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1 **First Ce-Nd isotope measurements of middle and lower**
2 **continental crust samples support massive lower crust recycling**
3 **over Earth's history**

4

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32 ABSTRACT

33 Long-lived radioactive isotopes provide valuable information on the evolution of
34 Earth's geological reservoirs. Coupled measurements of the ^{138}La - ^{138}Ce and ^{147}Sm -
35 ^{143}Nd systems have attracted much interest, but some critical reservoirs, such as the
36 deep continental crust, have yet to be investigated. To address this gap, we report Ce-
37 Nd isotope measurements of 35 crustal samples from Canada, western Europe, and
38 Siberia, with Archean to Phanerozoic ages. Most samples from western Europe and
39 Siberia are interpreted to represent the deepest continental crust because of low SiO_2
40 content (<55 wt.%) and generally mafic compositions. In contrast, Precambrian
41 composites from the Canadian shield have highly felsic compositions (61–71 wt.%
42 SiO_2) and represent the old upper continental crust. Xenoliths from the Massif Central
43 (France) and samples from uplifted massifs in the Ivrea-Verbano zone (Italy) plot on
44 the Ce-Nd mantle array. Precambrian Canadian composites and xenoliths from
45 Udachnaya (Siberian Craton) plot to the left of the mantle array, with the Siberian
46 samples farthest from the array. The La-Ce system yields a ca. 1.8 Ga age for the
47 Siberian xenoliths, distinct from the ca. 2.7 Ga Sm-Nd errorchron age. The La-Ce
48 system was most likely reset during a large-scale episode of delamination and
49 rejuvenation of the Archean lower lithosphere established in Siberia. A change in the
50 La/Ce ratio during this event explains an increasing deviation with time of the Ce-Nd
51 isotopic composition of the Siberian deep crust from the mantle array. We introduce a
52 new parameter (θ) to quantify the likelihood of any rock evolving away from the mantle
53 array. It represents the angle between the evolution vector of a sample and the mantle
54 array, and it is calculated from measured La/Ce and Sm/Nd ratios. Samples that plot to
55 the right of the mantle array have $\theta > 0$, whereas samples that plot to the left of the
56 mantle array have $\theta < 0$. The angle θ was used to compare our samples to a worldwide

57 granulite compilation (1581 samples) because it is independent of the age and the initial
58 isotopic composition of the samples. The majority of lower crust rocks have negative
59 θ , suggesting they are prone to evolve to the left of the mantle array, but to a lesser
60 extent than the Siberian samples that are characterized by the most negative θ values.
61 Thus, the Siberian samples with the most unusual Ce-Nd isotopic compositions are the
62 only group to plot close to the deep crust end-member calculated from classical mass-
63 balance budget of the bulk silicate Earth. These results suggest that the lower crust
64 sampled by Siberian xenoliths is only a minor component in the terrestrial deep crust.
65 We use this database to estimate new parent/daughter ratios for the lower continental
66 crust: $^{138}\text{La}/^{142}\text{Ce} = 0.00380 \pm 0.00007$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.128 \pm 0.007$. Measurements
67 and models are finally reconciled when considering massive recycling of lower
68 continental crust through Earth's history, totaling 3 to 4 present-day, continental crust
69 masses.

70

71

72 KEYWORDS

73 Rare earth elements, ^{138}La - ^{138}Ce , ^{147}Sm - ^{143}Nd , lower continental crust recycling.

74

75

76 1. Introduction

77

78 The continental crust (CC) is a low-mass reservoir accounting for a large share of the
79 highly incompatible elements in the silicate Earth. This share increases with greater
80 incompatibility (preferential partitioning to the melt during magmatic processes) so that
81 the CC concentrates 6 to 25% of the light rare earth elements (LREE: La to Nd) of the

82 bulk silicate Earth (BSE – using REE values from McDonough and Sun, 1995 and
83 Rudnick and Gao, 2014). The upper continental crust (UCC) is the most accessible
84 layer of the continental crust, and its average composition of refractory elements is
85 essentially inferred from fine sediments such as loess and diamictites that sample large
86 areas (McLennan, 2001). The REE compositions in these sediments reflect those of
87 their sources because mechanical weathering has a negligible effect on these elements
88 (Chauvel et al., 2014; Taylor and McLennan, 1981). While representing 70 wt.% of the
89 total CC, the middle and lower continental crust (MCC and LCC) is much less
90 characterized than the UCC. In particular, very few LCC sections are exposed
91 tectonically, and LCC samples are mostly xenoliths in volcanic rocks and have
92 essentially mafic compositions (<53 wt.% SiO₂). Most LCC samples are affected by
93 granulite-facies metamorphism (±pyroxene, ±plagioclase feldspar, ±garnet, ±oxides)
94 occurring at high-pressure – high-temperature conditions in the deep crust. The
95 compositions of these deep crust reservoirs were estimated from mid-crustal rocks (e.g.,
96 MCC exposed in China – Gao et al., 1998), granulites exposed at the surface, and
97 xenoliths (Bohlen and Mezger, 1989; Downes, 1993; Rudnick, 1992) together with
98 geophysical constraints (Weaver and Tarney, 1984; and references therein). However,
99 the heterogeneous nature of the deep CC has made it challenging to determine its
100 average composition with certainty. The estimates vary between studies but all seem to
101 agree on a more mafic composition for LCC than for MCC (Hacker et al. 2015; Rudnick
102 and Gao, 2014).

103 This study provides the first measurements of the ¹³⁸La-¹³⁸Ce ($T_{1/2} = 292.5$ Ga –
104 Tanimizu, 2000) and ¹⁴⁷Sm-¹⁴³Nd isotope systems ($T_{1/2} = 106$ Ga – Begemann et al.,
105 2001) in deep crustal rocks. During melt extraction from the mantle, melting residues
106 have lower La/Ce and higher Sm/Nd ratios than the melt because Sm and Ce are more

107 compatible than Nd and La, respectively (Hofmann, 1988). As a result, magmas
108 extracted from initially melt-depleted reservoirs define a negative correlation in the
109 ^{138}Ce - ^{143}Nd isotopic space. The “ ϵCe - ϵNd mantle array” has been precisely defined
110 using a large number of isotope measurements of mid-ocean ridge basalts (MORB) and
111 ocean island basalts (OIB – Israel et al., 2020; Willig and Stracke, 2019; Willig et al.,
112 2020). The Ce-Nd isotopic composition of the UCC was defined from loess
113 measurements in a previous study (Israel et al., 2020). Because the UCC plots on the
114 ϵCe - ϵNd mantle array, the deep crust end-member calculated from mass-balance
115 calculations in previous studies has negative ϵCe - ϵNd values (Israel et al., 2020; Willig
116 and Stracke 2019; Willig et al., 2020). Like many studies that attempted to characterize
117 large-scale reservoirs, they mainly base their assumptions on trace element
118 compositions of these reservoirs reported in review studies. This approach is however
119 biased due to large uncertainties on the mean concentrations and the absence of isotopic
120 constraints. To address this, we explore the Ce-Nd isotopic composition of the deep
121 continental crust by analyzing 35 middle to lower continental crust samples from three
122 localities: (1) xenoliths of Permo-Triassic rocks in basaltic breccias from Neogene
123 maars in Massif Central, France; (2) uplifted deep Permian crust from the Ivrea-
124 Verbano zone, Italy, and (3) Neoproterozoic to Paleoproterozoic xenoliths from the
125 Devonian Udachnaya kimberlite in the central Siberian craton, Russia. Our UCC
126 dataset is complemented by new analyses of Precambrian composites from the
127 Canadian shield. Our data are compared to a large dataset of REE contents in worldwide
128 granulites to evaluate their significance in the lower crust budget. In particular, we
129 investigate the distribution of $^{138}\text{La}/^{142}\text{Ce}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios in lower crust samples
130 and their impact on the isotope evolution of the lower crust. The study of ^{138}La - ^{138}Ce
131 and ^{147}Sm - ^{143}Nd isotopic systems in the deep crustal rocks offers a new perspective on

132 the REE composition of the continental crust. It brings new information to re-evaluate
133 the long-term evolution of the continental crust.

134

135

136 **2. Samples and methods**

137 2.1. Geological context and sample description

138 *Ivrea Verbano Zone, Italy*

139 The five samples from the Ivrea-Verbano zone (IVZ – Alps) in northwestern Italy are
140 the only samples in our set from tectonically exhumed deep crust (see Fig. 1 in Quick
141 et al., 2003). They sample two major local lower crust units: the Kinzigite Formation
142 (amphibolite to granulite-facies paragneiss) and the Basic Formation (mafic complex
143 and lenses of mantle peridotite). The mafic complex results from underplating on, and
144 intrusions of mafic magmas into, the base of the pre-existing crust (Quick et al., 1994;
145 Voshage et al., 1990 – main magmatic phase dated at 288 Ma by U-Pb dating on zircons
146 and monazites – Peressini et al., 2007; Voshage et al., 1990). It caused a perturbation
147 of deep crust geotherms which delayed the Sm-Nd closure age by about 18 Ma (270
148 Ma in garnet-free mafic rocks – Downes, 1993). The magmatism favored the intra-
149 crustal differentiation and drove metamorphic events in the lower crust (granulite and
150 amphibolite facies) to upper crust conditions (greenschist facies - Schuster and Stüwe,
151 2008). Vertical uplift, crustal thinning, and lithosphere wedging during the Alpine
152 collision (from late Paleozoic to early Mesozoic) are responsible for the ascent of the
153 LCC to the surface (Handy et al., 1999) and for multiple high-temperature events that
154 affected the MCC to LCC. The IVZ records a long-lasting, 300 Ma tectonic,
155 metamorphic, and magmatic history that preserves its igneous structure (Langone et al.,
156 2018; Peressini et al., 2007).

157 The rocks in this study are metabasite (IV1 – plagioclase-hornblende-clinopyroxene-
158 orthopyroxene), granulite-facies layered charnockite (IV5 – plagioclase-garnet-quartz-
159 hornblende), granulite-facies migmatite (IV9 – biotite-sillimanite-garnet-quartz) and
160 metapelite (IV10 – garnet-sillimanite-biotite). They have been affected by medium to
161 high-grade metamorphism and deformation.

162

163 *French Massif Central, France*

164 Three xenoliths from Bournac and eight xenoliths from Beaunit were analyzed during
165 the course of this study (Eastern French Massif Central – FMC – see Fig. 1 in Rossi et
166 al., 2006). In this locality, xenoliths from the upper crust to the shallow mantle were
167 brought to the surface during Miocene and Eocene explosive volcanic activity
168 (Féménias et al., 2004; Rossi et al., 2006). Zircons in metasedimentary granulites from
169 Bournac were dated between 150 and 630 Ma (Rossi et al., 2006). The oldest zircons
170 (>400 Ma) have a detrital origin and the youngest ones were formed by crustal
171 reworking in a lower crust environment during the Hercynian orogeny (See Rossi et al.,
172 2006 and references therein). Garnet-feldspar-whole rock Sm-Nd isochrons give an age
173 of 200 Ma in agreement with the age of the metamorphism (Downes et al., 1990).

174 The Beaunit maar is settled on the Permian Beaunit layered complex which was
175 emplaced at the crust-mantle transition at 257 Ma (U-Pb zircon age – Féménias et al.,
176 2003). This plutonic complex corresponds to a stratified intrusion located about 30 km
177 below the surface at the mantle-crust interface (Berger et al., 2007; Féménias et al.,
178 2003).

179 Bournac samples are the most felsic samples of our collection and all of them are felsic,
180 garnet-rich metasedimentary rocks (plagioclase-garnet-biotite-amphibole assembly).

181 Beaunit samples range from ultramafic plutonic amphibole-rich rocks (BPG2) to mafic

182 and felsic charnockites (B152). Mafic and ultramafic samples show no clear evidence
183 of high-degree metamorphism or deformation, whereas two felsic samples (BG6 and
184 B2-gneiss) show deformation and a mineralogical organization into bedding planes.

185

186 *Udachnaya, Central Siberian craton, Russia*

187 The fifteen samples from Siberia are xenoliths from the Udachnaya kimberlite pipe in
188 the central Siberian craton (Markha terrane, East of the Anabar Province). Udachnaya
189 is well known for its unaltered mantle and deep crustal xenoliths suitable for
190 petrological and geochronological studies (Ionov et al., 2010; Moyen et al., 2017). The
191 host kimberlites were dated at ca. 360 Ma (Kinny et al., 1997).

192 The age and origin of the crust beneath the Anabar province are still a matter of debate.
193 The CC formation involved two major events: (1) the first at 2.7–3.0 Ga (Moreira et
194 al., 2023; Moyen, 2017) and (2) the second at 1.9-1.8 Ga (U-Pb dating on zircons –
195 Moreira et al., 2023; Moyen et al., 2017; Shatsky et al., 2019) by plume upwelling,
196 underplating of basaltic magmas. Moyen et al. (2017) and Moreira et al. (2023) argued
197 that the LCC was strongly affected by a rejuvenation event at 2.0–1.8 Ga, whereas the
198 MCC and UCC remained largely unaffected after their formation at 2.7 Ga. Shatsky et
199 al. (2018, 2019) suggested that the 1.8 Ga-old juvenile materials are also present in the
200 LCC and the UCC. These studies suggest that Paleoproterozoic delamination and
201 rejuvenation of the lower Archean lithosphere had major effects on the structure and
202 composition of the continental crust in the Anabar province (Moyen et al., 2017). The
203 craton remained then thermally undisturbed since 1.8 Ga.

204 All 15 Udachnaya samples, collected at depths over 400m in the open mine, consist of
205 fresh minerals and have no eruption-related or alteration materials. Six most mafic
206 samples (246-17, 1003-14, 1010-13, 226-03, 232-17, and 360-13) are rich in garnet,

207 clinopyroxene, and plagioclase (\pm amphibole) and thus equilibrated at amphibolite to
208 granulite facies conditions. They likely represent the deepest parts of the crust. Sample
209 1001-16 is a picritic gabbro mainly composed of olivine, pyroxene, and amphibole;
210 sample 1006-14 is a mantle-like olivine-pyroxenite. All the other samples have more
211 felsic mineral assemblages, from amphibole-rich granitoid to felsic granulite. Three of
212 them contain abundant feldspar (370-13, 1014-14, and 98-13). 85% of the samples have
213 more than 40 wt.% plagioclase according to their CIPW norm.

214

215 *Canadian Precambrian Shield, Canada*

216 Lastly, we analyzed four composite samples from the Canadian Precambrian Shield.
217 Shaw et al. (1967; 1976) prepared the composite samples to estimate the major- and
218 trace-element composition of the Canadian Precambrian shield. They were derived by
219 sampling rocks across broad geographic regions of Canada, and composite powders
220 were made from 122 rocks from Northern Quebec (NQ), 116 from Baffin Island (BI),
221 18 from Saskatchewan (SS), and 116 from Southwestern Quebec (SQ). These provinces
222 have ages ranging between 0.9 and 2.7 Ga (McCulloch and Wasserburg, 1978).

223

224

225 2.2. Analytical methods

226 *Sample preparation*

227 All Phanerozoic samples (from IVZ and FMC) were cut with a rock saw and crushed
228 in Laboratoire Magmas and Volcans (LMV), Clermont-Ferrand, France. Precambrian
229 xenoliths from Udachnaya were cut and crushed at Montpellier University, France. To
230 avoid contamination by the host lava, the rims (one centimeter) of each xenolith
231 (initially 5 to 15 cm large) were removed, including veins inside the xenoliths (due to

232 possible kimberlite interaction or fluid percolation). The Canadian composite samples
233 were provided in powder form (Shaw et al., 1967, 1976). The IVZ and FMC samples
234 were processed and analyzed for major elements at the LMV using a Jobin-Yvon
235 ULTIMA C[®] ICP-AES and alkali fusion procedure, whereas analyses of the Siberian
236 samples were made by XRF analyses of beads produced by fusion of rock powders with
237 lithium-metaborate at the University of Mainz, Germany. Major- and trace-element
238 compositions of the Canadian samples were reported by Shaw et al. (1967, 1976), and
239 the compositions are nicely matched by new data reported here (see below).

240

241 Between 50 to 800 mg of sample powders were first acid-digested using a 3:1, 65% HF
242 / 48% HNO₃ mixture maintained at 75 °C on a hot plate for 48 hours. Once dried they
243 underwent a second step of digestion with 6M HCl, before breaking down fluorides by
244 three dissolutions with 1:1, 48% HNO₃ / 6M HCl, and slow evaporation at 70 °C.
245 Refractory mineral-rich samples were then re-digested in a concentrated 10:1, HF /
246 HNO₃ mixture using Teflon[®] vessels that were placed within Parr[®] bomb apparatus (48
247 hours at 180 °C), or in double distilled NH₄HF₂ (crystal form) within Savillex[®] beakers
248 (48 to 72 hours at 220 °C). Once dried they again underwent a 6M HCl digestion. Once
249 dissolved, a small portion (1%) of the solution was aliquoted for trace element and
250 La/Ce ratio measurements.

251

252 Cerium and Nd were separated following procedures described by Garçon et al. (2018),
253 Bonnand et al. (2019) and Israel et al. (2020). Using the AG50W-X8 resin, the major
254 elements were eluted in 2.5M HCl and Ba in 2M HNO₃ before collecting the REE
255 fraction in 6M HCl. The REE fraction was processed in Ln-Spec resin (50-100 mesh)
256 using an oxidation technique (20mM NaBrO₃ / 10M HNO₃) to oxidize Ce (tetravalent)

257 while eluting the other trivalent REE; then the Ce fraction was collected by reducing
258 the environment (20mM H₂O₂ / 6M HCl). The Ce fraction was purified in a final step
259 using AG50W-X8 (200-400 mesh, 1 ml) to remove residual Na, Br and Ba. Similarly,
260 the REE fraction was purified before it was processed using Ln-Spec resin to isolate
261 Nd. Mean procedural blanks for Ce and Nd were 113 pg and 14 pg, respectively.

262

263 *Mass spectrometry*

264 Trace-element abundances were measured with the LMV Agilent 7500[®] quadrupole
265 ICP-MS instrument in collision cell mode. Concentrations were calculated using an
266 external calibration (CMS reference material, Inorganic Venture) and the associated
267 errors are about 2-6% (2sd) for REE and up to 28% for Li, Sr and Ba. Certified USGS
268 reference materials BHVO-2 and BCR-2 were analyzed with our samples to assess the
269 accuracy of our analytical protocol. Our results for BHVO-2 and BCR-2 differ from
270 accepted reference concentrations (Jochum et al., 2016) by less than 10% for REE.
271 Errors calculated from ratios are significantly reduced and we obtained a reproducibility
272 of 1% on 7 repeated measurements of the CMS standard solution (2sd). A distinct
273 analytical session was dedicated to the measurement of La/Ce ratios. They were
274 estimated using a calibration curve defined from four gravimetrically prepared
275 standards with different La/Ce ratios (0.2681, 0.3712, 0.5703, 0.7878) produced from
276 CMS elementary standards. The reproducibility errors calculated from three repeated
277 measurements of the four standards are \approx 0.3% (2sd).

278 Cerium isotope ratios were measured in oxide form on a ThermoScientific Triton Plus[®]
279 TIMS at LMV, using a static mode method and double 99.99% Re filaments (Bonnand
280 et al., 2019). Oxygen correction, correction for mass-discrimination using ¹³⁶Ce/¹⁴²Ce
281 = 0.01688, and correction for the tailing effect due to the overabundant signal of

282 $^{140}\text{Ce}^{16}\text{O}$ affecting $^{136}\text{Ce}^{16}\text{O}$ and $^{142}\text{Ce}^{16}\text{O}$ signals (extrapolation from half-masse
283 measurements – details for corrections are given in Bonnard et al., 2019) were
284 performed offline. The mass fractionation of the CeO^+ beam is assumed to follow an
285 exponential law. Uncertainties reported below are 2 standard deviations. Cerium
286 isotope measurements of this study were acquired during three distinct sessions. The
287 mean tailing correction was equal to $\Delta\epsilon_{\text{Ce}} = 1.01 \pm 0.25$ ($n = 73$, samples and standards).
288 Repeated measurements of our Ce_{LMV} synthetic reference material gave $^{138}\text{Ce}/^{142}\text{Ce} =$
289 0.02257036 ± 74 (33 ppm; $n = 24$). All $^{138}\text{Ce}/^{142}\text{Ce}$ ratios measured in samples and rocks
290 standards are normalized to the Ce_{LMV} value $^{138}\text{Ce}/^{142}\text{Ce} = 0.002257063$ (Israel et al.,
291 2020 – $^{138}\text{Ce}/^{142}\text{Ce}_{\text{Ce}_{\text{LMV}}} / ^{138}\text{Ce}/^{142}\text{Ce}_{\text{Ce}_{\text{AMES}}} = 0.999835$). $^{138}\text{Ce}/^{142}\text{Ce}$ ratios measured
292 for BCR-2 and BHVO-2 are 0.02256694 ± 92 (41 ppm, $n = 3$) and 0.02256465 ± 71 (31
293 ppm, $n = 6$), respectively.

294

295 Neodymium isotope ratios were measured on a ThermoScientific Triton[®] TIMS at
296 LMV during three analytical sessions, using either a one-line or a two-line method and
297 double 99.999% Re filaments. Mass discrimination was corrected using an exponential
298 law and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for the JNdi-1 standard
299 reference material and the two rock samples BCR-2 and BHVO-2 are 0.512108 ± 7 (15
300 ppm; $n = 21$), 0.512619 ± 9 (18 ppm, $n = 3$), and 0.512972 ± 9 (15 ppm, $n = 2$),
301 respectively. Since the JNdi-1 values increased during the three sessions, $^{143}\text{Nd}/^{144}\text{Nd}$
302 ratios of the analyzed samples and rocks standards were normalized to the JNdi-1
303 reference value of Garçon et al. (2018), i.e., $^{143}\text{Nd}/^{144}\text{Nd} = 0.512099$.

304

305

306 **3. Results**

307 3.1. Major and trace element compositions

308 Major and trace element compositions measured in this study are reported in
309 [Supplementary data 1](#). All metaigneous and metasedimentary samples in our study are
310 presented on a total alkali ($\text{Na}_2\text{O}+\text{K}_2\text{O}$) *versus* silica diagram and compared with
311 literature granulites ([Fig. 1](#)).

312 Samples from Bournac and Canada have the highest SiO_2 content, with values ranging
313 from 58 to 71 wt.%. Ivrea and Beaunit samples are highly variable in SiO_2 (32 to 68
314 wt.% and 44 to 62 wt.%, respectively) but they contain the most mafic samples of our
315 dataset (BPG2 and IV9). Siberian samples have 47 to 55 wt.% SiO_2 with one exception
316 (62 wt.%). The more felsic samples show high $\text{Na}_2\text{O}+\text{K}_2\text{O}$ values (up to 9.5 wt.%, SiO_2
317 = 53 wt.%). Loss on ignition (LOI) values in the Siberian samples range from 0.1 to 2.4
318 wt.%, with the highest values measured in samples that show veins, re-crystallization,
319 or altered feldspar (322-13, 370-13 and 386-13). All the other samples have LOI lower
320 than 0.86, with LOI attributed to the presence of primary hydrous minerals (biotite,
321 amphibole). No clear correlation can be observed with any major or trace elements
322 sensitive to alteration (e.g., Sr) or La/Ce and Sm/Nd ratios. LOI values of the West
323 European samples range from 0.1 to 1 wt.%.

324 Bulk-CC normalized REE patterns ([Fig. 2](#)) show LREE depletions to LREE
325 enrichments, as indicated by the moderate to high $\text{La}/\text{Yb}_{\text{Bulk CC}}$ ratios (where the
326 subscript “Bulk CC” stands for ratio normalized to the bulk continental crust from
327 Rudnick and Gao, 2014 – $\text{La}/\text{Yb}_{\text{Bulk CC}} = 0.30 - 4.9$; except IV1, 246-17, B4g-lite and
328 370-13 samples that show $\text{La}/\text{Yb}_{\text{Bulk CC}} = 0.07, 0.13, 0.18$ and 12, respectively).

329 The Siberian samples show the largest range of REE fractionation with $\text{La}/\text{Yb}_{\text{Bulk CC}}$
330 ratios varying from 0.13 to 12, which is a great range compared to West European
331 samples ($\text{La}/\text{Yb}_{\text{Bulk CC}} = 0.07 - 4.0$). For better visualization, Siberian samples are

332 presented in two diagrams (Figs. 2b,d) based on their Sm/Nd ratio. All the samples with
333 a Sm/Nd>0.24 are mafic (SiO₂<50 wt.%) and contain garnet in their mineral
334 assemblage. Thirteen Siberian samples show a moderate to high depletion in LREE
335 compared to the MREE (La/Gd_{Bulk CC} / Gd/Yb_{Bulk CC} = 0.08 to 0.63 vs. 1.14 and 3.73 in
336 1014-14 and 370-13, respectively - Figs. 2b,d). Most of them show no significant
337 cerium anomaly and a small negative europium anomaly (Ce/Ce* = 0.81 – 1.09 and
338 Eu/Eu* = 0.58 – 0.98, where Ce/Ce* = Ce_N/(0.5×(La_N+Nd_N)) and Eu/Eu* =
339 Eu_N/(0.5×(Sm_N+Gd_N)) where the subscript “N” stands for concentration normalized to
340 CI chondrite – Barrat et al., 2012). Samples 98-13, 370-13 and 1014-14 have positive
341 Eu anomalies (Eu/Eu* = 4.38, 1.35 and 1.27) consistent with their strong enrichment
342 in feldspar, and they show a strong depletion in HREE compared to the other Siberian
343 samples (Fig. 2d). Among them, only 370-13 has a high LOI of 2.4 (vs. 0.2 and 0.6 for
344 98-13 and 1014-14, respectively). All the other Siberian samples have LOI ranging
345 between 0.1 and 1.4, except 322-13 whose LOI is 2.3.

346

347

348 3.2. ¹³⁸La-¹³⁸Ce and ¹⁴⁷Sm-¹⁴³Nd systematics

349 Measured Ce and Nd isotopic compositions are given in Table 1 and reported in epsilon
350 (ε) notation in Figure 3. Most of the data for FMC, IVZ and Canadian samples plot
351 within or very close to the Ce-Nd mantle array (for the FCM and IVZ samples εCe = -
352 0.65 to 3.83 and εNd = -14.72 to 6.73; for Canadian samples εCe = 0.02 to 2.71 and
353 εNd = -30.69 to -6.19). Bournac xenoliths, Ivrea samples and Canadian composites are
354 located at the end of the mantle array toward the most radiogenic Ce and the least
355 radiogenic Nd isotopic compositions, except BOU3 which plots to the right of the
356 mantle array. Because the three Bournac samples have very similar Nd isotopic

357 compositions, the Ce isotopic composition of this sample seems anomalously
358 radiogenic. Beaunit xenoliths range between the MORB and loess endmembers defined
359 in Israel et al. (2020), in agreement with their large range of SiO₂ contents.

360 The Siberian samples mostly plot to the left of the mantle array in the ϵCe - ϵNd diagram.
361 They cover a wider range of ϵCe values than FMC and IVZ samples, with ϵCe values
362 from -1.75 to 5.78 for and ϵNd from -41.61 to -4.69. They define two nearly horizontal
363 sub-parallel trends, with slopes distinct from that of the mantle array. The Siberian
364 samples are reported in $^{138}\text{La}/^{142}\text{Ce}$ - $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ - $^{143}\text{Nd}/^{144}\text{Nd}$ diagrams
365 (Fig. 4). They define a single regression line for each isotope system. Our data agree
366 with literature ^{147}Sm - ^{143}Nd data on granulites from the same area (Fig. 4b) but
367 regressions are not sufficiently well defined to provide robust information on ages and
368 form errorchrons (MSWD>10). The La-Ce errorchron age is nevertheless significantly
369 younger than that for the Sm-Nd system (1.8 ± 0.4 Ga and 2.7 ± 0.3 Ga, respectively –
370 calculated with IsoplotR – Vermeesch, 2018 – Fig. 4). These two ages are consistent
371 with the chronology established using other methods. For example, U-Pb ages
372 measured on zircons from both Udachnaya and Obnazhennaya kimberlites defined two
373 peaks at 1.8 and 2.7 Ga (Moyen et al., 2017), which are similar to the U-Pb zircon ages
374 from granulites of the Anabar province (Koreshkova and Downes, 2021; Moreira et al.,
375 2023) and the Re-Os depletion ages of peridotite xenoliths from these pipes (Ionov et
376 al., 2015a, 2015b). This is consistent with a common history for the lithospheric mantle
377 and deep crust of the Siberian craton.

378 Isochron diagrams are not presented for Beaunit, Bournac and Ivrea samples. They are
379 too young to extract relevant information from long-lived systems.

380

381

382 4. Discussion

383 4.1. Data from this study compared to crustal reservoirs

384 Recent publications, such as Rudnick and Gao (2014) and Hacker et al. (2015),
385 provided estimates for the chemical composition of the deep crust. These compositions
386 differ due to the relative weight given to measurements (e.g., abundance of mafic and
387 felsic components) and geophysical constraints. Figure 1 reports the SiO₂ and alkalis
388 for these reference compositions but also a large literature dataset composed of Archean
389 and post-Archean granulites (grey and pink squares in Fig. 1).

390 The crustal samples in this study range from ultramafic to felsic compositions as shown
391 in Figure 1 and fall within the range defined in the literature. The Siberian xenoliths
392 from this study fall within the range of those reported by Koreshkova et al. (2011),
393 Moyen et al. (2017) and Shatsky et al. (2019, 2018). However, they are more enriched
394 in alkalis than most of the literature samples for similar SiO₂ contents, suggesting that
395 this is typical of the Siberian craton. Samples 1001-16, 1014-14 and 370-13 have the
396 highest Na₂O+K₂O (7.8, 7.0 and 9.5 wt.%, respectively), beyond the compositions
397 commonly observed in literature lower crust samples (Figure 1).

398 Koreshkova et al. (2011) and Moyen et al. (2017) grouped Siberian xenoliths based on
399 HREE/LREE ratios and K₂O that were unrelated to LOI. Koreshkova et al. (2011)
400 suggested that most of the xenoliths in their study (collected in other parts of the
401 kimberlite pipe than those in this study) were modified by interaction with kimberlite
402 magmas, resulting in enrichments in LILE. Many of their samples were also modified
403 by post-eruption processes such as alteration and interaction with fluids mobilized from
404 local sedimentary country rocks. Since kimberlites are low in alkalis (Kamenetsky et
405 al., 2012) and strongly enriched in LREE relative to HREE ($La/Yb_{Bulk\ CC} = 14$ to 20),
406 contamination by a kimberlitic melt for our samples can be ruled out. This process

407 cannot explain the relative depletion in LREE relative to HREE in the Udachnaya
408 xenoliths ($\text{La}/\text{Yb}_{\text{Bulk CC}} = 0.13$ to 1.8; except samples 1014-14, 1001-16 and 370-13
409 with $\text{La}/\text{Yb}_{\text{Bulk CC}} = 3.1, 4.9$ and 12, respectively – Fig. 2b,d). Moreover, our samples
410 plot far from Udachnaya kimberlites on the Sm-Nd errorchron diagram whereas
411 contamination by the host kimberlite is clearly identified for one xenolith analyzed by
412 Koreshkova et al. (2011) (Fig. 4b). Therefore, the Ce-Nd isotopic compositions of the
413 Siberian xenoliths are unlikely to be affected by kimberlite contamination.

414

415

416 4.2. Ce-Nd isotopic evolution of crustal samples

417 The isotopic composition of rocks evolves with time as a function of their
418 parent/daughter ratios. Figure 5 shows the initial isotopic compositions of the samples
419 from this study based on their measured parent/daughter ratios and published ages. The
420 initial isotopic composition is unrelated to this discussion, and we focus here on the
421 evolution paths of the samples, represented as arrows from initial to present-day
422 isotopic compositions.

423 The majority of the Phanerozoic samples from the FMC and the IVZ evolve along the
424 Ce-Nd mantle array. Because these samples are young, both their present-day and initial
425 isotopic compositions are close to each other in the $\epsilon\text{Ce}-\epsilon\text{Nd}$ diagram (Fig. 5a). In
426 contrast, the much older Canadian and Siberian samples plot to the left of the mantle
427 array (Fig. 5b). While the age and thermal history of the Canadian samples are uncertain
428 due to their composite nature, their epsilon values plot close to the mantle array after
429 recalculation back to 3 Ga (maximum presumed age of the sampled terrains – Fig. 5a).
430 Their evolution paths are close to the slope of the mantle array, creating a slight
431 deviation from the mantle array integrated over 3 Ga. Using younger ages for correction

432 does not affect their evolution paths and results in similar conclusions. The isotopic
433 compositions of the Siberian samples also move closer to the mantle array (Fig. 5b)
434 when back-calculated up to 2.7 Ga (Moyen et al., 2017), except sample 370-13 that
435 moves further from the mantle array. This sample has the highest LOI value and it
436 contains altered feldspar suggesting alteration affected its La/Ce ratio. The evolution
437 paths of the Siberian samples are much steeper than the slope of the mantle array.
438 However, previous results suggest the Siberian crust formed during the Archean at ~2.7
439 Ga followed by a major event of delamination and rejuvenation at 1.8 Ga (Moyen et al.,
440 2017; Shatsky et al., 2019), which is consistent with chronological insights from La-Ce
441 and Sm-Nd systematics (Fig. 4). The disturbance of the La-Ce systematics in the
442 Siberian samples at 1.8 Ga suggest their evolution paths are probably not linear but
443 should be subdivided into at least two segments in Figure 5b.

444

445 The observed depletion in LREE relative to MREE and the disturbance of the La-Ce
446 systematics in the Siberian samples at 1.8 Ga suggest high-grade metamorphism may
447 have affected the entire crustal section (Fig. 2) and produced a decrease in the La/Ce
448 ratios. The La-Ce system is more prone to disturbances during fluid circulation
449 accompanying the metamorphism than the Sm-Nd system because the REE mobility
450 decreases with increasing atomic number. Remarkably, lanthanum appears to be the
451 most mobile REE during fluid interaction in granulite facies (e.g., dehydration of
452 amphibole – Ague, 2017 and references therein). Cerium changes valence from 3+ to
453 4+ under oxidizing conditions and thus is decoupled from other REE, as seen in modern
454 seawater and chemical marine sediments (Bau, 1999). The percolation of an oxidized
455 fluid may reduce cerium mobility relative to other REEs, although this is not
456 documented in the literature at LCC conditions. Therefore, a decrease in the La/Ce

457 ratios in Siberian samples is more likely due to the higher mobility of La during high-
458 grade metamorphism.

459

460

461 4.3. Deviation from the ϵCe - ϵNd mantle array: comparing our data with literature

462 The isotopic evolution of samples is usually compared by calculating their $f_{P/D}$
463 parameter (Vervoort et al., 2000), where $f_{P/D}$ represents the deviation of the
464 parent/daughter ratio of a sample from this ratio in a chondritic reservoir. The values
465 for $f_{\text{Sm/Nd}}$ and $f_{\text{La/Ce}}$ can be either positive or negative and indicate the direction and
466 amplitude of the isotopic evolution relative to CHUR in an epsilon-epsilon diagram
467 (Fig. 5c). The ratio $F = f_{\text{Sm/Nd}} / f_{\text{La/Ce}}$ integrates the effects of both $f_{\text{Sm/Nd}}$ and $f_{\text{La/Ce}}$. This
468 parameter is relevant for quantifying the deviation from the CHUR as a point but not
469 from the mantle array line on epsilon-epsilon diagrams. As a handy alternative, we
470 compare the evolution vectors of the samples with the vector formed by the mantle
471 array trend (Fig. 5c). These vectors are distinct by the oriented angle θ calculated on an
472 orthonormal epsilon-epsilon diagram. Samples with evolution vectors to the left of the
473 mantle array will exhibit negative θ values (Fig. 5c). The rate of deviation of the
474 samples from the mantle array is also calculated in the form of the horizontal deviation
475 of the Ce isotopic composition over a billion-year period ($\Delta\epsilon\text{Ce/Ga}$ – Fig. 7a). Both θ
476 and $\Delta\epsilon\text{Ce/Ga}$ parameters only depend on the La/Ce and Sm/Nd ratios of a sample.
477 Disregarding isotopic or age constraints, θ and $\Delta\epsilon\text{Ce/Ga}$ provide quantitative insights
478 into how samples diverge from the mantle array with time, indicating the direction (\approx
479 degree of decoupling of La/Ce and Sm/Nd ratios) and rate of deviation per time unit,
480 respectively (calculations detailed in the [Supplementary material](#)). These parameters
481 calculated for our samples are reported in [Supplementary data 2](#)).

482 The evolution vectors of the West European samples display slopes that diverge slightly
483 from the mantle array, with θ values ranging from -4.0 to $+3.0^\circ$ (Fig. 7a), except sample
484 BOU2 showing a higher θ value at $+5.6^\circ$. While it also slightly deviates from the mantle
485 array, IV1 evolves upward ($\theta = -176$). The Canadian composites have slightly negative
486 θ values from -2.3 to -3.9° . SQ has a higher θ value (-7.8°) but it also shows a much
487 younger Nd model age than the other Canadian samples ($T_{DM} = 1$ Ga vs. $T_{DM} = 2.1$ - 2.5
488 Ga – details are given in Supplementary data 1), suggesting a late disturbance. The
489 Siberian samples from this study and the literature have a large range of θ values, and
490 most of them are strongly negative (down to -21.0°), except two samples with the
491 highest La/Ce ratios (1014-14 and 370-13 with $\theta = -0.5$ and $+2.8^\circ$, respectively).
492 While the samples from Europe mostly show $\Delta\epsilon_{Ce}/Ga$ between -0.7 and 0.5 , and
493 Canadian samples between -1.5 and -0.5 . Siberian samples deviate more significantly
494 from the mantle array with $\Delta\epsilon_{Ce}/Ga$ from -2.3 to -0.3 (except 1014-14 and 370-13 with
495 $\Delta\epsilon_{Ce}/Ga = -0.1$ and 0.8 , respectively).
496
497 To further explore the significance of our data and inferences, and how representative
498 the Siberian xenoliths could be of the CC, we calculated θ and $\Delta\epsilon_{Ce}/Ga$ values using
499 the elemental concentrations of 445 Archean and 1136 post-Archean granulites from
500 the literature. We used the database compiled by Hacker et al. (2015) and added new
501 values from the PetDB database. Figure 6 presents the relative numbers of samples from
502 each region for the Archean and post-Archean datasets. All cratons are incorporated
503 into both the Archean and post-Archean datasets. Compared to the global ages
504 distribution of the continental lithosphere (Fig. 7 in Poupinet and Shapiro, 2009) our
505 database shows an under-representation of post-Archean samples from Siberia relative
506 to their Archean equivalents and an over-representation of West European samples

507 relative to Antarctica, Australia and South America that are under-represented. The
508 calculated θ and $\Delta\epsilon_{\text{Ce/Ga}}$ values of the complete database are reported in
509 [Supplementary data 2](#) and shown in [Figure 7a](#). Archean and post-Archean granulites
510 present similar, normal distributions of θ and $\Delta\epsilon_{\text{Ce/Ga}}$ values with peaks at -3° and -
511 0.4, respectively. These slightly negative values will result in isotopic compositions
512 increasingly deviating to the left of the mantle array over time. When all data are plotted
513 in a θ versus $\Delta\epsilon_{\text{Ce/Ga}}$ diagram, a positive correlation is observed. The linear regression
514 is defined by the equation $\Delta\epsilon_{\text{Ce/Ga}} = 0.15 (\pm 0.03) \times \theta - 0.01 (\pm 0.05)$. For $\theta = -3^\circ$, it
515 intercepts $\Delta\epsilon_{\text{Ce/Ga}} = -0.46 \pm 0.05$, consistent with the peak of $\Delta\epsilon_{\text{Ce/Ga}}$. We note that
516 the Siberian xenoliths have strongly negative θ and $\Delta\epsilon_{\text{Ce/Ga}}$ values ([Fig. 7a](#)) which are
517 found among the most extreme values documented for granulites in the literature.
518 The θ and $\Delta\epsilon_{\text{Ce/Ga}}$ values calculated from reference compositions of the LCC
519 (Rudnick and Gao, 2014 and Hacker et al., 2015 – mafic and felsic models) are more
520 negative than the distribution peaks of literature granulites ($\theta = -6.6$ to -5.6° ; $\Delta\epsilon_{\text{Ce/Ga}}$
521 = -1.1 to -0.6). According to these reference compositions, the LCC should deviate
522 significantly from the mantle array with time, to a greater extent than most granulites,
523 but significantly less than the Siberian xenoliths.

524

525

526 4.4. La/Ce and Sm/Nd ratios of the lower crust

527 To better understand the relative influence of the parent/daughter ratios on the θ values
528 of the Siberian samples and literature granulites, their present-day $^{138}\text{La}/^{142}\text{Ce}$ and
529 $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are plotted in [Figure 7b](#), together with their frequency distribution
530 histograms. Siberian samples have lower $^{138}\text{La}/^{142}\text{Ce}$ values (maximum distribution at
531 0.0033) than other granulites that show distribution peaks at 0.0035 and 0.0039 for

532 Archean and post-Archean granulites, respectively, with a larger range for Archean
533 samples. Post-Archean granulites have a normal $^{147}\text{Sm}/^{144}\text{Nd}$ distribution with a peak
534 at 0.125, while Archean granulites show a flatter distribution. Siberian samples also
535 show a wide range of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios without clear peaks.

536

537 Two regression lines intersect the CHUR composition in [Figure 7b](#). The first one
538 represents parent/daughter ratios for samples with isotopic compositions that evolve
539 along the mantle array ($\theta = 0^\circ$ – black line) and the other one with an angle $\theta = -3^\circ$
540 (purple line) corresponds to the peak value in the histogram of [Figure 7a](#). The
541 distribution of the parent/daughter isotope ratios of granulites in the histograms of
542 [Figure 7b](#) raises questions about the LREE concentrations of the LCC. Parent/daughter
543 ratios obtained using reference compositions do not plot on the $\theta = -3^\circ$ line nor the
544 mantle array line. Their $^{147}\text{Sm}/^{144}\text{Nd}$ ratios range from 0.113 to 0.154 (Rudnick and
545 Gao, 2014 and Hacker et al., 2015 – see [Supplementary data 2](#)), encompassing a
546 significant portion of granulite compositions. The peak of $^{147}\text{Sm}/^{144}\text{Nd}$ observed in
547 granulites is however close to a mafic composition of the LCC, between the felsic and
548 mafic composition models of Hacker et al. (2015). Their $^{138}\text{La}/^{142}\text{Ce}$ ratios range from
549 0.00350 to 0.00322, in agreement with the peak for Archean granulites but lower than
550 the peak observed for post-Archean granulites ([Figure 7b](#)).

551 Our observations are based on a comprehensive set of granulite compositions, however,
552 weighting the parent/daughter ratios by the relative surface area of different continents
553 is unlikely to change significantly our observations. In any case, a more mafic LCC
554 than the Rudnick and Gao (2014) reference is suggested by the literature on granulites.
555 The granulite database ([Fig. 7](#)) indicates the most likely parent/daughter ratios of the

556 LCC that result in $\theta = -3^\circ$ and $\Delta\epsilon_{\text{Ce/Ga}} = -0.46 \pm 0.05$ are $^{138}\text{La}/^{142}\text{Ce} = 0.00380$
557 ± 0.00007 and $^{147}\text{Sm}/^{144}\text{Nd} = 0.128 \pm 0.007$.

558

559 The atypical isotope evolution of Siberian samples likely results from La/Ce
560 decrease due to enhanced mobility of LREE during high-grade metamorphic conditions
561 (granulite facies – Ague, 2017). However, generalizing this conclusion to all Archean
562 granulites from the literature may be oversimplistic since it is difficult to assess which
563 parent/daughter ratio has greater effects on their isotope evolution. Shifting
564 parent/daughter ratios from the mantle array line to the -3° line can be achieved either
565 by decreasing the $^{138}\text{La}/^{142}\text{Ce}$ or $^{147}\text{Sm}/^{144}\text{Nd}$ ratio by $\approx 11\%$ and 18% , respectively,
566 which are both plausible. Such decreases may be caused by partial melting of crustal
567 material, fractional crystallization or metamorphism generating inhomogeneous
568 enrichment or depletion in the REE pattern in lower crust conditions. Both ratios may
569 even decrease simultaneously during metamorphism involving fluid-rock interaction,
570 alteration, or incorporation of hydrothermally-related material or altered sediments in
571 the melt (tetrad effect – Lee et al., 2010 and reference therein).

572

573

574 4.5. Evidence for massive recycling of lower continental crust

575 *The continental crust in the mass-balance budget of the bulk silicate Earth*

576 The composition of the bulk silicate Earth (BSE) can be expressed as the
577 complementarity of the CC and depleted MORB mantle (DMM), i.e. $\text{BSE} = \text{CC} +$
578 DMM (Allègre and Lewin, 1989). Mantle geochemists have emphasized the
579 importance of recycling oceanic crust (OC) throughout Earth's history to understand
580 the present-day composition of the convecting mantle and the signification of the

581 mantle array (Stracke et al., 2003). While it represents only a small fraction of the crust
582 (3-30 wt.%), the OC was subducted over geologic time and its current share in the
583 mantle is difficult to constrain. Moreover, the REE content of the OC is about four
584 times lower than in the LCC (White and Klein, 2014) and the calculated Ce-Nd isotopic
585 composition of the OC evolves very slightly with time and remains on the mantle array
586 (see Figure 2 in Willig et al., 2020). The bulk OC is then supposed to have little impact
587 on the mass-balance budget of Ce and Nd in the BSE.

588 The mass-balance budget of the BSE was estimated by Israel et al. (2020) using the
589 measured Ce-Nd isotopic composition of the DMM and reference isotopic
590 compositions and Ce and Nd contents for the BSE and CC (Table 2; Supplementary
591 material – details about the input parameters are given in Israel et al., 2019). The
592 calculated Ce-Nd isotopic range for the bulk CC (orange field in Fig. 8) is located to
593 the left of the mantle array and is distinct from the UCC estimates based on mean loess
594 values. As a result, the deep continental crust (MCC+LCC) must plot even further to
595 the left of the mantle array, in the negative $\epsilon_{\text{Ce}}-\epsilon_{\text{Nd}}$ quadrant (grey field in Fig. 8) to
596 fulfill the complementarity bulk $\text{CC} = \text{UCC} + (\text{MCC} + \text{LCC})$. Willig and Stracke (2019)
597 and Willig et al (2020) showed similar results for their modeled LCC. The horizontal
598 distances ($\Delta\epsilon_{\text{Ce}}$) of the bulk CC and the deep continental crust from the mantle array
599 are -1.5 ± 0.8 and -2.9 ± 1.2 , respectively (mean values and two standard deviations).

600 These estimates consider: (1) three reference compositions of the CC after Rudnick and
601 Gao, 2014 and Hacker et al., 2015 and (2) the range of Nd isotopic composition of the
602 bulk CC – $\epsilon_{\text{Nd}} = -21$ to -10 after Allègre and Lewin, 1989 and Chauvel et al., 2014,
603 respectively). Only the Ce-Nd isotopic compositions for the Siberian samples plot near
604 the modeled MCC+LCC reservoir. The peak θ values in the literature dataset (-3° , Fig.
605 7a) and the associated $\Delta\epsilon_{\text{Ce}}$ per billion years, enable to estimate the deviation of the Ce

606 isotopic composition from the mantle array for the LCC at about -0.8 to -1.1, for a mean
607 age of the CC between 1.8 and 2.4 Ga (Chauvel et al., 2014; Taylor and McLennan,
608 1995). The LCC is then potentially much less distant from the Ce-Nd mantle array than
609 the MCC+LCC reservoir calculated from the mass-balance budget (Fig. 8).

610 The mass fraction of bulk CC relative to the BSE ($m_{\text{bulk CC}}/m_{\text{BSE}} = (^{143}\text{Nd}/^{144}\text{Nd}_{\text{BSE}} -$
611 $^{143}\text{Nd}/^{144}\text{Nd}_{\text{DMM}}) / (^{143}\text{Nd}/^{144}\text{Nd}_{\text{CC}} - ^{143}\text{Nd}/^{144}\text{Nd}_{\text{DMM}}) \times [\text{Nd}]_{\text{BSE}}/[\text{Nd}]_{\text{CC}}$) can be estimated
612 using a mass-balance budget, and is calculated to be 0.026 ± 0.013 . However, the mass
613 fraction of the present-day CC relative to the mantle ($m_{\text{present-day CC}}/m_{\text{present-day mantle}} =$
614 0.006 : $m_{\text{present-day CC}} = 2.367 \times 10^{25} \text{g}$ and $m_{\text{mantle}} = 4.007 \times 10^{27} \text{g}$ – Lodders and Fegley,
615 1998) is 4.4 times lower than the fraction estimated from the BSE mass-balance. Thus,
616 about 3.4 times the present-day mass of the continental crust may have been recycled
617 to the mantle, which is larger than recent estimates of 1–1.6 times the present-day mass
618 of CC (e.g., Dhuime et al., 2018; Kumari et al., 2016).

619 While these calculations imply a chondritic BSE, two recent studies have provided
620 compelling evidence that the BSE (or primitive mantle) is slightly depleted in
621 incompatible elements relative to chondrites (Frossard et al., 2022; Johnston et al.,
622 2022). Recent mass balance models have also reevaluated the global crust-mantle
623 differentiation of the Silicate Earth and propose the existence of an early depleted
624 reservoir (EDR) formed prior to the extraction of the continental crust (Hofmann et al.,
625 2022). To reconcile a 7.9 ppm excess in ^{142}Nd compared to chondrites (Frossard et al.,
626 2022), we consider a 2.65% higher Sm/Nd ratio than chondrites ($^{147}\text{Sm}/^{144}\text{Nd}_{\text{EDR}} =$
627 0.2012) and we reevaluate the LREE content of this EDR. Based on a 4.568 Ga
628 formation age, we estimate that the present-day values for the primitive mantle are
629 $^{138}\text{La}/^{142}\text{Ce}_{\text{EDR}} = 0.00306$, $\varepsilon_{\text{Ce}_{\text{EDR}}} = -0.3$, and $\varepsilon_{\text{Nd}_{\text{EDR}}} = 3.1$. With these new parameters,

630 the mass fraction of bulk CC relative to the BSE is lower than for a chondritic BSE
631 ($m_{\text{bulk CC}}/m_{\text{BSE}} = 0.016 \pm 0.008$) and corresponds to $2.7 \times m_{\text{present-day CC}}/m_{\text{present-day mantle}}$.

632

633 *Impact of lower continental crust recycling on the mass-balance budget of the BSE*

634 Tang et al. (2015) suggested that Eu anomalies in the UCC, MCC and LCC cannot be
635 explained without considering a greater proportion of the LCC than the proportion
636 observed in the present-day CC. They suggested different relative proportions of the
637 different sub-reservoirs of the CC with the LCC representing 84 wt.% rather than the
638 10% recommended by Rudnick and Gao (2014). This implies that 88 wt.% of the LCC
639 was recycled to the mantle, and represents about $2.9 \times m_{\text{present-day CC}}$. The UCC and MCC
640 would then represent only 8 wt.% and 8 wt.%, respectively, of the bulk CC (vs. 32 wt.%
641 and 30 wt.%, respectively, according to Rudnick and Gao, 2014).

642 The massive recycling of LCC proposed by Tang et al. (2015) affects the mass-balance
643 calculations for the Ce-Nd systematics. The resultant bulk CC and MCC+LCC ϵ_{Ce} -
644 ϵ_{Nd} isotopic compositions are closer to the mantle array than the previous reservoir
645 estimates (with $\Delta\epsilon_{\text{Ce}}$ ranging from -1.2 to -1.6 (± 0.9) – see bulk CC and MCC+LCC
646 represented as red and black fields in Fig. 8). The MCC+LCC reservoir fits with the
647 granulite database, suggesting that the Ce-Nd isotopic composition of the LCC is
648 located to the left of the mantle array, but not as far as the Siberian samples. Our
649 estimates indicate a mass fraction of bulk CC relative to the BSE ($m_{\text{bulk CC}}/m_{\text{BSE}} = 0.024$
650 ± 0.011 and 0.033 ± 0.022 for depleted and chondritic BSE, respectively) that is 4.1 to
651 5.6 times higher than the mass fraction of the present-day CC. Consequently, we
652 suggest that 2.6 to $3.9 \times m_{\text{present-day CC}}$ of LCC was recycled in the mantle during Earth's
653 history (total of 3.1 to $4.6 \times m_{\text{present-day CC}}$ of CC was recycled in the mantle, including 84
654 wt.% of LCC).

655 Continental growth models remain challenged by the difficulty in measuring the rates
656 of formation and destruction of the continental crust through time (e.g., Dhuime et al.,
657 2018; Kumari et al., 2016; Reimink et al., 2023; Rosas and Korenaga, 2018). Our study
658 suggests a large amount of crustal recycling, since we estimated that the portion of CC
659 derived from the Earth's mantle is four to five times larger than the current mass of CC,
660 and most of the recycled crust is from its deepest mafic part. Geological processes, such
661 as crustal delamination, play a crucial role in explaining this substantial LCC recycling
662 while considering the contemporary structure of CC.

663 In this context, Hacker et al. (2011, 2015) have highlighted that the lowermost mafic
664 crust can become unstable and detach, sinking into the mantle beneath rifts and volcanic
665 arcs. Particularly during subduction, the densest mafic crust descends into the mantle
666 while some of the silica-rich crust may be metamorphized into felsic gneiss, rise,
667 undergo partial melting and finally relaminate at the base of the crust. Consequently, it
668 is plausible that most of the LCC lost into the mantle may have a more mafic
669 composition compared to the rocks found at the base of the lithosphere.

670 The recycling of substantial masses of CC within the mantle can also have a significant
671 impact on the mantle's composition. The recycled CC may represent a few percent of
672 the mantle's mass, estimated at 1.6-2.3 wt%, and contribute to its enrichment in
673 refractory elements. Research focusing on isotopic variations in ocean island basalts
674 suggests that recycled CC may persist within the mantle and could be sampled through
675 the hotspot-related volcanism. The predominant influence of recycled LCC has been
676 proposed as an explanation for the characteristics of EM-I-like OIB (Boyet et al., 2019;
677 Frey et al., 2002), thereby supporting the hypothesis of abundant LCC storing in the
678 mantle.

679

680

681 5. Conclusions

682

683 We analyzed the Ce-Nd isotope compositions of Precambrian samples from Canada
684 (composite in nature), Phanerozoic samples from western Europe, and Archean
685 xenoliths from Siberia that represent the upper to lower parts of the continental crust.
686 Both the Canadian upper crust and the West European deep crust closely align with the
687 $\epsilon_{\text{Ce}}-\epsilon_{\text{Nd}}$ mantle array whereas the deep crust of the Siberian craton plots to the left of
688 the array. The peculiar composition of the deep crust in the Siberian craton can be
689 explained by high grade-metamorphism related to large-scale delamination and
690 rejuvenation of the Archean lower lithosphere at 1.8 Ga (Moyen et al., 2017). This
691 process likely caused a preferential loss of La, resulting in decreased La/Ce ratios, while
692 preserving the Archean Sm-Nd age systematics. This is consistent with the greater
693 mobility of light REE relative to medium REE previously observed under granulite-
694 facies conditions (Ague, 2017).

695

696 Comparing the measured parent/daughter ratios with a large set of granulites from the
697 literature, we found that only Siberian xenoliths deviate significantly to the left of the
698 $\epsilon_{\text{Ce}}-\epsilon_{\text{Nd}}$ mantle array with time (high negative θ and high negative $\Delta\epsilon_{\text{Ce}}/\text{Ga}$,
699 representing the degree and rate of deviation, respectively). As a comparison, Archean
700 and post-Archean literature granulites also have negative θ and $\Delta\epsilon_{\text{Ce}}/\text{Ga}$ but essentially
701 to a lesser extent than the Siberian samples, making the latter exceptional cases in the
702 LCC database. Most worldwide granulites exhibit a θ of -3° and can deviate from the
703 $\epsilon_{\text{Ce}}-\epsilon_{\text{Nd}}$ mantle array by ≈ 0.46 epsilon Ce units per billion years. Using this
704 compilation, we propose new parent/daughter ratios for the LCC: $^{138}\text{La}/^{142}\text{Ce} = 0.00380$

705 ± 0.00007 and $^{147}\text{Sm}/^{144}\text{Nd} = 0.128 \pm 0.007$. These findings suggest that high-grade
706 metamorphism and/or reworking occurring in LCC conditions may lead to enhanced
707 mobility of certain LREE in LCC rocks and deviation of the La-Ce and Sm-Nd isotopic
708 systems from the mantle array over time.

709

710 The LCC represented by the granulite database cannot be reproduced by a typical mass-
711 balance budget of the BSE. The later results in the isotope composition of the deep
712 continental crust (MCC+LCC) far to the left of the ϵCe - ϵNd mantle array; it would
713 require to incorporate a substantial proportion of Siberian-like granulites within the
714 continents, although they are rare in the LCC database. Alternatively, incorporating a
715 substantial proportion of LCC in mass-balance calculations, considering the massive
716 recycling of LCC back into the mantle, provides a more reliable explanation. We
717 estimate that approximately 3 to 5 times the mass of the continental crust has been
718 recycled into the mantle throughout Earth's history, mostly comprising the LCC. This
719 modeling brings the deep crust composition closer to the mantle array and aligns better
720 with the constraints from the granulite database.

721

722

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724

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736

737

738 **Appendix A. Supplementary material**

739

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

741 Supplementary data 1: Major-, trace-element contents, and Ce-Nd isotopes.

742 Supplementary data 2: Database including Archean and post-Archean granulites from
743 the literature.

744 Supplementary material: 1) Estimating the θ angle; 2) Parameters and equations used
745 in mass-balance budget calculations.

746

747

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1027

1028 **Table caption:**

1029

1030 **Table 1.** La-Ce and Sm-Nd isotope measurements. Uncertainties reported on Ce and
1031 Nd measured isotope ratios are 2se analytical errors in the last decimal place. Cerium

1032 and Nd isotopic compositions are expressed in present-day $\epsilon\text{Ce} = \left(\frac{\frac{^{138}\text{Ce}}{^{142}\text{Ce}}_{\text{sample}}}{\frac{^{138}\text{Ce}}{^{142}\text{Ce}}_{\text{CHUR}}} - 1 \right) \times$

1033 10,000 and $\epsilon\text{Nd} = \left(\frac{\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{sample}}}{\frac{^{143}\text{Nd}}{^{144}\text{Nd}}_{\text{CHUR}}} - 1 \right) \times 10,000$ using the following CHUR

1034 references: $^{138}\text{Ce}/^{142}\text{Ce} = 0.02256577$ (Israel et al., 2020) and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630$

1035 (Bouvier et al., 2008). ϵCe_t and ϵNd_t are isotopic compositions corrected from

1036 radioactive decay using published ages for the West European samples, 3.0 Ga for the

1037 Canadian samples (see section 2.1) and the 2.7 Ga Sm-Nd errorchron age for the

1038 Siberian rocks (Fig. 4). Parent/daughter ratios were obtained using the natural isotope

1039 abundances of Meija et al. (2016): $^{138}\text{La}/^{142}\text{Ce} = \text{La}/\text{Ce} \times 0.00804772$; $^{147}\text{Sm}/^{144}\text{Nd} =$

1040 $\text{Sm}/\text{Nd} \times 0.60455923$. CHUR values for parent/daughter ratios are $^{138}\text{La}/^{142}\text{Ce} =$

1041 0.00311 and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1960$ (Bouvier et al., 2008 ; Israel et al., 2020). Decay

1042 constant values are $\lambda_{\beta, 138\text{La}} = 2.37 \times 10^{-12} \text{ yr}^{-1}$, $\lambda_{\text{EC}, 138\text{La}} = 4.44 \times 10^{-12} \text{ yr}^{-1}$ (Sato and
1043 Hirose, 1981; Shimizu et al., 1984; Tanimizu, 2000) and $\lambda_{147\text{Sm}} = 6.539 \times 10^{-12} \text{ yr}^{-1}$
1044 (Begemann et al., 2001).

1045

1046 **Table 2.** Elemental and isotopic compositions of Earth's main silicate reservoirs. BSE,
1047 bulk silicate Earth; EDR, early depleted reservoir; DMM, depleted MORB mantle; CC,
1048 continental crust; UCC, upper continental crust; MCC, middle continental crust; LCC,
1049 lower continental crust. Isotopic compositions for CC and MCC+LCC reservoirs are
1050 estimated using mass-balance calculations for a chondritic BSE and an EDR. Errors
1051 given for the mass-balance calculated isotopic compositions (CC, MCC+LCC) and the
1052 mass fraction of the continental crust ($m_{\text{bulkCC}}/m_{\text{BSE}}$) correspond to the standard
1053 deviation on the mean value calculated for the composition models of Rudnick and Gao
1054 (2014) and Hacker et al. (2015 – mafic and felsic model). Errors on literature data are
1055 2 sd. Values in italics refer to literature data: ^{a*} based on Lu content from McDonough
1056 and Sun, 1995 and chondritic REE ratios from Israel et al., 2020 and Bouvier et al.,
1057 2008; ^b from Israel et al., 2020; ^c from Bouvier et al., 2008; ^d from Rudnick and Gao,
1058 2014; ^e and ^f correspond to felsic and mafic compositions from Hacker et al., 2015, ^g
1059 from Allègre and Lewin, 1989; Chauvel et al., 2014; Goldstein and Jacobsen, 1988. ^{d*},
1060 ^{e*}, and ^{f*} are recalculated after modification of the relative proportions of CC sub-
1061 reservoirs. ^{h*}Cerium and Nd concentrations and $\epsilon_{\text{Ce}}-\epsilon_{\text{Nd}}$ values of the EDR are
1062 estimated using the method suggested in Jackson and Jellinek, 2013 for a Sm/Nd ratio
1063 increased by 2.65%

1064

1065 **Figure captions**

1066

1067 **Fig. 1.** Total alkali *versus* silica (TAS) diagram for West European, Canadian and
1068 Siberian samples from this study (colored large circles and diamonds) and literature
1069 (white squares – Koreshkova et al., 2011; Moyen et al., 2017; Shatsky et al., 2019,
1070 2018). Literature granulites are from Hacker et al., 2015 with an additional 670 new
1071 data points from the literature (grey squares are Archean granulites and pink squares
1072 are post-Archean granulites – see [Supplementary data 2](#) for references). Stars represent
1073 reference composition for LCC, MCC and UCC from Rudnick and Gao, 2014 (R&G)
1074 and Hacker et al., 2015 (most mafic and felsic models – H^{+}_{mafic} and H^{+}_{felsic}). We chose
1075 not to represent any subdivision in the TAS diagram to compare the silica and alkali
1076 contents in all our metaigneous and metasedimentary samples with literature data,
1077 without consideration of their rock type. IV9 is out of limits of this diagram (SiO_2
1078 content is 32 wt.% and $\text{Na}_2\text{O}+\text{K}_2\text{O}$ content is 3.3 wt.%)

1079

1080 **Fig. 2.** Bulk-CC normalized REE patterns for samples from this study together with
1081 values for UCC, MCC and LCC from Rudnick and Gao (2014). The Siberian samples
1082 are divided into two distinct graphs according to their Sm/Nd ratio (samples with
1083 $\text{Sm/Nd} > 0.24$ and < 0.24 are in graphs b and d respectively), and their felsic or mafic
1084 composition. Three Udachnaya kimberlites from Maas et al., 2005 are also represented.

1085

1086 **Fig. 3.** ϵNd *versus* ϵCe measured in the Siberian, Canadian, and West European
1087 samples. CC samples from literature are reported for comparison (Gao et al., 2016;
1088 Hasenstab et al., 2020; Hayashi et al., 2004; Israel et al., 2020; Lee et al., 2010, 2001;
1089 Liu et al., 1990; Minami et al., 1995; Shimizu et al., 1996, 1990, 1988, 1988; Tanaka
1090 et al., 1987; Tazoe et al., 2007; Tusch et al., 2022). The black line is the mantle array
1091 regression line (Israel et al., 2020 – $\epsilon\text{Nd} = -7.3 (\pm 0.5) \times \epsilon\text{Ce} + 0.4 (\pm 0.3)$), the dark grey

1092 area shows the mean dispersion of OIB on both sides of the mantle array ($\pm 0.2 \epsilon\text{Ce}$ and
1093 $\pm 1.3 \epsilon\text{Nd}$) and light grey area shows their maximum dispersion ($\pm 0.9 \epsilon\text{Ce}$ and $\pm 6.3 \epsilon\text{Nd}$).

1094

1095 **Fig. 4.** (a) La-Ce and (b) Sm-Nd errorchron diagrams for the Siberian samples and for
1096 granulite xenoliths from Udachnaya (Koreshkova et al., 2011). Regression lines and
1097 errorchron ages (± 2 sd) are calculated using model 3 of IsoplotR with 1% errors on
1098 Sm/Nd ratios and 0.3% errors on La/Ce ratios. None of the regressions define an
1099 isochron (MSWD values of 11 and 28 for (a) and (b), respectively). Two Udachnaya
1100 kimberlites from Maas et al., 2005 are also represented.

1101

1102 **Fig. 5.** $\epsilon\text{Nd}_{(0 \rightarrow t)}$ versus $\epsilon\text{Ce}_{(0 \rightarrow t)}$ diagram representing Ce-Nd isotopic paths (arrows)
1103 calculated from measured La/Ce and Sm/Nd ratios and present-day Ce-Nd isotopic
1104 compositions. (a) Correction for radioactive decay was done using published ages of
1105 0.257, 0.200, and 0.270 Ga for the samples from Beaunit, Bournac, and Ivrea,
1106 respectively, and 3.0 Ga for the Canadian samples (see section 2.1). (b) Correction for
1107 radioactive decay was done using the 2.7 Ga Sm-Nd errorchron age for the Siberian
1108 rocks. The Ce-Nd mantle array regression line is from Israel et al. (2020). (c)
1109 Representation of hypothetical isotopic paths (arrows) related to their oriented angle θ ,
1110 with the mantle array (thick grey line), estimated in degrees in an orthonormal system.
1111 The θ value depends only on the La/Ce and Sm/Nd ratios. Evolution trends pointing
1112 toward the left of the mantle array have negative θ values, or positive θ values if they
1113 point to the right of the mantle array. The zero (or 180°) value means the evolution
1114 trend of the sample is parallel to the mantle array. $f_{\text{Sm/Nd}}$ and $f_{\text{La/Ce}}$ describe the evolution
1115 of a sample relative to the chondritic reference, where $f_{\text{Sm/Nd}} =$
1116 $((^{147}\text{Sm}/^{144}\text{Nd}_{\text{sample}}/^{147}\text{Sm}/^{144}\text{Nd}_{\text{CHUR}})-1)$ and $f_{\text{La/Ce}} =$

1117 $((^{138}\text{La}/^{142}\text{Ce}_{\text{sample}}/^{138}\text{La}/^{142}\text{Ce}_{\text{CHUR}})-1)$. Sample 386-13 is presented as an example. Its
1118 isotopic path shows an angle with the mantle array equal to -9.8° . Note that angles
1119 observed in a classical $\epsilon\text{Ce}-\epsilon\text{Nd}$ space are distorted due to the large difference of scale
1120 between the x and y axes of the diagram (see miniature for angles represented in an
1121 orthonormal diagram).

1122

1123 **Fig. 6.** Geographical distribution of literature samples used for their La, Ce, Nd and Sm
1124 contents, presented in pie charts (a) for Archean samples and (b) for post-Archean
1125 samples.

1126

1127 **Fig. 7.** (a) $\Delta\epsilon\text{Ce}$ per billion years *versus* θ and (b) $^{138}\text{La}/^{142}\text{Ce}$ *versus* $^{147}\text{Sm}/^{144}\text{Nd}$
1128 diagrams estimated for the European, Canadian and Siberian samples from this study
1129 and compared to Archean ($n = 445$) and post-Archean granulites ($n = 1136$) from
1130 literature. Histograms are also associated with both variables of the diagram for
1131 Archean and post-Archean granulites, and Siberian crustal xenoliths (data from this
1132 study and Koreshkova et al., 2011 and Shatsky et al., 2019) together with their Kernel
1133 Density Estimation (KDE – calculated using IsoplotR – grey, pink and red curves,
1134 respectively). $\Delta\epsilon\text{Ce}$ is calculated as the relative horizontal deviation from the mantle
1135 array after one billion years of evolution, using initial isotopic compositions located on
1136 the mantle array and measured parent/daughter ratios. The dark grey and light grey
1137 fields in (a) represent the mean and maximum horizontal scatter of OIBs that are used
1138 to define the $\epsilon\text{Ce}-\epsilon\text{Nd}$ mantle array, respectively. The dotted line represents the linear
1139 regression calculated from Archean and post-Archean samples using IsoplotR for θ
1140 values between -5 and -1° ($n = 411$). Its equation is $\Delta\epsilon\text{Ce}/\text{Ga} = 0.15 (\pm 0.03) \times \theta - 0.01$
1141 (± 0.05) . Reference parent/daughter values for the LCC from Rudnick and Gao, 2014

1142 (R&G) and Hacker et al., 2015 (mafic and felsic models – H^{+}_{mafic} and H^{+}_{felsic} ,
1143 respectively) are represented in (b) as black, blue and green lines and stars, respectively.
1144 Parent/daughter ratios resulting in isotopic compositions evolving along the mantle
1145 array ($\theta = 0^\circ$) and with an angle of -3° relative to the mantle array are represented as
1146 black and purple lines, respectively.

1147 Scale for θ is limited between -20 and 20° to improve readability (bin size 1° – 249
1148 samples out of scale, including IV1 with $\theta = -176^\circ$). Scales are also limited between
1149 0.001 and 0.010 for $^{138}\text{La}/^{142}\text{Ce}$ (bin size 0.0002 – 17 samples out of scale) and between
1150 0.025 and 0.25 for $^{147}\text{Sm}/^{144}\text{Nd}$ (bin size 0.005 – 53 samples out of scale) to improve
1151 readability.

1152

1153 **Fig. 8.** ϵCe versus ϵNd measured in mantle-derived samples (Bellot et al., 2018, 2015;
1154 Dickin et al., 1987; Israel et al., 2020; Makishima and Masuda, 1994; Tanaka et al.,
1155 1987; Willig and Stracke, 2019; Willig et al., 2020) and in crustal samples (references
1156 in Fig. 3). The orange and grey fields represent mass-balance calculated isotopic
1157 compositions for the bulk CC and for the MCC+LCC, respectively, for both chondritic
1158 and non-chondritic compositions of the BSE, using parameters in Table 2 and relative
1159 proportions of the CC sub-reservoirs from Rudnick and Gao, 2014. The red and black
1160 fields represent mass-balance calculated isotopic compositions for the bulk CC and for
1161 the MCC+LCC, respectively, using parameters in Table 2 for a bulk CC after modifying
1162 the relative proportions of UCC, MCC and LCC (8.1, 7.6 and 84.3%, respectively –
1163 thick lines for Rudnick and Gao based compositions). The purple lines represent the
1164 equidistant lines from the mantle array for $\Delta\epsilon\text{Ce} = -0.8$ and -1.1 , estimated for 1.8 and
1165 2.4 Ga-old granulites, using $\Delta\epsilon\text{Ce}/\text{Ga} = -0.46$.

Sample	$^{138}\text{La}/^{142}\text{Ce}$	$^{138}\text{Ce}/^{142}\text{Ce}$	2se	ϵCe	ϵCe_t	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	2se	ϵNd	ϵNd_t
Bournac – Crustal xenoliths										
BOU2	0.00428	0.02256804	37	1.01	0.8	0.155	0.512308	5	-6.28	-5.2
BOU3	0.00374	0.02257441	24	3.83	3.7	0.118	0.512240	6	-7.61	-5.6
BOU4	0.00385	0.02256812	21	1.04	0.9	0.121	0.512251	6	-7.39	-5.5
Ivrea – Verbano zone - Uplifted crust										
IV1	0.00254	0.02256429	22	-0.65	-0.5	0.219	0.512975	4	6.73	5.9
IV5a	0.00407	0.02256904	24	1.45	1.2	0.121	0.512183	4	-8.72	-6.1
IV5b	0.00486	0.02256883	22	1.36	0.9	0.115	0.512113	4	-10.09	-7.3
IV9	0.00410	0.02256910	14	1.47	1.2	0.140	0.511876	3	-14.72	-12.8
IV10	0.00401	0.02256961	19	1.70	1.4	0.107	0.512391	4	-4.66	-1.6
Puy Beaunit – Crustal xenoliths										
B4-Glite	0.00387	0.02256509	22	-0.30	-0.5	0.147	0.512778	5	2.89	4.5
B6	0.00477	0.02256668	20	0.40	-0.0	0.096	0.512572	6	-1.12	2.2
B152	0.00388	0.02256895	24	1.41	1.2	0.109	0.512101	5	-10.31	-7.5
BG4	0.00434	0.02256718	22	0.62	0.3	0.117	0.512556	4	-1.44	1.1
BPG1	0.00372	0.02256718	17	0.63	0.5	0.149	0.512391	5	-4.67	-3.1
BPG2	0.00368	0.02256490	22	-0.39	-0.5	0.156	0.512718	3	1.72	3.0
BG6	0.00483	0.02256894	23	1.41	0.9	0.122	0.512216	6	-8.08	-5.6
B2-gneiss	0.00448	0.02256892	23	1.39	1.0	0.081	0.512020	4	-11.90	-8.1
Udachnaya pipe, Siberian craton – Crustal xenoliths										
1001-16	0.00363	0.02257045	25	2.07	0.6	0.094	0.510823	1	-35.25	0.1
1003-14	0.00283	0.02256514	23	-0.28	0.5	0.150	0.512000	1	-12.30	3.8
1006-14	0.00187	0.02256183	19	-1.75	1.8	0.140	0.511519	2	-21.48	-2.6
1006-16	0.00329	0.02256663	27	0.38	-0.1	0.115	0.511147	1	-28.93	-0.8
1010-13	0.00314	0.02256687	20	0.49	0.4	0.150	0.511923	2	-13.80	2.0
1014-14	0.00461	0.02257248	20	2.97	-1.3	0.099	0.511155	2	-28.78	5.1
226-03	0.00357	0.02256808	19	1.03	-0.3	0.149	0.511979	2	-12.70	3.8
231-17	0.00325	0.02256714	22	0.61	0.2	0.118	0.511197	2	-27.95	-0.7
232-17	0.00336	0.02256859	26	1.25	0.5	0.155	0.511932	1	-13.62	0.7
246-17	0.00242	0.02256238	21	-1.50	0.5	0.172	0.512390	1	-4.69	3.7
322-13	0.00362	0.02256835	22	1.14	-0.3	0.113	0.511202	1	-27.86	0.9
360-13	0.00373	0.02257041	20	2.05	0.3	0.121	0.511220	2	-27.51	-1.3
370-13	0.00600	0.02257880	19	5.78	-2.5	0.069	0.510497	2	-41.61	2.6
386-13	0.00284	0.02256410	23	-0.74	0.0	0.132	0.511520	1	-21.66	0.5
98-13	0.00270	0.02256459	27	-0.52	0.6	0.111	0.511188	2	-28.14	1.6
Precambrian shield, Canadian craton – Crustal composite										
NQ	0.00392	0.02257114	32	2.38	-0.2	0.109	0.511368	2	-24.38	9.2
BI	0.00387	0.02257188	31	2.71	0.3	0.105	0.511033	1	-30.91	4.2
SS	0.00423	0.02257179	38	2.67	-0.9	0.100	0.511044	2	-30.69	6.4
SQ	0.00311	0.02256581	30	0.02	0.0	0.113	0.512300	1	-6.19	25.4

Table 1

Chondritic		Earth									
	BSE	DMM (mean MORB)	UCC (mean loess)	CC	MCC	LCC	CC	MCC	LCC		
							84% LCC				
% of CC				100	29.6 ^d	38.8 ^c	100			7.6	84.3
Ce (µg/g)	1.7 ^{a*}		63 ^d	43 ^d 49 ^e 36 ^f	53 ^d 39 ^e 27 ^f	20 ^d 46 ^e 19 ^f	26 ^{d*} 47 ^{e*} 23 ^{f*}				
Nd (µg/g)	1.3 ^{a*}		27 ^d	20 ^d 23 ^e 19 ^f	25 ^d 19 ^e 16 ^f	11 ^d 22 ^e 13 ^f	13 ^{d*} 22 ^{e*} 14 ^{f*}				
εCe	0.00 ± 0.29 ^b	-1.1 ± 0.6 ^b	1.8 ± 0.3 ^b	1.1 ± 0.3 to 0.2 ± 0.2	0.4 ± 0.3 to -1.1 ± 0.5		1.3 ± 0.7 to 0.4 ± 0.4			1.2 ± 0.8 to 0.1 ± 0.4	
εNd	0.00 ± 0.21 ^c	9.7 ± 2.3 ^b	-11.2 ± 3.0 ^b	-21 to -10 ^g	-28.1 ± 2.4 to -9.2 ± 0.2		-21 to -10 ^g			-22.6 ± 0.8 to -9.8 ± 0.1	
m _{bulkCC} /m _{BSE}				0.026 ± 0.013			0.033 ± 0.022				
Early	Depleted	Earth									
	EDR	DMM (mean MORB)	UCC (mean loess)	CC	MCC	LCC	CC	MCC	LCC		
							84% LCC				
% of CC				100	29.6 ^d	38.8 ^c	100			7.6	84.3
Ce (µg/g)	1.5 ^{h*}		63 ^d	43 ^d 49 ^e 36 ^f	53 ^d 39 ^e 27 ^f	20 ^d 46 ^e 19 ^f	26 ^{d*} 47 ^{e*} 23 ^{f*}				
Nd (µg/g)	1.2 ^{h*}		27 ^d	20 ^d 23 ^e 19 ^f	25 ^d 19 ^e 16 ^f	11 ^d 22 ^e 13 ^f	13 ^{d*} 22 ^{e*} 14 ^{f*}				
εCe	-0.3 ^{h*}	-1.1 ± 0.6 ^b	1.8 ± 0.3 ^b	1.2 ± 0.3 to 0.4 ± 0.2	0.7 ± 0.42 to -0.9 ± 0.4		1.5 ± 0.7 to 0.5 ± 0.5			1.4 ± 0.9 to 0.3 ± 0.4	
εNd	3.1 ^{h*}	9.7 ± 2.3 ^b	-11.2 ± 3.0 ^b	-21 to -10 ^g	-28.1 ± 2.4 to -9.2 ± 0.2		-21 to -10 ^g			-22.6 ± 0.8 to -9.8 ± 0.1	
m _{bulkCC} /m _{EDR}				0.016 ± 0.008			0.024 ± 0.011				

Table 2

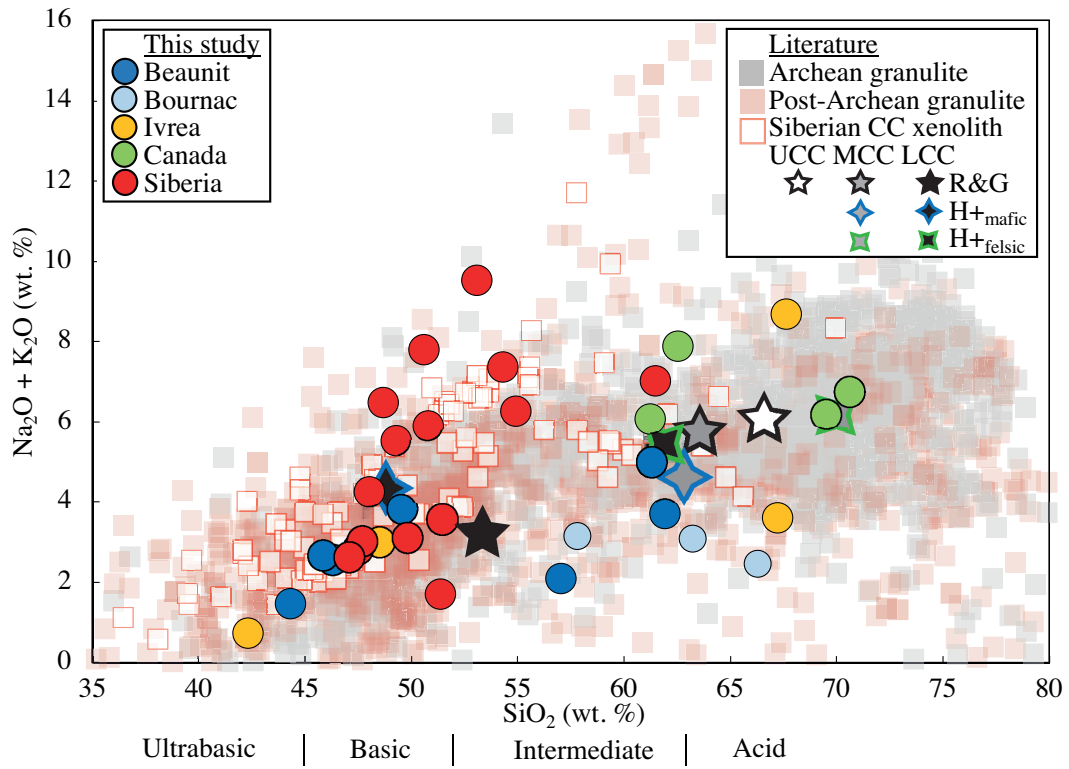


Figure 1

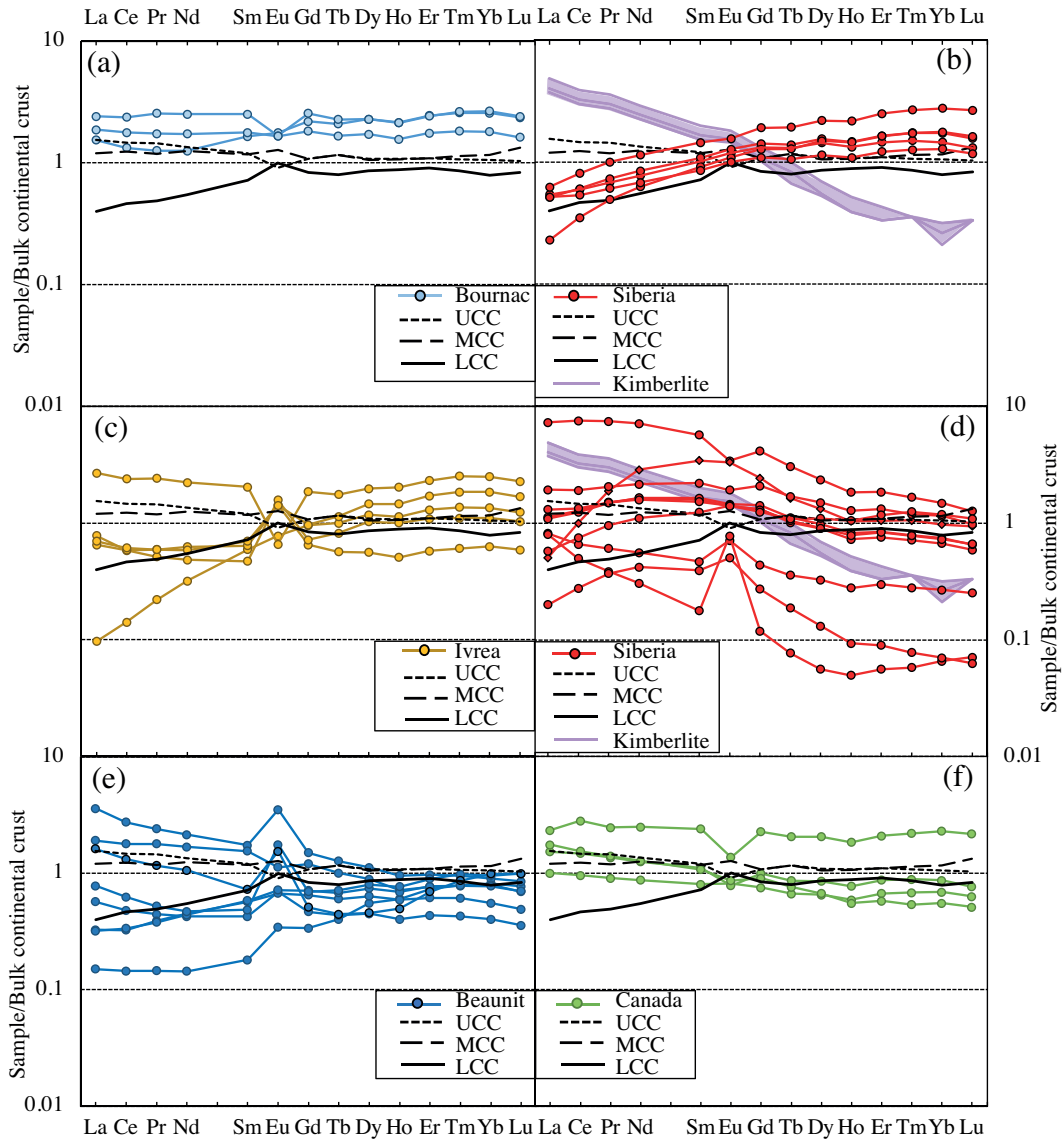


Figure 2

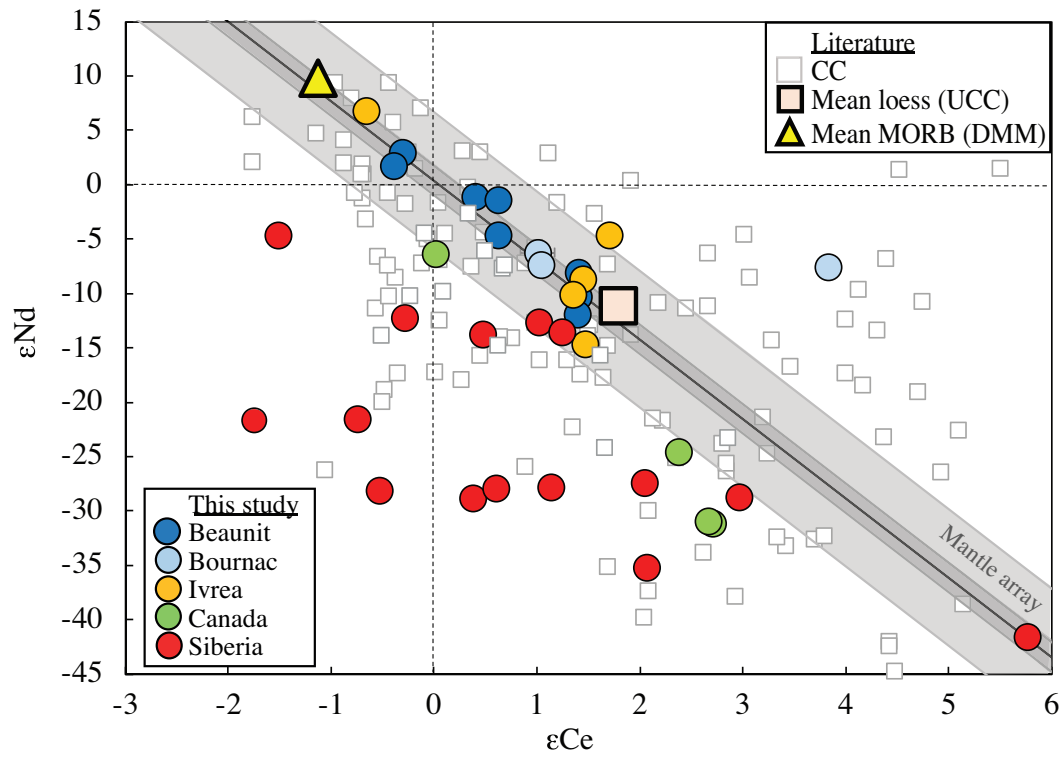


Figure 3

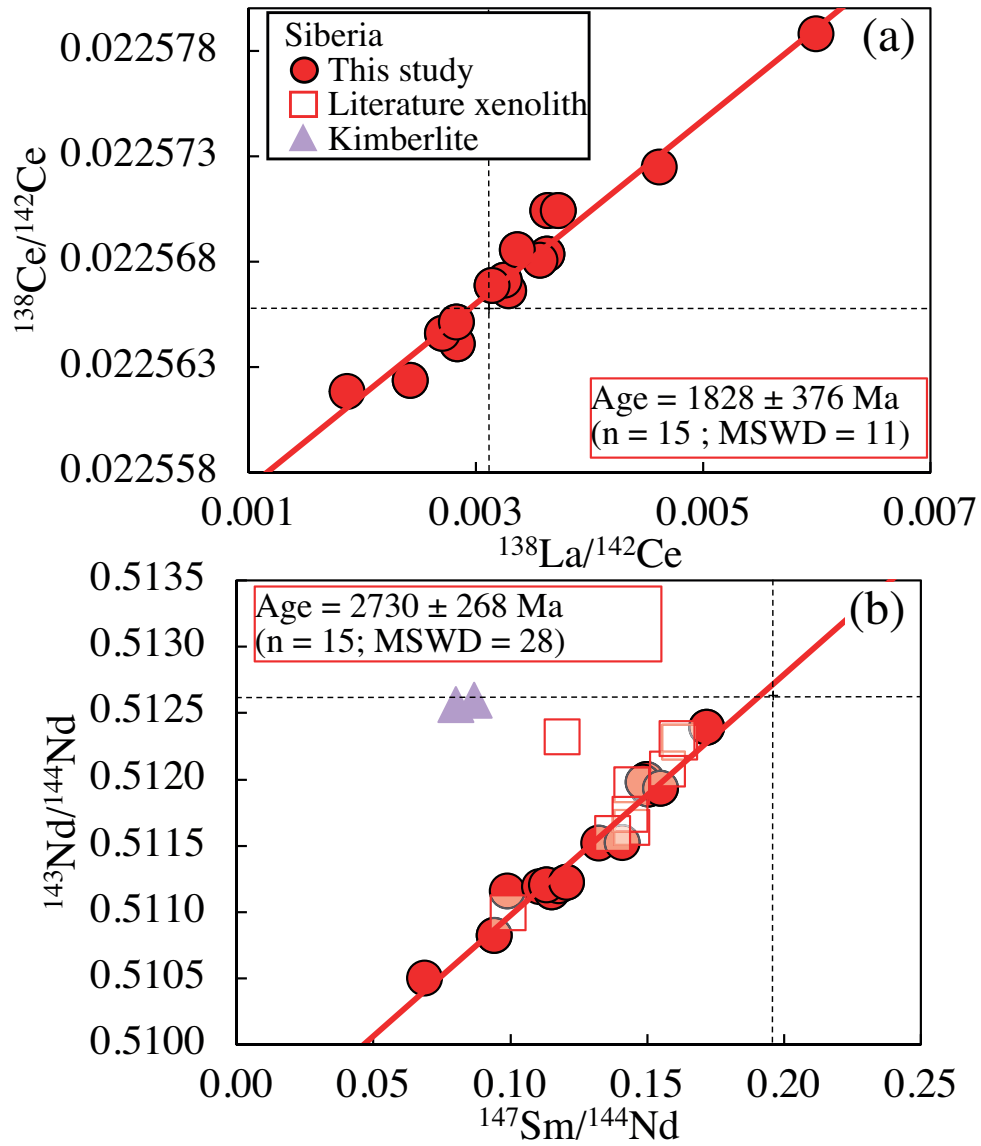


Figure 4

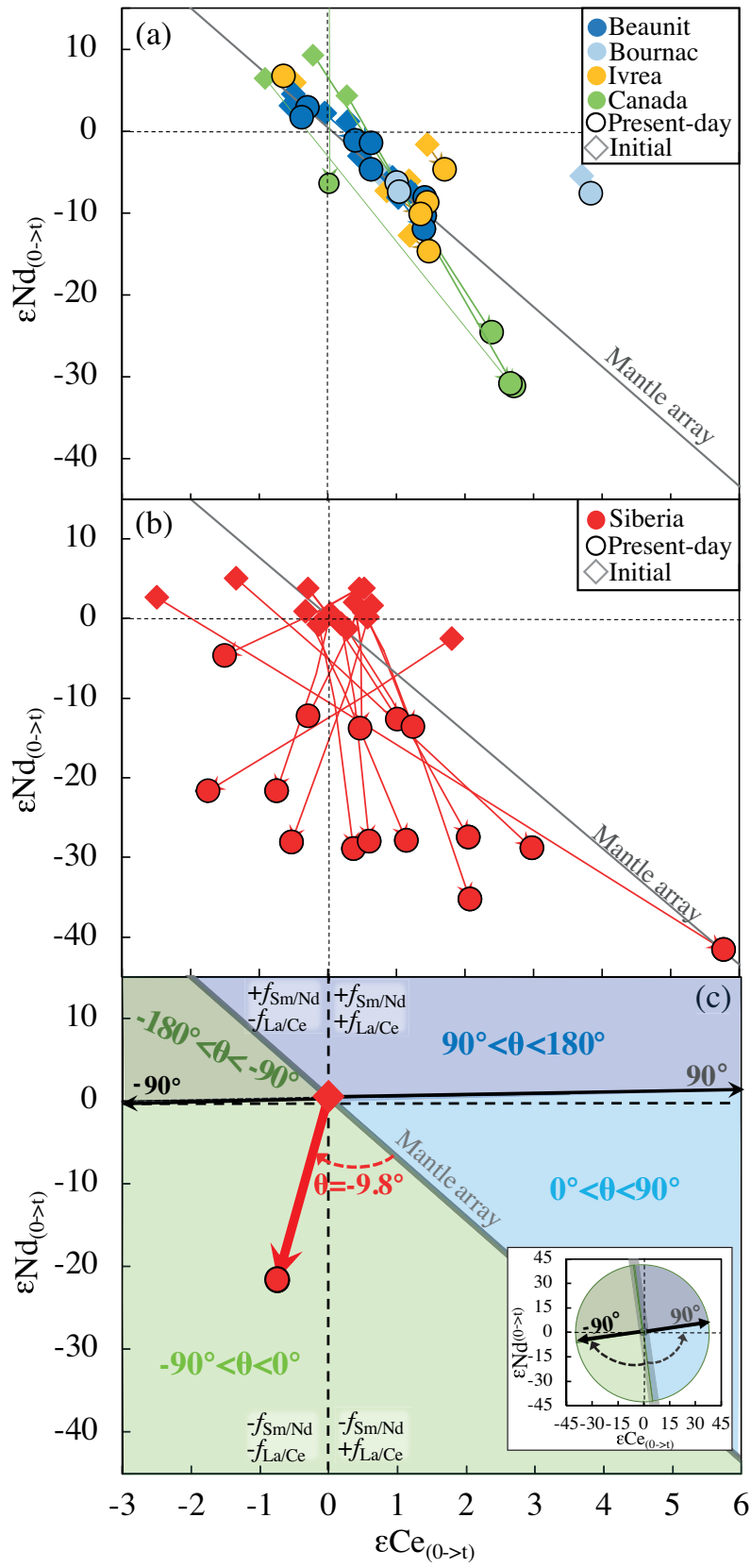


Figure 5

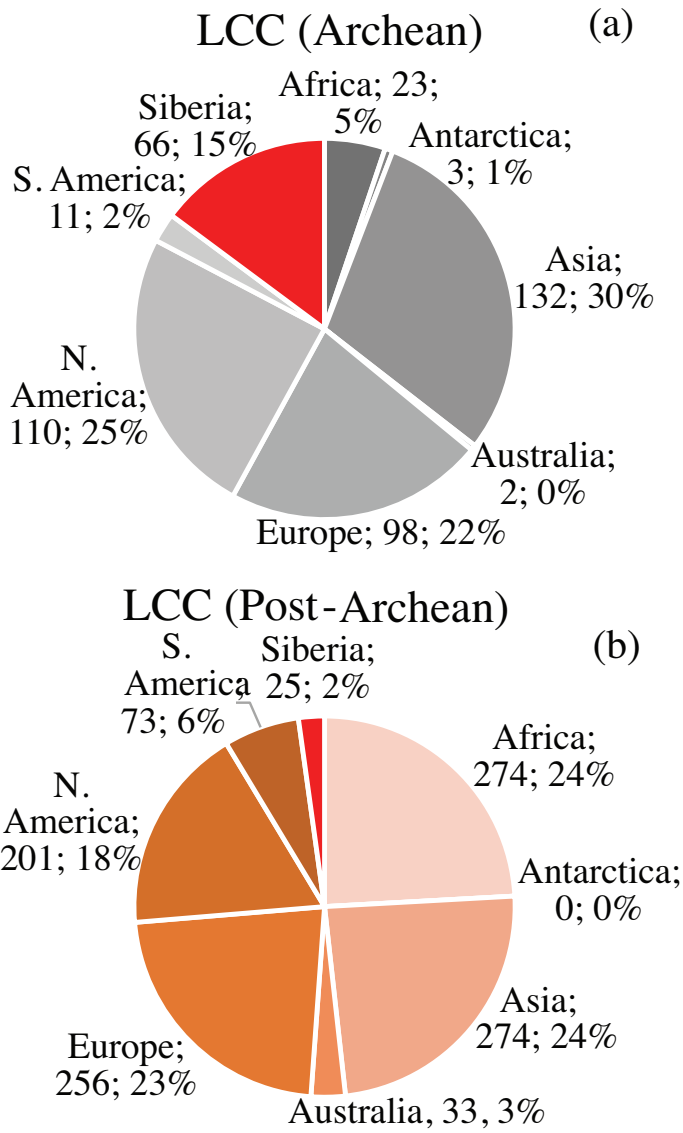


Figure 6

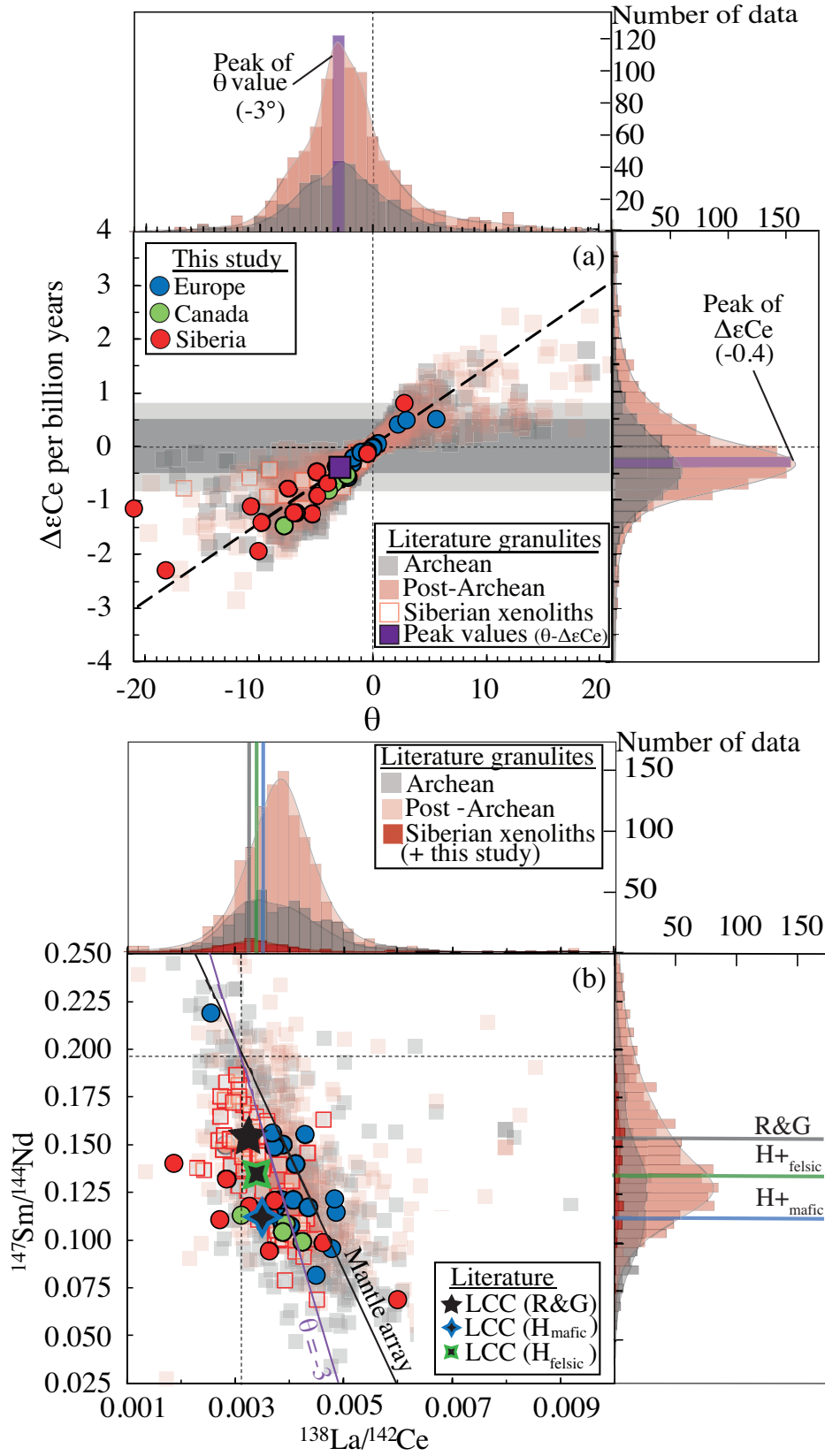


Figure 7

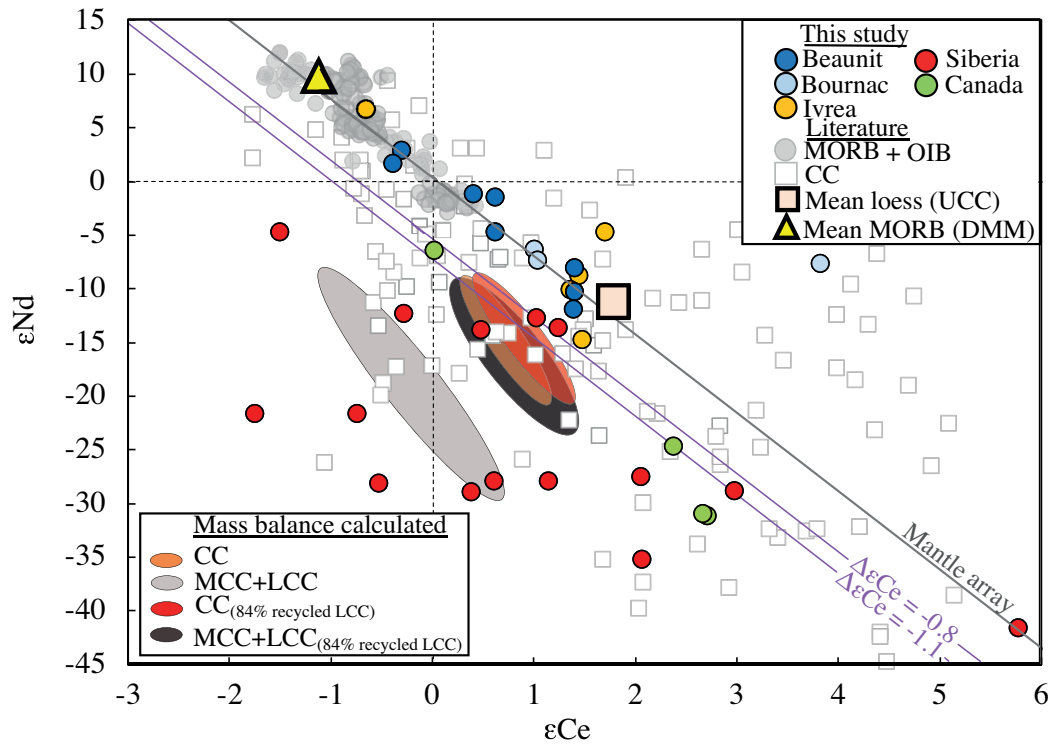


Figure 8

SUPPLEMENTARY MATERIAL

**FIRST CE-ND ISOTOPE MEASUREMENTS OF MIDDLE AND LOWER
CONTINENTAL CRUST SAMPLES SUPPORT MASSIVE LOWER CRUST
RECYCLING OVER EARTH'S HISTORY**

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1. Estimating the θ angle

The $\theta_{\text{sample-mantle array}}$ angle is the angle existing between the evolution vector of any sample and the vector representing the mantle array, in a $\epsilon\text{Ce}-\epsilon\text{Nd}$ diagram (epsilon values calculated at zero for the present-day value of the sample and at any time t by using the CHUR value at the same time t). The equation of the mantle array is $\epsilon\text{Nd} = \epsilon\text{Ce} \times -7.3 + 0.4$ (Israel et al., 2020)

We first fix the initial isotopic composition of any sample on the mantle array. In this case, we chose $\epsilon\text{Ce}_i=0$ and $\epsilon\text{Nd}_i=0.4$ as the intercept of the mantle array. We use the CHUR value for cerium when calculating ϵCe .

We estimate the isotopic composition of a sample as the result of radioactive decay over a period t (here fixed at 1 Ga), using the measured parent/daughter ratios (ϵCe_t and ϵNd_t).

The horizontal distance $\Delta\epsilon\text{Ce}_{\text{sample-MA}}$ between a sample and the mantle array is solely due to the radioactive decay, and is expressed as:

$$\Delta\epsilon\text{Ce}_{\text{sample-MA}} = \epsilon\text{Ce}_t - \frac{\epsilon\text{Nd}_t - 0.4}{-7.3}$$

The norm of the evolution vector of a sample in an orthonormal diagram is:

$$N_{\text{Ve,sample}} = \sqrt{(\epsilon\text{Ce}_t - \epsilon\text{Ce}_i)^2 + (\epsilon\text{Nd}_t - \epsilon\text{Nd}_i)^2}$$

Similarly, we estimate the norm of the mantle array as a vector, by considering $\epsilon\text{Ce}_A - \epsilon\text{Ce}_B = 1$ and $\epsilon\text{Nd}_A - \epsilon\text{Nd}_B = -7.3$ because for a variation of ϵCe of +1 between a point A and a point B, the variation of ϵNd is -7.3, according to the equation of the mantle array in a plot of ϵNd vs ϵCe :

$$N_{\text{Ve,MA}} = \sqrt{(\epsilon\text{Ce}_A - \epsilon\text{Ce}_B)^2 + (\epsilon\text{Nd}_A - \epsilon\text{Nd}_B)^2} = \sqrt{1^2 + (-7.3)^2}$$

We then estimate the vector product of these vectors:

$$P_{\text{Ve}} = (\epsilon\text{Ce}_A - \epsilon\text{Ce}_B) \times (\epsilon\text{Ce}_t - \epsilon\text{Ce}_i) + (\epsilon\text{Nd}_A - \epsilon\text{Nd}_B) \times (\epsilon\text{Nd}_t - \epsilon\text{Nd}_i)$$

The cosine of the angle between these two vectors is:

$$\text{Cos}(\theta) = \frac{P_{\text{Ve}}}{\sqrt{N_{\text{Ve,sample}} \times N_{\text{Ve,MA}}}}$$

And finally the angle is $\text{Arc}(\text{Cos}(\theta))$.

However, the calculated angle is not oriented. We set θ to be negative if $\Delta\epsilon\text{Ce}_{\text{sample-MA}}$ is negative (the isotopic composition of the sample tends to evolve below the mantle array). Or θ is positive if $\Delta\epsilon\text{Ce}_{\text{sample-MA}}$ is positive (the isotopic composition of the sample tends to evolve above the mantle array).

2. Parameters and equations used in mass-balance budget calculations

Table S1: Elemental and isotopic compositions of Earth's silicate reservoirs used in mass-balance calculations: BSE, bulk silicate Earth; DMM, depleted MORB mantle (DMM = mean MORB); CC, continental crust; UCC, upper continental crust; MCC, middle continental crust; LCC, lower continental crust. Values in italics refer to literature data: Ce, Nd contents and Ce/Nd ratios are from Rudnick and Gao (R&G) and Hacker et al., 2015 (H et al. - for both mafic and felsic model) for CC, UCC and MCC+LCC reservoirs and they are calculated from Lu contents from McDonough and Sun, 1995 and chondritic REE ratios (see Israel et al., 2020 for further details). ϵCe and ϵNd values for DMM (mean MORB) and UCC (mean loess) are from Israel et al., 2020. ϵNd values for the bulk CC correspond to the entire range of suggested compositions for this reservoir in the literature ($\epsilon\text{Nd} = -21$ to -10 according to Allègre and Lewin, 1989 and Chauvel et al., 2014, respectively). Note that the LCC accounts for 56.7 wt% of the MCC+LCC reservoir.

	Reservoir	Ce ($\mu\text{g/g}$)	Nd ($\mu\text{g/g}$)	Ce/Nd	ϵCe	ϵNd	W
	BSE	<i>1.7</i>	<i>1.3</i>	<i>1.28</i>	<i>0.00</i>	<i>0.00</i>	
	DMM				<i>-1.1</i>	<i>9.7</i>	
R&G	Bulk CC	<i>43</i>	<i>20</i>	<i>2.15</i>	<i>1.0 - 0.2</i>	<i>-21 - -10</i>	<i>0.020 - 0.032</i>
	UCC	<i>63</i>	<i>27</i>	<i>2.33</i>	<i>1.8</i>	<i>-11.2</i>	
	MCC+LCC	<i>34</i>	<i>17</i>	<i>2.01</i>	<i>-1.1 - 0.3</i>	<i>-28 - -9</i>	
H et al.,	Bulk CC	<i>36</i>	<i>19</i>	<i>1.89</i>	<i>1.3 - 0.4</i>	<i>-21 - -10</i>	<i>0.022 - 0.034</i>
Most mafic model	MCC+LCC	<i>22</i>	<i>14</i>	<i>1.57</i>	<i>0.6 - -1.3</i>	<i>-29 - -9</i>	
H et al.,	Bulk CC	<i>49</i>	<i>23</i>	<i>2.13</i>	<i>1.0 - 0.2</i>	<i>-21 - -10</i>	<i>0.018 - 0.028</i>
Most felsic model	MCC+LCC	<i>43</i>	<i>21</i>	<i>2.08</i>	<i>0.5 - -0.8</i>	<i>-27 - -9</i>	

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, where the mass fraction of DMM = 1 - mass fraction of CC.

The mass fraction of mantle depleted by the extraction of the continental crust is then:

$$\frac{m_{DM}}{m_{PM}} = \frac{m_{CC}}{m_{PM}} \times \frac{1-W}{W} \quad (7)$$

Where the typical present-day mass of the continental crust (m_{cc}) is 2.367×10^{25} g and the mass of the primitive mantle (m_{PM}) is 4.007×10^{27} g (Lodders and Fegley, 1998).

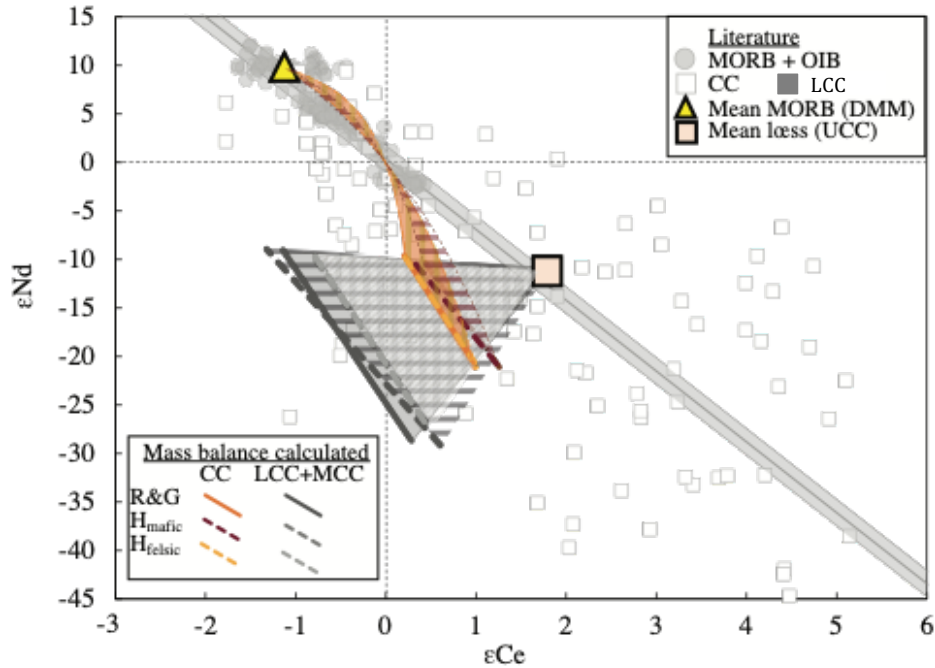


Figure S1: (a) ϵ_{Ce} vs. ϵ_{Nd} diagram representing the calculated crustal reservoirs by mass-balance calculation. Epsilon values are normalized according to the CHUR references defined for Nd with $^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}} = 0.512630$, $^{147}\text{Sm}/^{144}\text{Nd} = 0.196$. The orange, striped dark red and striped light orange fields represent the different hyperbolic DMM–CC mixing curves calculated for a chondritic BSE with Nd and Ce contents from Rudnick and Gao and Hacker et al., 2015 for extremely mafic and felsic CC models, respectively. Similarly, the grey, striped dark grey and striped light grey fields represent the UCC–(MCC–LCC) mixing lines using Nd and Ce contents from Rudnick and Gao, 2003 and Hacker et al., 2015. Note that the information given by the parent/daughter ratios of the UCC, MCC and LCC requires the MCC and LCC to have a higher Nd isotopic composition ($\text{Sm}/\text{Nd}_{\text{LCC}} > \text{Sm}/\text{Nd}_{\text{MCC}} > \text{Sm}/\text{Nd}_{\text{UCC}}$) and lower Ce isotopic composition ($\text{La}/\text{Ce}_{\text{LCC}} < \text{La}/\text{Ce}_{\text{MCC}} < \text{La}/\text{Ce}_{\text{UCC}}$) than the UCC. Our calculations are based on the entire range of literature estimates for the Nd isotopic composition of the bulk CC.