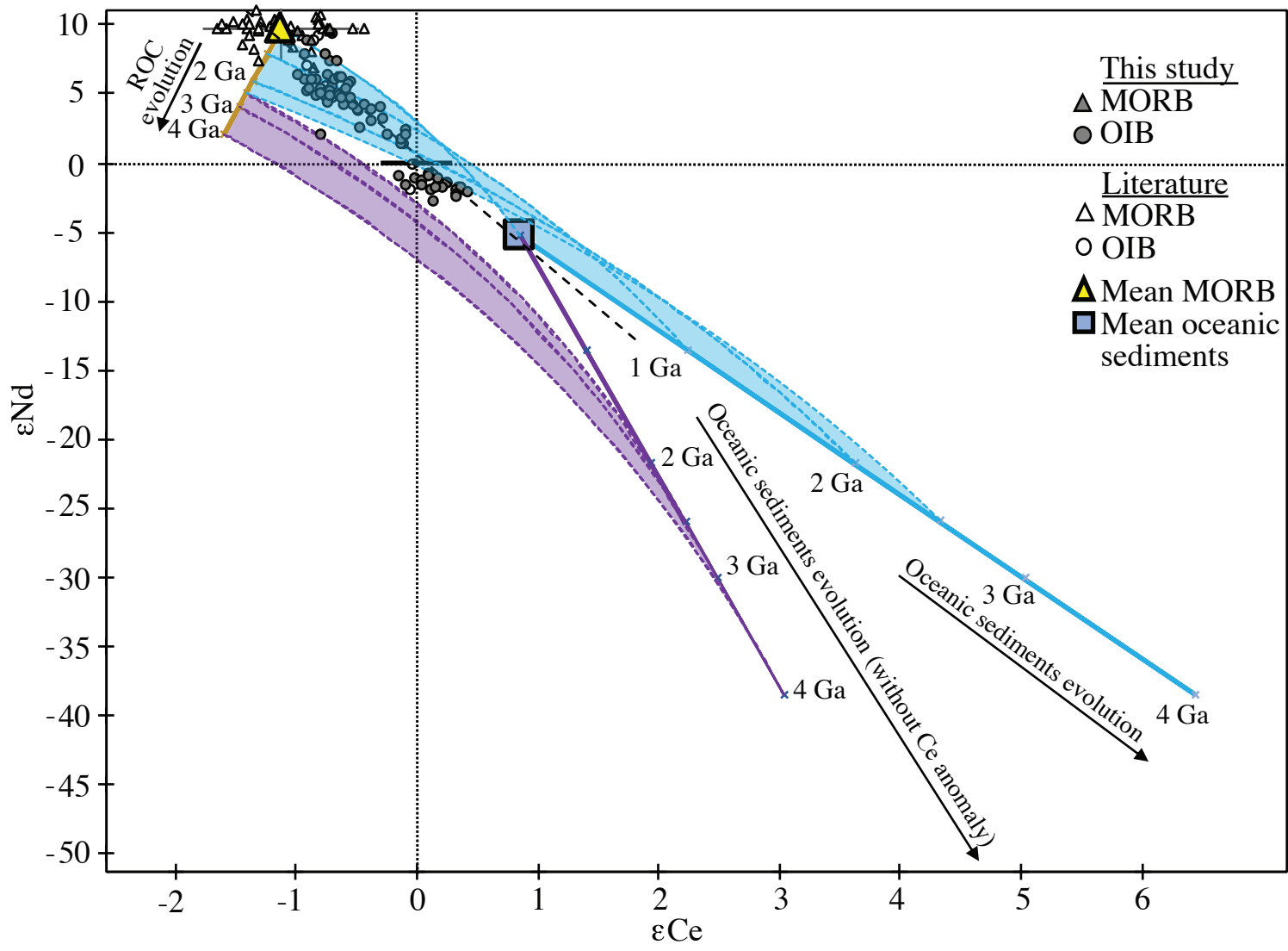


Fig.6

Table 1

| Type | Sample | Location | Volcano | $^{138}\text{Ce}/^{142}\text{Ce}$ | 2se | ϵCe | La/Ce | $^{143}\text{Nd}/^{144}\text{Nd}$ | 2se | ϵNd | Sm/Nd | |
|------------------|--------------------|-----------------|---------------|-----------------------------------|------------|---------------------|-----------|-----------------------------------|----------|---------------------|-------|-------|
| OIB | E38 | Ethiopia | | 0.02256395 | 20 | -0.81 | 0.305 | 0.512935 | 2 | 5.95 | 0.220 | |
| | E39 | | | 0.02256372 | 14 | -0.91 | 0.318 | 0.512936 | 2 | 5.96 | 0.218 | |
| | E95 | | | 0.02256393 | 21 | -0.81 | 0.318 | 0.512871 | 2 | 4.71 | 0.273 | |
| | E156 | | | 0.02256421 | 16 | -0.69 | 0.375 | 0.512907 | 2 | 5.40 | 0.190 | |
| | E202 | | | 0.02256401 | 20 | -0.78 | 0.310 | 0.512728 | 2 | 1.92 | 0.257 | |
| | E266 | | | 0.02256469 | 16 | -0.48 | 0.399 | 0.512824 | 1 | 3.78 | 0.199 | |
| | E268 | | | 0.02256497 | 16 | -0.35 | 0.459 | 0.512779 | 1 | 2.90 | 0.209 | |
| | E271 | | | 0.02256558 | 18 | -0.08 | 0.478 | 0.512746 | 2 | 2.26 | 0.205 | |
| | RRTO 06 | Austral Islands | Rututu | 0.02256437 | 19 | -0.62 | 0.474 | 0.512877 | 2 | 4.81 | 0.208 | |
| | TBA-IH | | Tubuai | 0.02256375 | 20 | -0.89 | 0.355 | 0.512894 | 2 | 5.15 | 0.193 | |
| | MCD201 | | McDonald | 0.02256514 | 27 | -0.28 | 0.145 | 0.512834 | 2 | 3.98 | 0.280 | |
| | 13K | Society | Tahaa | 0.02256578 | 14 | 0.00 | 0.361 | 0.512563 | 2 | -1.30 | 0.261 | |
| | F107 | Tuamotu | | 0.02256382 | 22 | -0.86 | 0.440 | 0.512929 | 2 | 5.83 | 0.236 | |
| | F124 | | | 0.02256379 | 21 | -0.87 | 0.443 | 0.512902 | 2 | 5.30 | 0.219 | |
| | F128 | | Fangataufa | 0.02256456 | 20 | -0.53 | 0.460 | 0.512923 | 1 | 5.73 | 0.239 | |
| | F129 | | | 0.02256415 | 20 | -0.72 | 0.436 | 0.512951 | 2 | 6.25 | 0.229 | |
| | F176 | | | 0.02256400 | 25 | -0.78 | 0.494 | 0.512902 | 2 | 5.31 | 0.210 | |
| | SP1 | St-Paul | | 0.02256416 | 16 | -0.71 | 0.445 | 0.512876 | 2 | 4.79 | 0.251 | |
| | 1804-1 | Hawaii | Loihi | 0.02256428 | 15 | -0.66 | 0.295 | 0.512934 | 1 | 5.94 | 0.249 | |
| | 1804-21 | | | 0.02256427 | 20 | -0.66 | 0.308 | 0.512935 | 2 | 5.96 | 0.240 | |
| | 1804-19 | | | 0.02256435 | 19 | -0.63 | 0.275 | 0.512940 | 1 | 6.04 | 0.247 | |
| | Haw-2000-04 | | Mauna Loa | 0.02256451 | 20 | -0.55 | 0.387 | 0.512913 | 1 | 5.52 | 0.282 | |
| | Haw-2000-19 | | | 0.02256483 | 20 | -0.41 | 0.401 | 0.512838 | 2 | 4.06 | 0.270 | |
| | Haw-2000-13 | | Kohala | 0.02256417 | 22 | -0.71 | 0.417 | 0.512999 | 1 | 7.20 | 0.214 | |
| | Haw-2000-28 | | Kilauea | 0.02256442 | 20 | -0.60 | 0.407 | 0.512944 | 2 | 6.13 | 0.285 | |
| | Haw-2000-17 | | Mauna Kea | 0.02256430 | 15 | -0.65 | 0.414 | 0.513000 | 1 | 7.21 | 0.233 | |
| | 0608-021 | | Reunion | Piton de la | 0.02256414 | 19 | -0.72 | 0.436 | 0.512851 | 2 | 4.32 | 0.236 |
| 80-76 | Fournaise | | | 0.02256463 | 18 | -0.50 | 0.446 | 0.512841 | 2 | 4.11 | 0.229 | |
| 989/036 | | 0.02256450 | | 19 | -0.56 | 0.445 | 0.512859 | 2 | 4.46 | 0.242 | | |
| 986/115 | | 0.02256445 | | 20 | -0.58 | 0.440 | 0.512837 | 2 | 4.03 | 0.230 | | |
| 070406-1 | | 0.02256457 | | 20 | -0.53 | 0.429 | 0.512862 | 2 | 4.53 | 0.250 | | |
| 67a | Cape Verde | Fogo | 0.02256517 | 23 | -0.26 | 0.459 | 0.512786 | 1 | 3.03 | 0.175 | | |
| F10 | | | 0.02256524 | 23 | -0.23 | 0.475 | 0.512730 | 3 | 1.94 | 0.179 | | |
| F16 | | | 0.02256473 | 20 | -0.46 | 0.466 | 0.512752 | 2 | 2.37 | 0.185 | | |
| CY-165 | | | 0.02256448 | 23 | -0.57 | 0.421 | 0.512901 | 1 | 5.30 | 0.186 | | |
| SV-01 | | Sao Vicente | 0.02256415 | 20 | -0.72 | 0.456 | 0.512890 | 1 | 5.08 | 0.191 | | |
| SV-12 | | | 0.02256417 | 22 | -0.71 | 0.479 | 0.512889 | 2 | 5.05 | 0.202 | | |
| S-06 | | Sal | 0.02256442 | 20 | -0.60 | 0.469 | 0.512862 | 2 | 4.53 | 0.214 | | |
| SN-09 | | Sao Nicolau | 0.02256356 | 19 | -0.98 | 0.481 | 0.512952 | 2 | 6.29 | 0.190 | | |
| ST08 | | Santiago | 0.02256495 | 21 | -0.36 | 0.486 | 0.512822 | 1 | 3.74 | 0.200 | | |
| 93(07)77 | | Iceland | Höfud Reidarm | 0.02256424 | 22 | -0.67 | 0.336 | 0.513102 | 1 | 9.20 | 0.188 | |
| 93(07)76 | úli | | 0.02256377 | 24 | -0.88 | 0.359 | 0.513077 | 1 | 8.71 | 0.381 | | |
| 93(07)24 | Asbyrgi | | 0.02256408 | 17 | -0.75 | 0.377 | 0.513027 | 2 | 7.74 | 0.352 | | |
| 93(07)23 | | | 0.02256371 | 22 | -0.91 | 0.372 | 0.513030 | 2 | 7.81 | 0.285 | | |
| 93(07)56 | Langaviti | | 0.02256340 | 20 | -1.05 | 0.350 | 0.513097 | 1 | 9.12 | 0.298 | | |
| ACO 95-3 | Sao Miguel | | 0.02256559 | 17 | -0.08 | 0.479 | 0.512733 | 1 | 2.00 | 0.190 | | |
| BM1962 128 (114) | Tristan Da Cunha | | 0.02256653 | 19 | 0.34 | 0.448 | 0.512503 | 2 | -2.47 | 0.178 | | |
| BM1962 128 (112) | | | 0.02256654 | 18 | 0.34 | 0.489 | 0.512502 | 1 | -2.49 | 0.178 | | |
| BM1965 P5 (8) | St-Helena | | 0.02256401 | 21 | -0.78 | 0.741 | 0.512884 | 2 | 4.95 | 0.201 | | |
| BM1965 P5 (12) | | | 0.02256417 | 18 | -0.71 | 0.433 | 0.512872 | 2 | 4.73 | 0.208 | | |
| 65001 | Heard | | 0.02256604 | 20 | 0.12 | 0.456 | 0.512586 | 2 | -0.87 | 0.203 | | |
| 65151 | | | 0.02256674 | 22 | 0.43 | 0.468 | 0.512512 | 1 | -2.31 | 0.198 | | |
| 65171 | | | 0.02256620 | 21 | 0.19 | 0.545 | 0.512567 | 1 | -1.23 | 0.188 | | |
| 69230 | | | 0.02256555 | 22 | -0.09 | 0.491 | 0.512691 | 3 | 1.19 | 0.184 | | |
| 69244 | | | 0.02256551 | 18 | -0.11 | 0.464 | 0.512697 | 2 | 1.30 | 0.196 | | |
| 69254 | | | 0.02256550 | 20 | -0.12 | 0.463 | 0.512711 | 2 | 1.57 | 0.195 | | |
| LVF-98-107 | | Kerguelen | | 0.02256577 | 23 | 0.00 | | | | | | |
| MPC-99-103 | | | 0.02256611 | 17 | 0.15 | | 0.512484* | 12* | -2.85 | | | |
| RR08-121 | | | 0.02256603 | 17 | 0.12 | | 0.512579* | 2* | -0.99 | | | |
| MORB | Searise-1 DR05-102 | MORB | Pacific Ocean | 0.02256309 | 23 | -1.19 | 0.310 | 0.513164 | 2 | 10.42 | 0.349 | |
| | MD23 Site 4 | | | | 0.02256380 | 21 | -0.87 | 0.289 | 0.513084 | 1 | 8.85 | 0.308 |
| | Clipperton DR01 | | | | 0.02256355 | 33 | -0.98 | 0.343 | 0.513122 | 2 | 9.59 | 0.321 |
| | CY82-0903 | Indian Ocean | | 0.02256310 | 20 | -1.18 | 0.391 | 0.513118 | 1 | 9.52 | 0.278 | |
| | MD34-D3 | | | 0.02256414 | 27 | -0.72 | 0.297 | 0.513122 | 2 | 9.60 | 0.393 | |
| | MD34-D4 | | | 0.02256409 | 22 | -0.74 | 0.372 | 0.513133 | 1 | 9.81 | 0.336 | |
| | MD34-D6 | | | 0.02256416 | 20 | -0.71 | 0.411 | 0.513133 | 1 | 9.81 | 0.305 | |
| Loess | R11 | W Europe | Belgium | 0.02257001 | 59 | 1.88 | | 0.512035* | 9* | -11.61 | | |
| | LO94 | | Svalbard | 0.02257026 | 40 | 1.99 | | 0.511937* | 10* | -13.52 | | |
| | XN-4 | China | Xining | 0.02256952 | 50 | 1.66 | | 0.512120* | 11* | -9.95 | | |
| | Sahara 2900m | Sahara | Alpes, France | 0.02256946 | 41 | 1.64 | | 0.512011* | 7* | -12.07 | | |
| | TJK3198 | Tajikistan | Chashmanigar | 0.02257004 | 46 | 1.89 | | 0.512131* | 8* | -9.73 | | |
| | TJK3165 | | | 0.02256955 | 32 | 1.68 | | 0.512117* | 9* | -10.01 | | |

Table 2

| Sample | Location | Type | $^{138}\text{Ce}/^{142}\text{Ce}$ | 2se | ϵCe | La/Ce |
|---------------|-----------|------------|-----------------------------------|-----|---------------------|-------|
| Sahara 97072 | Sahara | EH3 - Find | 0.02256613 | 21 | 0.16 | 0.410 |
| Sahara 97158 | Sahara | EH3 - Find | 0.02256571 | 24 | -0.02 | 0.385 |
| Oudiyat Sbaa | W Sahara | EH5 - Fall | 0.02256633 | 26 | 0.25 | 0.371 |
| Adrar Bous | Niger | EL5 - Find | 0.02256591 | 21 | 0.06 | 0.384 |
| Yilmia | Australia | EL6 - Find | 0.02256251 | 20 | -1.44 | 0.362 |
| Pillistfer | Estonia | EL6 - Fall | 0.02256272 | 20 | -1.35 | 0.354 |
| Agen | France | H5 - Find | 0.02256561 | 21 | -0.07 | 0.393 |
| NWA 8007 | Morocco | L3 - Find | 0.02256554 | 20 | -0.10 | 0.389 |
| NWA 10854 | NW Africa | L3 - Find | 0.02256560 | 23 | -0.07 | 0.382 |
| Saint-Severin | France | LL6 - Fall | 0.02256522 | 23 | -0.24 | 0.392 |
| Allende | Mexico | CV3 - Fall | 0.02256585 | 32 | 0.20 | 0.400 |

Table 3

| | Chondritic BSE | EDR | DMM | CC | UCC (1.8 Ga) | UCC (2.2 Ga) | Mafic crust (4.3 Ga) |
|--|-----------------------|------------|------------------|-----------|---------------------|---------------------|-----------------------------|
| Ce (μg/g) | 1.0-1.7 | | | 43 | 68 | 68 | 11.2 |
| Nd (μg/g) | 0.8-1.3 | | | 20 | 29 | 29 | 5.9 |
| Ce/Nd | 1.28 | 1.22 | | 2.15 | 2.33 | 2.33 | 1.9 |
| ¹³⁸Ce/¹⁴²Ce | 0.02256577 ± 66 | 0.02256492 | 0.02256325 ± 145 | | 0.02256981 ± 68 | 0.02257091 | 0.0225743 |
| εCe | 0.00 ± 0.29 | -0.4 | -1.1 ± 0.6 | | 1.8 ± 0.3 | 2.3 | 3.8 |
| ¹⁴³Nd/¹⁴⁴Nd | 0.512630 ± 11 | 0.512842 | 0.513129 ± 116 | | 0.512059 ± 155 | 0.511759 | 0.511745 |
| εNd | 0.00 ± 0.21 | 4.1 | 9.7 ± 2.3 | | -11.2 ± 3.0 | -17 | -17.3 |

Supplementary material

Formation of the Ce-Nd mantle array: crustal extraction vs. recycling by subduction

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Supplementary 1.

Trace element patterns and Ce anomalies

1. Trace element patterns

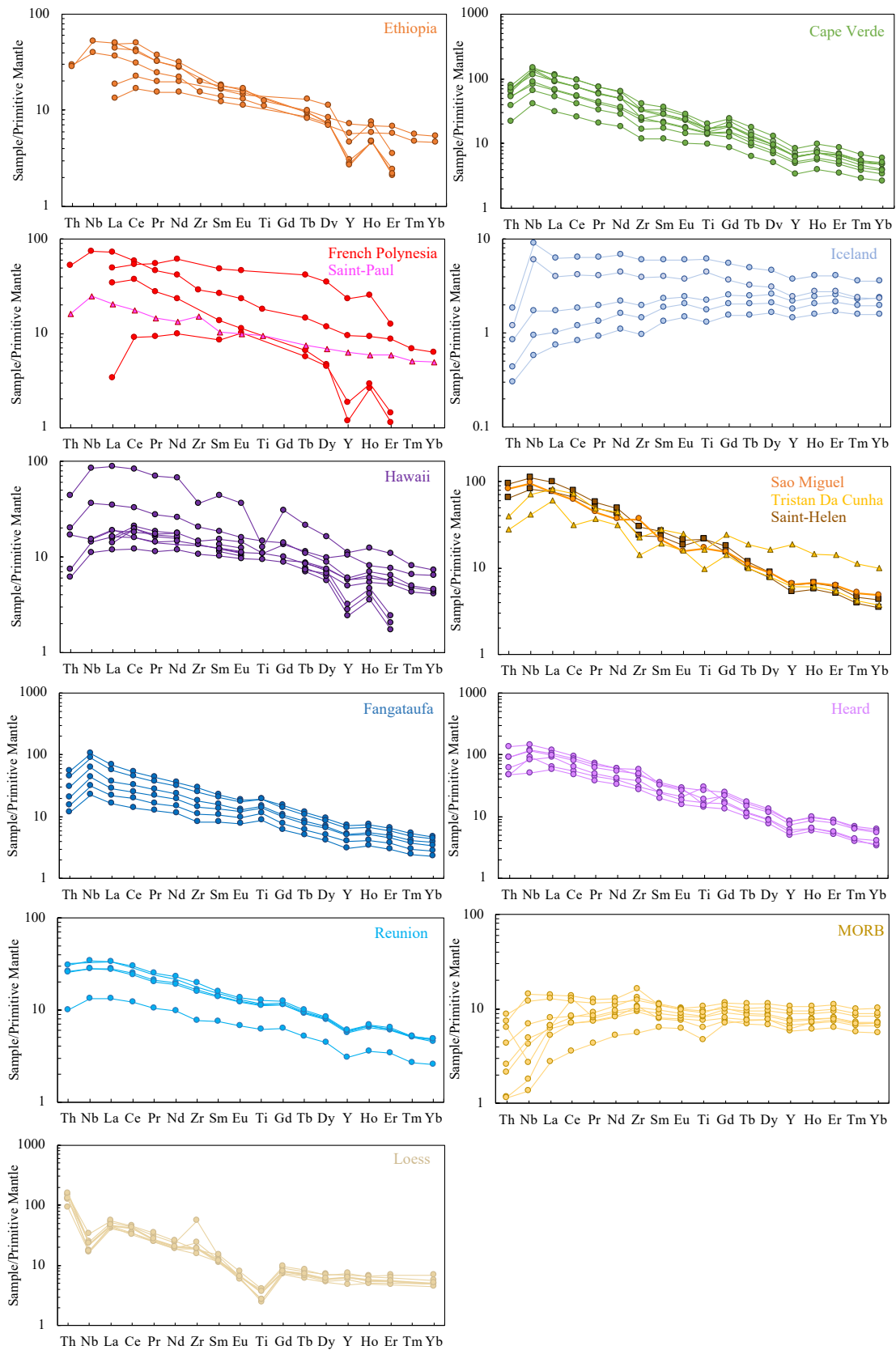


Fig. S1. Trace element patterns of OIBs, MORBs, and loesses. Concentrations are normalised to primitive mantle values (Sun and McDonough, 1989).

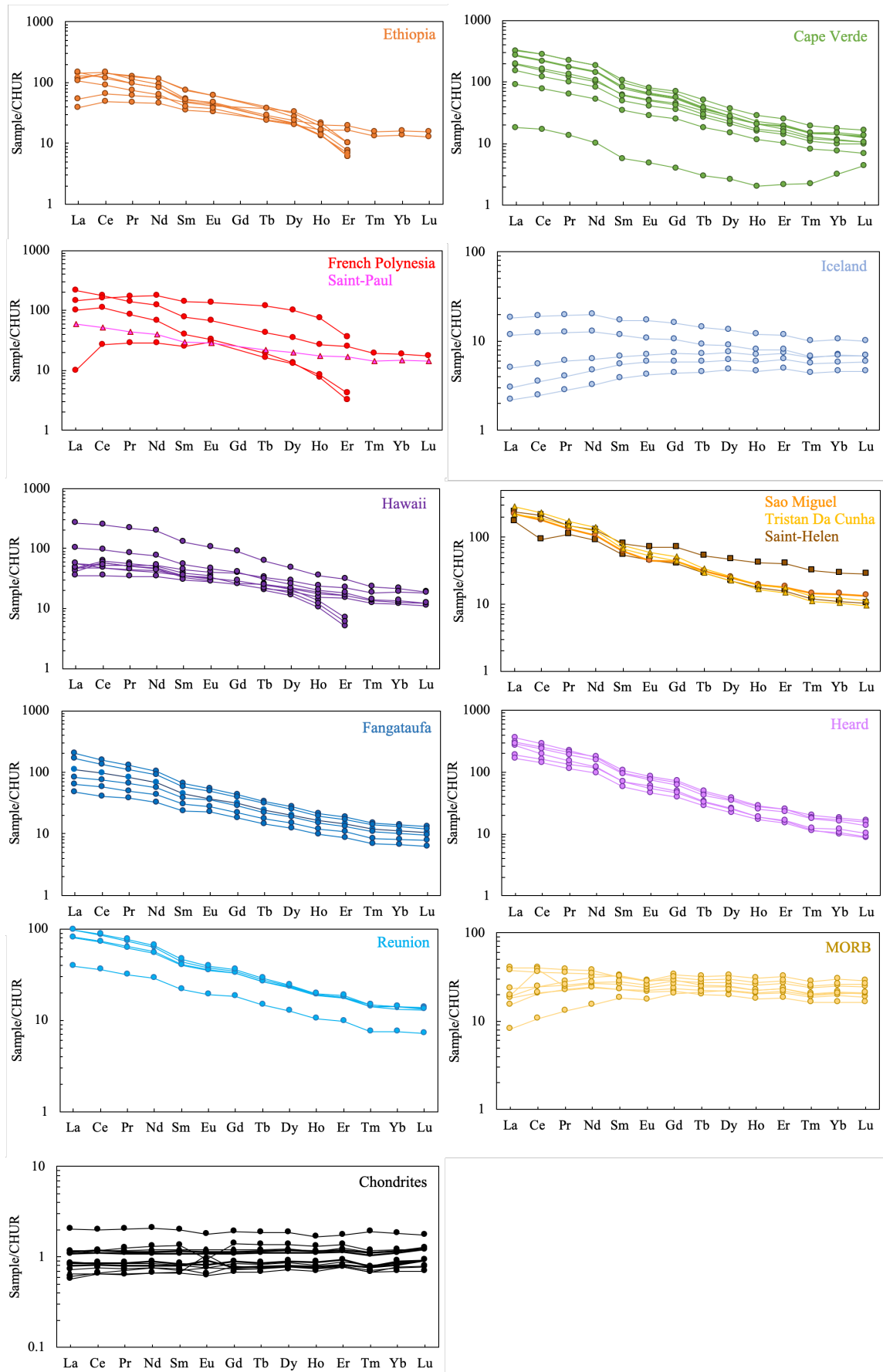


Fig S2. Rare earth element patterns of OIBs, MORBs, and chondrites. Concentrations are normalised to CI chondrite values (Barrat et al., 2012).

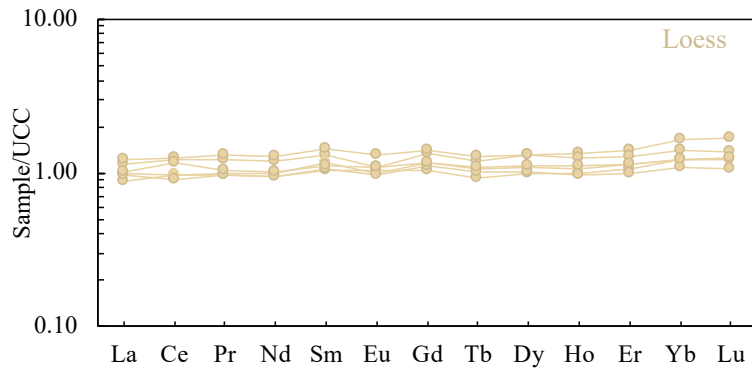


Fig. S3. Rare earth element patterns of loess samples. Concentrations are normalised to the upper continental crust (Rudnick and Gao, 2003).

2. Ce isotopic ratios as a function of elemental Ce anomalies

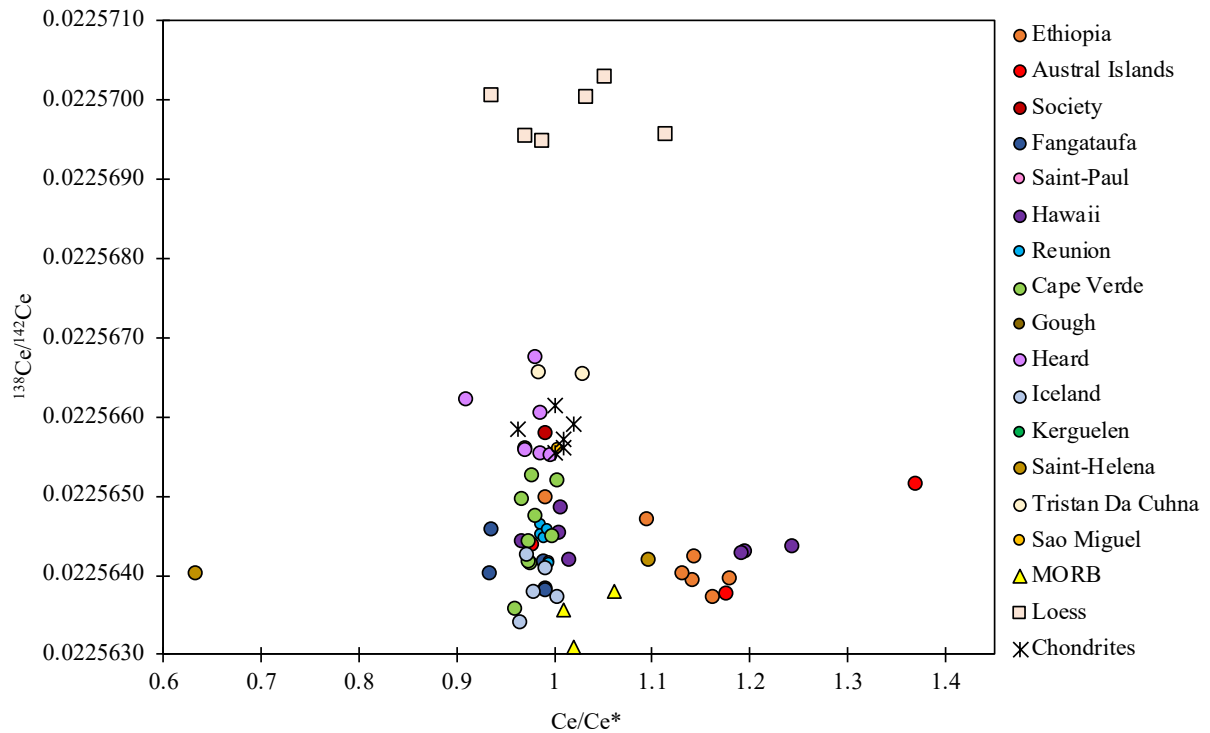


Fig. S4. $^{138}\text{Ce}/^{142}\text{Ce}$ vs Ce/Ce^* diagram for terrestrial samples analysed in this study. Ce/Ce^* represents the elemental Ce anomaly relative to the neighbouring REEs as $\frac{\text{Ce}}{\text{Ce}^*} = \frac{\text{Ce}_N}{\frac{1}{2}\text{La}_N + \frac{1}{2}\text{Pr}_N}$, where a_N , Ce_N , and Pr_N are the La, Ce, and Pr concentrations normalised to CI chondrite (Barrat et al., 2012). One sample from the Saint-Helena hotspot has a large negative Ce anomaly ($\text{Ce}/\text{Ce}^* = 0.64$), but its Ce isotopic composition is similar to that of other samples from the same location. This anomaly probably reflects the late alteration of the rock. Some samples from Ethiopia, Hawaii, and French Polynesia have significant positive anomalies. These anomalies reflect depletion in La (Fig. S2), and are not correlated with Ce isotopic ratios.

Supplementary 2. Literature $^{138}\text{Ce}/^{142}\text{Ce}$ ratios and data normalisation: example with MORB

We prefer to use the epsilon notation when comparing data from the literature. The most rigorous method for comparison is the use of CHUR values measured under the same analytical conditions (i.e., mass spectrometer, cup configuration, analytical protocol, etc.). This choice results from the difficulty in normalising data acquired with distinct protocols. In Fig. S5, we highlight the bias observed when comparing MORB samples from different studies (Bellot et al., 2015, 2018; Willig and Stracke, 2019) normalised using either BCR-2 or Ce_{AMES} . Isotopic compositions vary by up to 10 ppm for data from Willig and Stracke (2019) and by up to 20 ppm for data from Bellot et al. (2015, 2018).

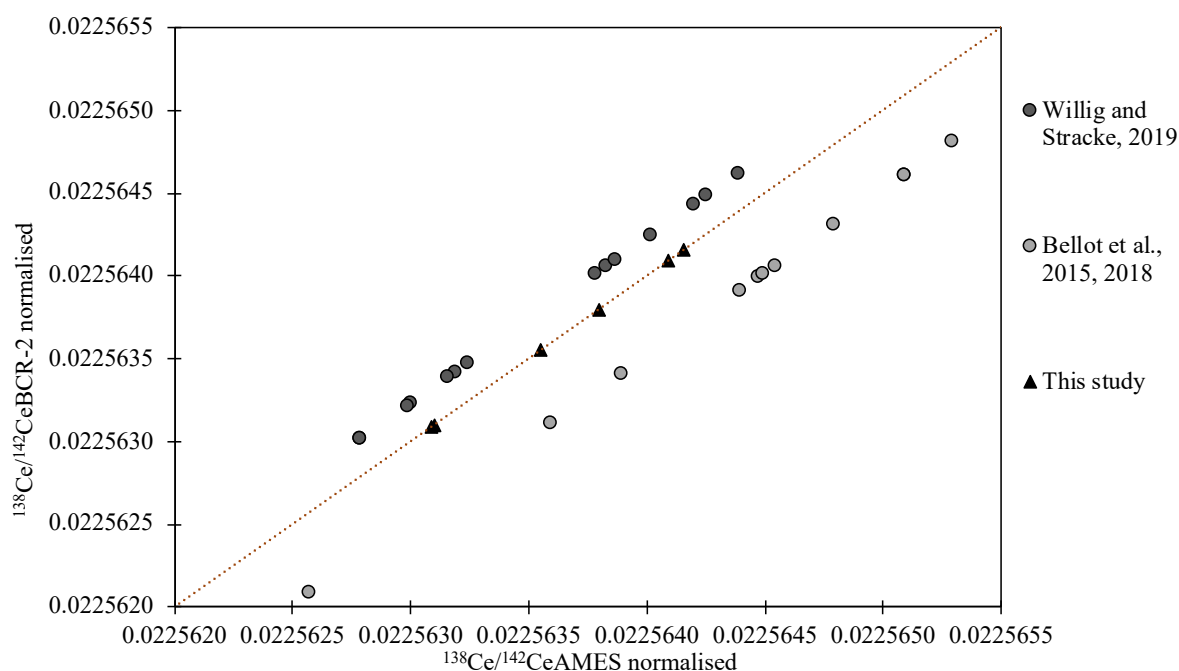


Fig. S5. Ce isotopic compositions of MORB samples from the literature normalised either to BCR-2 or to Ce_{AMES} and compared to data from this study. The dotted line indicates the 1-1 correspondence line.

Supplementary 3.
 $^{138}\text{Ce}/^{142}\text{Ce}$ ratios of crustal samples from literature

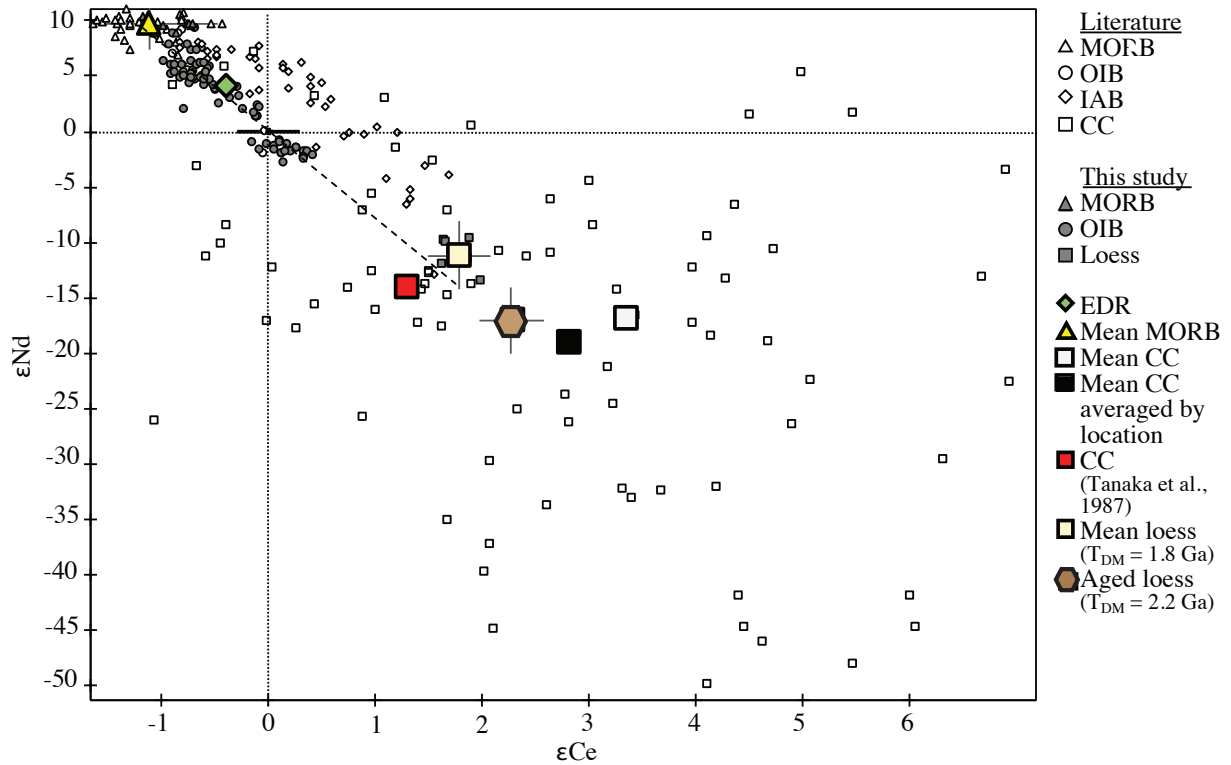


Fig. S6. $^{143}\text{Nd}/^{144}\text{Nd}$ vs $^{138}\text{Ce}/^{142}\text{Ce}$ ratios measured in mantle-derived samples (see Fig. 2) and continental crust samples (Dickin et al., 1987; Gao et al., 2016; Hayashi et al., 2004; Lee et al., 2001, 2010; Liu et al., 1990; Masuda et al., 1988; Minami et al., 1995; Shimizu et al., 1988, 1990, 1996; Tanaka et al., 1987; Tazoe et al., 2007). Large symbols represent reservoirs (as in Fig. 6). Note that the red square is the continental crust proposed by Tanaka et al. (1987). The black square is the mean value of all literature continental crust samples represented here ($n = 94$), and the open square is the mean continental crust value when samples are averaged by location ($n = 16$).

Supplementary 4. Mass-balance DMM-CC mixing calculations

Our single-stage differentiation model considers the continental crust (CC) and the depleted MORB mantle (DMM) to be complementary reservoirs developed from the primitive mantle (BSE).

The Nd sialic index (W_{Nd}) is defined as the amount of Nd in the continental crust relative to the total amount of Nd in the BSE (Allègre and Lewin, 1989). Its value can be obtained from the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the BSE, DMM, and CC as:

$$\frac{^{143}\text{Nd}}{^{144}\text{Nd}_{BSE}} = W_{Nd} \times \frac{^{143}\text{Nd}}{^{144}\text{Nd}_{CC}} + (1 - W_{Nd}) \times \frac{^{143}\text{Nd}}{^{144}\text{Nd}_{DMM}}. \quad (1)$$

The Nd sialic index can also be approximated as the product of the mass fraction of continental crust (W , relative to the BSE) and the ratio of the Nd contents in the continental crust and BSE as:

$$W_{Nd} = W \times \frac{[\text{Nd}]_{CC}}{[\text{Nd}]_{BSE}} \quad \text{where } W = \frac{m_{CC}}{m_{CC} + m_{DMM}}. \quad (2)$$

Using W as obtained above, the Ce sialic index (W_{Ce}) and the Ce isotopic composition of the continental crust can be deduced from equations similar to equations (1) and (2):

$$W_{Ce} = W \times \frac{[\text{Ce}]_{CC}}{[\text{Ce}]_{BSE}}, \quad (4)$$

$$\frac{^{138}\text{Ce}}{^{142}\text{Ce}_{BSE}} = W_{Ce} \times \frac{^{138}\text{Ce}}{^{142}\text{Ce}_{CC}} + (1 - W_{Ce}) \times \frac{^{138}\text{Ce}}{^{142}\text{Ce}_{DMM}}. \quad (3)$$

The mass fraction of continental crust W also allows us to recalculate the complementary Nd and Ce contents of the DMM using mass-balance equations for the trace element concentrations:

$$[\text{Nd}]_{BSE} = W \times [\text{Nd}]_{CC} + (1 - W) \times [\text{Nd}]_{DMM}, \quad (5)$$

$$[\text{Ce}]_{BSE} = W \times [\text{Ce}]_{CC} + (1 - W) \times [\text{Ce}]_{DMM}. \quad (6)$$

To maintain a consistent dataset between isotopic and elemental ratios, the Ce and Nd concentrations of the DMM are recalculated using the BSE and CC contents and the mass fraction of DMM determined in step 2 (= 1 – mass fraction of CC). The Ce/Nd ratio is set to 1.28 for a chondritic BSE and to 1.22 for the EDR model. So that the Lu value chosen to anchor the REE pattern of the BSE has no consequence on the final ϵCe value. Using the Lu contents proposed by Lyubetskaya and Korenaga (2007), Allègre et al. (2001), and Palme and O'Neill (2014) gives uncertainties of ± 0.3 ppm on the Ce and Nd contents of the DMM. Corresponding DMM Ce and Nd concentrations are 0.1–1.0 and 0.6–1.0 ppm, respectively, in the chondritic case and 0.6–1.1 and 0.8–1.0 ppm, respectively, in the EDR model. We obtained restricted ϵNd_{CC} ranges of –13 to –21 (CHUR) and –10 to –12 (EDR) that are similar within errors to the values proposed by Salters and Stracke (2004) and Workman and Hart (2005).

Supplementary 5. Recycling models

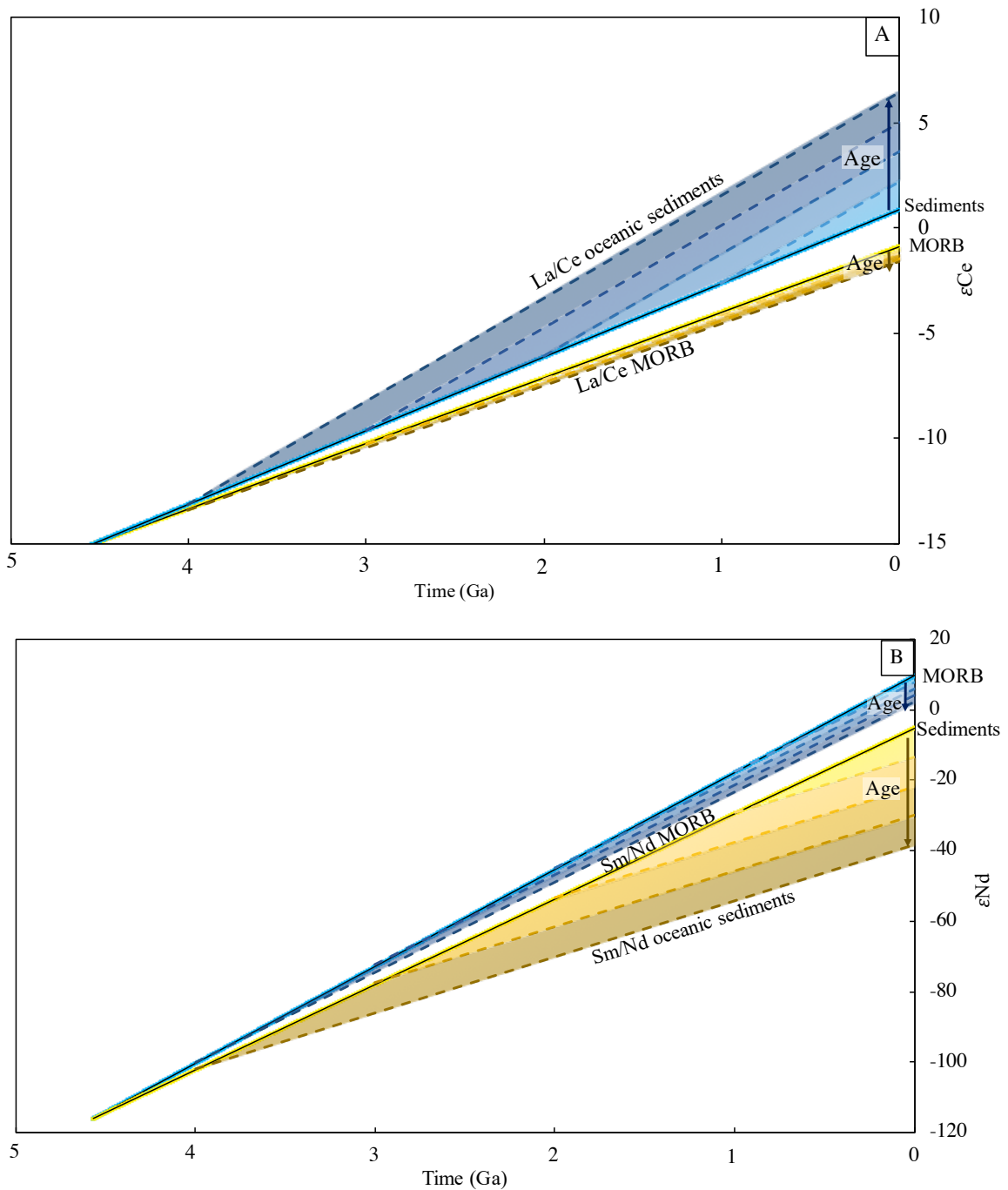


Fig. S7. Evolution models used to calculate the present (A) ϵ_{Nd} and (B) ϵ_{Ce} isotopic compositions of recycled MORBs (yellow) and oceanic sediments (blue) for ages of formation between 4 and 1 Ga. Solid lines connect the present-day isotopic compositions of MORBs and oceanic sediments to the initial CHUR ratio, and dashed lines represent their isotopic evolution since the reservoir formation times. MORBs are characterised by $\text{La}/\text{Ce}_{\text{MORB}} = 0.34$ and $\text{Sm}/\text{Nd}_{\text{MORB}} = 0.33$ (this study). Oceanic sediments formed after the Great Oxygenation Event are characterised by $\text{La}/\text{Ce}_{\text{OS}} = 0.57$ and $\text{Sm}/\text{Nd}_{\text{OS}} = 0.20$ (data from Bellot et al., 2015, 2018), and those that formed earlier are assumed to have $\text{La}/\text{Ce}_{\text{OS}} = 0.47$ (after Ce anomaly correction). MORB and oceanic sediments sources have constant chemical ratios extrapolated from the evolution of an initial chondritic reservoir until present-day composition. MORB source has $\text{La}/\text{Ce}_{\text{MORB source}} = 0.36$ and $\text{Sm}/\text{Nd}_{\text{MORB source}} = 0.35$. Oceanic sediments source has $\text{La}/\text{Ce}_{\text{sediments source}} = 0.41$ and $\text{Sm}/\text{Nd}_{\text{MORB source}} = 0.31$. Figure modified after Chauvel et al. (2008).

| | ROC (MORB) | MORB source | Oceanic sediments | Oceanic sediments (Pre-GOE) | Oceanic sediment source |
|--|------------------|-------------|-------------------|-----------------------------|-------------------------|
| La (μg/g) | 5 ± 5 | | 18 ± 9 | 18 ± 9 | |
| Ce (μg/g) | 15 ± 12 | | 33 ± 25 | 38 ± 22 | |
| La/Ce | 0.34 ± 0.10 | 0.36 | 0.57 ± 0.25 | 0.47 ± 0.05 | 0.41 |
| ¹³⁸Ce/¹⁴²Ce | 0.02256325 ± 145 | | 0.02256771 ± 310 | 0.02256771 ± 310 | |
| εCe | -1.1 ± 0.6 | | 0.9 ± 1.4 | 0.9 ± 1.4 | |
| Nd (μg/g) | 13 ± 7 | | 18 ± 13 | 18 ± 13 | |
| Sm (μg/g) | 4 ± 2 | | 4 ± 3 | 4 ± 3 | |
| Nd/Sm | 0.34 ± 0.07 | 0.38 | 0.20 ± 0.03 | 0.20 ± 0.03 | 0.19 |
| ¹⁴³Nd/¹⁴⁴Nd | 0.513129 ± 116 | | 0.512360 ± 653 | 0.512360 ± 653 | |
| εNd | 9.7 ± 2.3 | | -5.3 ± 12.7 | -5.3 ± 12.7 | |

Table S1: La, Ce, Sm and Nd contents, La/Ce and Sm/Nd ratios and Ce and Nd isotopic compositions of terrestrial reservoirs used in recycling models (Fig. 5 and Fig. S7). ROC, recycled oceanic crust; DMM, depleted MORB mantle; GOE, great oxygenation event. ROC and oceanic sediments isotopic and chemical compositions are based on measurements (MORB: this study, [Bellot et al., 2015, 2018](#), [Makishima and Masuda, 1994](#) and [Willig and Stracke, 2019](#); oceanic sediments: [Bellot et al., 2015, 2018](#)). ROC and oceanic sediments sources have constant chemical ratios extrapolated from the evolution of an initial chondritic reservoir until present-day isotopic compositions measured in MORB and oceanic sediments. Pre-GOE oceanic sediments La/Ce ratio and Ce contents are corrected from Ce anomaly.

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