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Ca-Sr isotope and chemical evidence for distinct sources of carbonatite and silicate mantle metasomatism

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1 **Abstract** (404 words)

2 Enrichments in light REE without concomitant enrichments in high-field-strength
3 elements in mantle peridotites are usually attributed to inputs from carbonate-rich
4 melts and referred to as ‘carbonatite’ metasomatism as opposed to interaction with
5 evolved silicate melts. Alternatively, both enrichment types are ascribed to percolating
6 volatile-bearing mafic liquids whose chemical signatures evolve from ‘silicate’ to
7 ‘carbonatite’. Here we compare these models for peridotites in which these
8 enrichment types are combined, as may be common in the mantle. We report new
9 Ca-Sr-Nd isotope and chemical data for lherzolite and harzburgite xenoliths from
10 Spitsbergen that were metasomatized, first, by silicate, then by carbonate-rich melts
11 that formed carbonate-bearing pockets replacing earlier minerals. Seven crushed
12 samples were treated with acetic acid that dissolved carbonates formed in the latest
13 event, but not silicates. The leachates (acid-removed carbonates making up 0.6–1.4%
14 of total sample mass) contain much more Sr than the residues after leaching
15 (277–2923 vs. 16–60 ppm), have a greater overall $^{87}\text{Sr}/^{86}\text{Sr}$ range (0.7049–0.7141 vs.
16 0.7036–0.7055) and higher $^{87}\text{Sr}/^{86}\text{Sr}$ in each sample than the residues. The leachates
17 have lower $\delta^{44/40}\text{Ca}$ range (0.17–0.68‰) than the residues (0.78–1.00‰), as well as
18 lower $\delta^{44/40}\text{Ca}$ than the residues in all samples but one. By and large, the carbonates
19 are out of Ca-Sr isotope equilibrium with the host peridotites implying that the older
20 silicate and younger carbonatite metasomatism were produced by different parental
21 melts, thus supporting the existence of distinctive carbonate-rich metasomatic media
22 in the lithospheric mantle, possibly including recycled materials.

23 The $\delta^{44/40}\text{Ca}$ in the leachates (i.e. carbonates, 0.17–0.68‰) are well below bulk
24 silicate Earth (BSE) estimates ($0.94 \pm 0.05\%$) and $\delta^{44/40}\text{Ca}$ in non-metasomatized
25 melt-depleted mantle. Yet, $\delta^{44/40}\text{Ca}$ in the non-leached whole rock (WR)
26 carbonate-bearing samples (0.75–0.95‰) fall within, or are only slightly lower than,
27 the BSE range. The $^{87}\text{Sr}/^{86}\text{Sr}$ range in these WR samples (0.7030–0.7112) includes
28 very high values for peridotites with large aggregates of dolomite and Mg-calcite. It

29 appears that both carbonatite and silicate metasomatism may produce $\delta^{44/40}\text{Ca}$ values
30 lower than the BSE such that Ca-isotope data cannot robustly tell apart these two
31 enrichment types, yet carbonatite metasomatism may yield the lowest $\delta^{44/40}\text{Ca}$.
32 Carbonates, even at small mass fractions, are significant hosts of Sr in the WR
33 Spitsbergen peridotites (8–51 wt.% of Sr mass) because of very high Sr
34 concentrations, but add little to WR Ca balance (3–12 wt.%). As a result, high Sr
35 content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may be indices (though not definitive proofs) of
36 carbonatite metasomatism in mantle rocks.

37

38 **Key words:** carbonatite metasomatism; silicate metasomatism; Ca isotopes; Sr
39 isotopes; mantle xenolith; peridotite; Spitsbergen

1. INTRODUCTION

40

41

42 Studies of chemical and mineralogical composition of mantle rocks suggested that
43 they were affected by two types of metasomatism, 'silicate' and 'carbonatite', the
44 latter characterized by strong enrichments in light rare earth elements (LREE) at low
45 high-field-strength elements (HFSE) (Ionov et al., 1993; Rudnick et al., 1993; Yaxley
46 et al., 1991). These results implied an important, widespread role for carbonatite melts
47 as agents of mantle metasomatism, despite the rarity of these melts at the Earth's
48 surface (Hauri et al., 1993). However, other studies on mantle xenoliths and peridotite
49 massifs inferred that enrichment patterns similar to those attributed to carbonate-rich
50 melts could be produced by reactive percolation of volatile-bearing silicate melts.
51 Numerical modeling of this process (Navon and Stolper, 1987) obtained a range of
52 chemical patterns from a single parental liquid at different distances from its source as
53 a result of chromatographic fractionation (due to different element compatibility),
54 with 'carbonatite' signatures at the percolation front (e.g. Bodinier et al., 1990; Ionov
55 et al., 2002a).

56 The existence of distinct, carbonatite and silicate, agents of mantle metasomatism
57 can be ascertained using isotope compositions, which may differ in samples affected
58 by media generated from different sources, but are similar in samples reworked by
59 derivatives of a single initial agent. Here we present new Ca-Sr-Nd isotope and trace
60 element data for a suite of mantle peridotites from the island of Spitsbergen that
61 contain carbonate-bearing pockets of mantle origin replacing earlier minerals (Ionov
62 et al., 1993; Ionov et al., 1996). Calcium and strontium are typical chemical
63 components of carbonatites. The main objective of this study is to distinguish the
64 Ca-Sr isotope inputs of the carbonates in the rocks using leaching with acetic acid that
65 dissolves only carbonates. The data are used to evaluate directly the effects of
66 carbonate-rich liquids on mantle metasomatism as well as to establish whether
67 different types and stages of metasomatism were produced by distinct types and

68 sources of media.

69 Calcium is a major lithophile element in the Earth's mantle and crust (e.g.
70 Hofmann, 1988). It has six naturally occurring stable isotopes (^{40}Ca , ^{42}Ca , ^{43}Ca , ^{44}Ca ,
71 ^{46}Ca and ^{48}Ca) with ~10% mass difference ($\Delta m/m$) between ^{40}Ca and ^{44}Ca (DePaolo,
72 2004). Calcium isotopic compositions are usually expressed as delta notation, e.g.
73 $\delta^{44/40}\text{Ca}$ relative to NIST SRM 915a: $[(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}/(^{44}\text{Ca}/^{40}\text{Ca})_{\text{NIST-SRM-915a}} - 1] \times$
74 1000.

75 The application of Ca stable isotopic composition in geosciences has rapidly
76 developed in the last two decades because Ca isotopes show important fractionation at
77 low temperatures near the Earth's surface, and are considered important indices of a
78 wide range of biological and chemical processes in sedimentology, environmental
79 geochemistry, weathering etc. (e.g. Blättler and Higgins, 2017; DePaolo, 2004; Fantle
80 and Tipper, 2014; Farkaš et al., 2007; Skulan et al., 1997). Ca isotopes may also give
81 new insights into global reservoirs and high-temperature processes in the Earth's
82 interior and extraterrestrial samples (see Antonelli and Simon (2020) for a review).

83 Recent studies revealed significant Ca isotope variations in mantle-derived mafic
84 igneous rocks (Huang et al., 2011; Liu et al., 2017a; Zhu et al., 2020; Zhu et al.,
85 2018b) and carbonatites (Amsellem et al., 2020; Banerjee and Chakrabarti, 2019;
86 Banerjee et al., 2021; Sun et al., 2021). Ca isotope variations were reported also for
87 the lithospheric mantle and ascribed to additions of recycled crustal materials (Chen et
88 al., 2018; Huang et al., 2011; Liu et al., 2017a; Zhu et al., 2020; Zhu et al., 2018b)
89 and/or equilibrium and disequilibrium isotope fractionation at high temperatures
90 during: (a) melt extraction (Chen et al., 2019; Kang et al., 2017), (b) reaction with
91 silicate and carbonate-rich melts or fluids (Ionov et al., 2019; Kang et al., 2017; Kang
92 et al., 2019; Kang et al., 2016; Zhao et al., 2017). This opens up new prospects in
93 mantle studies, but also creates new challenges, in particular how to distinguish Ca
94 isotope variations in mantle rocks produced by intra-mantle fractionation from those
95 caused by mixing with recycled crustal materials.

96 An important notion in mantle studies is that of the Bulk Silicate Earth (BSE),
97 sometimes called “primitive mantle” (PM), defined as silicate portion of the Earth as
98 it existed after separation of the core but before it was differentiated to crust and
99 heterogeneous mantle (Hofmann, 1997). Present-day mantle reservoirs were formed
100 by melt extraction from the BSE (Workman and Hart, 2005), metasomatism and
101 recycling of surface materials. The BSE composition may be evaluated using fertile
102 mantle peridotites that experienced no melt extraction or metasomatism (Palme &
103 O’Neill, 2003; McDonough & Sun, 1995). So far, the only robust $\delta^{44/40}\text{Ca}$ estimate for
104 the BSE ($0.94 \pm 0.05\%$, 2sd) has been given by Kang et al. (2017) based on 14
105 xenoliths of non-metasomatized fertile lherzolites with Al_2O_3 (3.7–4.7 wt.%) and CaO
106 (3.2–4.0 wt.%) overlapping the PM estimates (~4.5 and 3.6%, respectively).

107 Kang et al. (2017) obtained a higher than BSE average $\delta^{44/40}\text{Ca}$ ($1.06 \pm 0.06\%$, 2sd)
108 for strongly melt-depleted (1.3–1.7 wt.% Al_2O_3), non-metasomatized (LREE-depleted)
109 peridotites and suggested that high degrees of melt extraction produce slightly higher
110 (by ~0.12%) $\delta^{44/40}\text{Ca}$ in residues. A similar $\delta^{44/40}\text{Ca}$ range (and $\delta^{44/40}\text{Ca}$ evolution
111 trend during melting) was found by Chen et al. (2019) in melt-depleted lherzolites
112 from Alpine massifs. Kang et al. (2017) also reported usually lower $\delta^{44/40}\text{Ca}$ (0.25–
113 0.96%) in metasomatized (LREE-enriched) peridotites, in particular for low-CaO (≤ 1
114 wt.%) rocks with Ca budget dominated by metasomatic inputs.

115 Strontium, like Ca, is an alkali earth element, but its BSE abundance is three orders
116 of magnitude lower (20 vs. 25400 $\mu\text{g/g}$). Strontium is highly incompatible during
117 peridotite melting because cation Sr^{2+} is much larger than Ca^{2+} such that Sr partition
118 coefficients between clinopyroxene (major Sr host in common lherzolites) and mafic
119 melts are well below unity (<https://earthref.org/KDD/e:38/>). Using the Rb-Sr
120 radiogenic isotope system for dating mantle materials is problematic due to high
121 mobility of these elements (e.g. Pearson et al., 2014), but the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may
122 indicate the sources of mantle-derived rocks and magmas (Hofmann, 2003), as well as
123 recycling of crustal materials (e.g. Guo et al., 2020; Xu, 2002). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in

124 mantle rocks are affected both by their age and the evolution of the Rb/Sr ratio
125 that may be hard to disentangle to identify sources of metasomatism. By comparison,
126 Ca isotope compositions do not evolve with time, but may reveal mantle sources,
127 mixing or, alternatively, mass-dependent fractionation during mantle processes.
128 Overall, the evidence from Sr and Ca isotopes may be complementary.

129 Previous studies found carbonates usually associated with (Na,Al)-rich silicate
130 glass in some Spitsbergen xenoliths (Ionov et al., 1993; Ionov et al., 1996). The
131 carbonates do not represent quenched carbonatite liquids but are crystal cumulates
132 from carbonate-rich silicate melts reacting with host peridotites (Ionov and Harmer,
133 2002). Trace element patterns estimated for such liquids (Ionov, 1998) are consistent
134 with many features of ‘carbonatite’ metasomatism (enrichments in LREE, Sr, Ba and
135 negative HFSE anomalies). However, similar element patterns were found also in
136 peridotites that contain no carbonates and attributed to reactive percolation and
137 extreme fractionation of volatile-bearing silicate melts (Ionov et al., 2002a).

138 Overall, it remains uncertain whether the carbonates in mantle xenoliths from
139 Spitsbergen and other worldwide localities (e.g. Dautria et al., 1992; Ionov et al.,
140 2018; Laurora et al., 2001) originate from particular carbonate-rich liquids or are
141 late-stage derivatives of evolving volatile-bearing silicate melts. In a more general
142 sense, the ambiguity concerns the origin of chemical signatures usually seen as
143 evidence for ‘carbonatite’ mantle metasomatism (e.g. Rivalenti et al., 2004; Tappe et
144 al., 2017).

145 This uncertainty is addressed here using Ca-Sr isotope and chemical data on
146 carbonate-bearing Spitsbergen xenoliths, notably by treating WR samples with acetic
147 acid that dissolves only carbonates. Analyses of the leachates, residues and bulk-rocks
148 discern metasomatic inputs of late-stage carbonates (extracted by leaching) from those
149 of earlier events (hosted by residues). We show that trace element patterns and Ca-Sr
150 isotope compositions of the leachates, hence carbonates, are distinct from those in the
151 silicate minerals of the host peridotites. We infer that the carbonate pockets were

152 formed from specific carbonate-rich liquids responsible for ‘carbonatite’
153 metasomatism. We further discuss the application of Ca-Sr isotope data to gain
154 insights into the sources and mechanisms of metasomatism in the mantle.

155

156 **2. GEOLOGICAL SETTING AND SAMPLES**

157 Spitsbergen is the largest island of the Svalbard archipelago, the northwestern (NW)
158 edge of the Eurasian continent. It was connected to Greenland until the opening of the
159 North Atlantic Ocean, and is located now ~200 km east of the mid-ocean ridge (e.g.
160 [Vagnes and Amundsen, 1993](#)), between the North Atlantic and the Arctic Oceans at
161 similar distances from Norway, Greenland and the North Pole.

162 Mantle xenoliths reported here were collected in alkali basaltic rocks at three
163 Quaternary eruption centers in NW Spitsbergen: Sverre, Halvdan and Sigurd (e.g.
164 [Griffin et al., 2012](#)). Most of the xenoliths are coarse to medium-grained spinel
165 lherzolites containing 5–12% clinopyroxene ([Ionov et al., 2002a](#); [Ionov et al., 1996](#));
166 samples 26A and 318 are harzburgites ([Streckeisen, 1976](#)). The samples from Sverre
167 are mainly ‘anhydrous’ lherzolites, while the Halvdan peridotites usually contain
168 amphibole with modal abundances ranging from rare grains in sample 4-90-9 to 5–8%
169 in samples 318 and 315-6. Samples 21-6 and 43-86 have accessory apatite ([S-Fig. 1a](#)
170 in Electronic Appendix 2 (EA2)). The peridotites equilibrated at 840–990°C based on
171 two-pyroxene thermometry ([Ionov et al., 2002a](#)). Sample 4A-90-1 from Sigurd is a
172 coarse-grained clinopyroxene-amphibole vein.

173 The xenoliths contain carbonates as mosaic aggregates of dolomite and Mg-calcite
174 with smooth curvilinear boundaries made up of interlocking grains 20–50 µm in size
175 ([Ionov, 1998](#); [Ionov et al., 1993](#); [Ionov et al., 1996](#)). They mainly occur in irregularly
176 distributed pockets that typically make up ≤ 2–3% of the rock and are 0.2–2 mm in
177 size. The pockets also contain small (<100 µm) euhedral grains of clinopyroxene and
178 olivine, Fe-Ni sulfides and (Na,Al)-rich silicate glass with micro-phenocrysts of
179 Cr-rich spinel ([S-Fig. 1d-h](#), EA2). The pockets replace minerals of host peridotite,

180 usually orthopyroxene, amphibole and spinel, that have embayed, resorbed outlines
181 and spongy reaction zones. Less commonly the carbonates occur as mosaic aggregates
182 in veins and at grain junctions of silicates (S-Fig. 1b-c, EA2).

183 Such assemblages closely resemble experimental and natural evidence for
184 mantle-derived carbonatite metasomatism (e.g. Green and Wallace, 1988). Studies of
185 melt and fluid inclusions in other carbonate-bearing, metasomatized mantle xenoliths
186 suggest that carbonate segregations formed from initially homogeneous
187 silicate-carbonate melts that separate into carbonatite and silicate components when
188 they intrude and react with host peridotites (Frezzotti et al., 2002; Laurora et al.,
189 2001).

190 The carbonate globules are larger and more abundant in four out of seven xenoliths
191 selected for leaching (samples 43-86, 4-36-90, 4-90-9 and 21-6). Some carbonate
192 aggregates are altered at rims to fine grained and turbid materials consisting of
193 composite microcrystalline (usually magnesite-ankerite) spherules immersed in
194 amorphous Mg-rich silicate material with low totals (S-Fig. 1g). They are common in
195 samples SB-4 and 28B (Ionov et al., 1993), but their proportions relative to primary
196 carbonates are negligible in large pockets (samples 43-86, 4-36-90, 4-90-9 and 21-6).

197 Textural evidence suggests that the Mg-Fe-rich carbonates formed by alteration of
198 primary dolomite and Mg-calcite in contact with silicates during the eruption, likely
199 due to heating and pressure drop. However, no evidence exists for the formation of
200 additional carbonates in low-temperature processes. Na-rich silicate glass in contact
201 with carbonates is not altered and contains fresh sulfide globules (Ionov et al., 1996).
202 The silicate glass in the xenoliths is very different from the glass in the host basaltic
203 rocks in terms of color, phenocryst assemblage and chemical composition, which
204 rules out links with host magma infiltration (Ionov et al., 1993).

205 Previous chemical and isotope studies of Spitsbergen xenoliths, including those
206 that contain no carbonates, found combined effects of three discrete evolution stages.
207 (1) The protoliths for the lithospheric mantle were formed by melt extraction from

208 fertile mantle with melting degrees ranging from <10% for some lherzolites to 25%
209 for the harzburgites in the Paleoproterozoic that depleted the rocks in incompatible
210 elements (Choi et al., 2010; Ionov et al., 2002a). (2) The melting residues were then
211 metasomatized by silicate liquids to form amphibole and apatite as well as enrich the
212 residues in incompatible elements (Ionov et al., 2002a), radiogenic Sr isotopes
213 (0.7025–0.7036) and non-radiogenic Nd isotopes (0.5123–0.5136) (Ionov et al.,
214 2002b). (3) Ingress of carbonate-rich media formed discordant carbonate-bearing
215 pockets shortly before the eruption of host magma (Ionov, 1998).

216 Ionov et al. (2002a) outlined two types of trace element patterns in WR samples
217 and coarse silicate minerals of Spitsbergen xenoliths (Type-1 and Type-2) that
218 combine features attributed to silicate or carbonatite metasomatism, e.g. negative
219 Ti-Zr-Hf anomalies in Type-2 rocks and strongly fractionated LREE with high La/Ce
220 (and H₂O/Ce, Tang et al. (2020)) in Type-1 bulk-rocks and clinopyroxene. Ionov et al.
221 (2002a) argued that the remarkable enrichments in the least compatible elements,
222 along with fractionation of elements with similar compatibility, in Type 1 samples
223 may not be due to mixing of melting residues with common enriched mafic melts but
224 to extreme fractionation near melt percolation front. They used numerical modelling
225 of reactive porous flow of volatile-bearing silicate liquids in depleted peridotites to
226 explain their trace element patterns and Sr-Nd isotope ratios (Ionov et al., 2002a;
227 Ionov et al., 2002b). Those studies, however, did not address specifically xenoliths
228 containing late-stage carbonates and pockets of fine-grained minerals and silicate
229 glass. They did not establish the provenance of carbonate-rich media responsible for
230 carbonate formation, particularly whether they are related to late-stage derivatives of
231 silicate metasomatism in the Spitsbergen mantle.

232

233 3. SAMPLE TREATMENT AND ANALYTICAL METHODS

234

235 The xenoliths analyzed in this study are listed in Table 1, along with a summary of

236 information on available data from this and previous studies.

237 **3.1 Leaching experiments**

238 Acid-leaching experiments were done on seven carbonate-bearing peridotites to
239 obtain separately the compositions of carbonates and silicates (as well as spinel and
240 apatite) in each sample. Our approach is different from that employed by [Ionov et al.](#)
241 [\(1993\)](#) who leached two of these samples ([Table 1](#)) with 10% HNO₃ for about 20
242 minutes in an ultrasonic bath, which did not only dissolve carbonates but may have
243 also affected other phases, e.g. silicate glass. In this study, the samples were treated
244 with dilute acetic acid (HAc), which dissolves carbonates while leaving silicate and
245 oxide phases intact. Specifically, aliquots of 4–10 g of rock were crushed by hand to
246 ≤1 mm in an agate mortar. These samples were transferred to centrifuge tubes and
247 weighed. About 15 ml of 10% HAc were added to the centrifuge tubes, which usually
248 produced gas bubbles; the tubes were shaken for about 30 min. The samples were
249 centrifuged and the leachates (solutions with dissolved carbonates) extracted by
250 pipette; the leaching residues were washed twice with MQ water, which was added to
251 the initial leachates.

252 To convert the acetate salts in the leachates to nitrates and remove remaining HAc,
253 the leachate solutions were dried and treated with concentrated HNO₃ several times
254 on a hot plate at 150°C until clear solutions were obtained, then transferred to Teflon
255 beakers. The solutions were dried, and dissolved in 2M HNO₃ for major and trace
256 element and Sr-Nd-Ca isotopic analysis.

257 After the leachate extraction, the residues were dried overnight at 105°C and
258 weighed to calculate the mass loss on leaching, and the relative mass of the carbonate
259 and acid-resistant components in each sample. Finally, the leaching residues were
260 ground to 200 mesh powder for analyses.

261

262 **3.2 Major and trace elements**

263 Major and trace element concentrations were obtained in this study for leachates

264 and residues from seven xenoliths, as well as for six WR samples (non-leached).
265 Another six WR samples were analyzed for major elements only. We also use WR
266 major and trace element data on 17 Spitsbergen xenoliths reported earlier (Ionov et al.,
267 2002a; Ionov et al., 1993; Ionov et al., 1996).

268 The major and trace element analyses were done at the State Key Laboratory of
269 Isotope Geochemistry (SKLIG), Guangzhou Institute of Geochemistry (GIG),
270 Chinese Academy of Sciences (CAS). About 80 mg of residue or WR powder was
271 fully digested in Teflon beakers with HF-HNO₃ mixtures placed in steel-jacketed
272 PARR bombs following procedures reported in Wang et al. (2018). These solutions
273 were used for both major and trace element, and Ca-Sr-Nd isotopic analyses.

274 Major elements (except Si) were analyzed by inductively coupled plasma atomic
275 emission spectrometry (ICP-AES); Chinese reference samples GSR-1, GSR-2, GSR-3,
276 SARM-4 and SY-4 were used for external calibration. Repeated analyses of USGS
277 reference materials indicate external reproducibility better than 10%. Trace elements
278 were determined by ICP mass spectrometry (ICP-MS) following procedures reported
279 in Du et al. (2018) with reproducibility better than 5%.

280

281 3.3 Sr-Nd isotopes

282 Chemical separation and isotope analyses of Sr and Nd were done at the SKLIG-
283 GIG-CAS. Aliquots of sample solution containing ~800 ng of Sr were transferred to a
284 Teflon beaker, dried, and dissolved in 0.25 ml of 3 M HNO₃. To separate Sr from
285 sample matrix, the sample solution was loaded onto a column packed with 0.25 ml of
286 Sr Spec resin (Zhu et al., 2018b). After elution by 6.5 ml of 3 M HNO₃, Sr was
287 collected in 3 ml of 0.05 M HNO₃. Strontium isotopes were measured on a Nu Plasma
288 1700 multi-collector (MC) ICP-MS instrument. The ⁸⁷Sr/⁸⁶Sr ratios were corrected for
289 instrumental mass fractionation by normalizing to ⁸⁸Sr/⁸⁶Sr = 8.375209. The ⁸⁷Sr/⁸⁶Sr
290 values obtained for reference materials NBS-987 (0.710254 ± 0.000014; 2sd, n = 12)
291 and BHVO-2 (0.703503 ± 0.000009; n = 1, internal precision) are consistent with

292 literature data (Table 2) (Charlier et al., 2006; Meng et al., 2019; Thirlwall, 1991;
293 Weis et al., 2006).

294 More than half of the leachates, residues and WR samples are too low in Nd for
295 precise Nd isotope analyses. Neodymium was purified using a two-column procedure
296 reported in Du et al. (2019) and Ma et al. (2013). The first column filled with 1 g of
297 AG50W-X12 (200–400 mesh) resin was eluted with 2.5 M HCl to extract the REE.
298 Neodymium was separated from other REE on the second column filled with 1 g of
299 Ln Spec (50–100 mesh) resin and eluted with 0.25 M HCl. The isotopic ratios were
300 measured on a Nu Plasma 1700 MC-ICP-MS. The $^{143}\text{Nd}/^{144}\text{Nd}$ values for reference
301 materials JNdi (0.512111 ± 0.000013 ; 2sd, n = 13) and W-2 (0.512512 ± 0.000008 ; n
302 = 1, internal precision) agree within error with literature data (Li et al., 2012; Luo et
303 al., 2020; Tanaka et al., 2000) as shown in Table 2.

304

305 **3.4 Calcium isotopes**

306 Chemical purification and analyses of Ca isotope compositions were done at the
307 SKLIG-GIG-CAS following procedures in Zhu et al. (2018a), Zhu et al. (2016) and
308 Liu et al. (2017b). An aliquot of sample solution containing 30–50 μg of Ca was
309 mixed with a ^{42}Ca - ^{43}Ca double-spike solution containing 8 μg Ca, dried, re-dissolved
310 in 0.1 ml of 1.6 M HCl, loaded onto a column filled with 1 ml of AG MP-50
311 (100–200 mesh) and eluted with 1.6 M HCl. Most of the matrix was eluted with 17 ml
312 of 1.6 M HCl, then Ca was collected in 27 ml of 1.6 M HCl. Samples low in CaO (< 3
313 wt.%) were passed through the column twice. The Ca recovery was >99%. Column
314 chemistry was run in batches of 20 samples; at least one reference material and blank
315 were processed as unknowns with each batch. Total procedure blanks were 15–70 ng,
316 which is negligible compared to 30–50 μg of Ca loaded onto the column.

317 Calcium isotopic compositions were measured on a ‘Thermo Triton’ thermal
318 ionization mass-spectrometer (TIMS). About 1 μl 10% HNO_3 containing 5 μg Ca was
319 loaded onto the center of out-degassed single Ta (99.995%) filament. A droplet of 1 μl

320 activator (10% H₃PO₄) was loaded to cover the sample spot. A single sequence of cup
321 configuration was adopted with ⁴⁰Ca, ⁴¹K, ⁴²Ca, ⁴³Ca and ⁴⁴Ca collected in L2, C, H1,
322 H2 and H3 Faraday cups, respectively. ⁴¹K was measured to evaluate isobaric
323 interference of ⁴⁰K on ⁴⁰Ca, and an online correction was done using ⁴⁰K/⁴¹K = 1.7384
324 × 10⁻³ Heuser et al. (2002). Instrumental fractionation was corrected using the
325 ⁴²Ca-⁴³Ca double spike method similar to that of Heuser et al. (2002) with the
326 exponential fractionation law. The Ca isotope data are reported as δ^{44/40}Ca relative to
327 NIST SRM 915a. NIST SRM 915a and IAPSO seawater reference materials were
328 routinely measured to monitor instrumental stability. Two standard deviation (2sd) of
329 average δ^{44/40}Ca for NIST SRM 915a analyzed in the course of this study was 0.12‰
330 (n = 34). Three to seven aliquots of each sample solution were loaded on different
331 filaments and measured separately; the reproducibility of δ^{44/40}Ca in the duplicate
332 analyses of each sample is ± 0.08‰ (2SE, see footnote of Table 3).

333 The δ^{44/40}Ca values for NIST SRM 915a, IAPSO seawater and four USGS
334 reference materials (DTS-1, DTS-2, PCC-1 and BHVO-2) measured in the same
335 session, and literature data are listed in Table 2. Average δ^{44/40}Ca values obtained for
336 NIST SRM 915a and IAPSO seawater are -0.02 ± 0.12‰ (2sd, n = 21) and 1.82 ±
337 0.10‰ (2sd, n = 10), respectively; those of DTS-1, DTS-2, PCC-1 and BHVO-2 are
338 1.61 ± 0.09‰ (2sd, n = 3), 1.10 ± 0.11‰ (2sd, n = 3), 1.10 ± 0.08‰ (2sd, n = 3) and
339 0.84 ± 0.09‰ (2sd, n = 5), respectively. These results are consistent with data
340 reported in the literature (Amini et al., 2009; Farkaš et al., 2007; Feng et al., 2017; He
341 et al., 2017; Huang et al., 2010; Valdes et al., 2014). Two WR samples were replicated
342 by digestion of a separate powder batch; one leachate was duplicated by processing in
343 column chemistry (Table 3). Duplicate δ^{44/40}Ca values for all the three samples are
344 within analytical uncertainty (Table 3).

345

346

4. RESULTS

347

348 Major and trace element compositions of leachates, residues and WR xenoliths in
349 this study are listed in [S-Tables 1 and 2](#) of Electronic Appendix 1 (EA1) along with
350 relevant literature data ([Ionov et al., 2002a](#); [Ionov et al., 1993](#); [Ionov et al., 1996](#)). The
351 Ca-Sr-Nd isotope compositions obtained in this study are given in [Tables 3 and 4](#).
352 Acid leaching was used here to separate the metasomatic inputs of late-stage
353 carbonates (extracted by leaching) from those of earlier melt extraction and silicate
354 metasomatism hosted by residues ([Ionov et al., 2002a](#); [Ionov et al., 2002b](#)).

355

356 **4.1 Chemical compositions**

357 The totals of the leachate analyses are low (46–63 wt.%) due to release of CO₂
358 from carbonates (44–48 wt.% in pure calcite and dolomite). The main components of
359 the leachates are CaO, MgO and FeO. Their proportions range broadly and outline
360 two end-members. Leachates from xenoliths 4-36-90, 4-90-9 and 21-6 contain 21–33
361 wt.% CaO, 12–20% MgO and 2.2–3.4% FeO, with higher CaO than for MgO in each
362 case. The leachate 43-86 has less CaO (20 wt.%) than MgO (27 wt.%). Leachates
363 from the other three xenoliths (63-90-18, SB-4 and 28B) are low in CaO (9–15 wt.%)
364 and have two to four times more MgO (34–37 wt.%) and 11–14 wt.% FeO.

365 Selected chemical data on WR samples and residues after leaching are plotted in
366 [Fig. 1](#) vs. Al₂O₃ together with data on fertile to melt-depleted peridotites from Tariat
367 in Mongolia ([Ionov and Hofmann, 2007](#)). Leached residues of the Spitsbergen
368 xenoliths generally have lower Sr, CaO and Ca/Al ratios than the WR samples, in line
369 with the removal of Ca-Sr-rich carbonates. However, all but one residues have higher
370 CaO and Ca/Al than melt-depleted mantle ([Fig. 1a](#)), but show no Sr enrichments ([Fig.](#)
371 [1c](#)). The leachates contain much more Sr (277–2923 ppm) than the residues (16–60
372 ppm) ([S-Table 2](#)). The Ca-rich leachates from three xenoliths have much more Sr
373 (2337–2923 ppm) than the other four (277–455 ppm). Mass fractions of the leachates
374 range from 0.6 to 1.4% of the bulk rocks ([Table 3](#)), in line with the mass fractions of
375 carbonates (~1%) estimated by [Ionov et al. \(1993\)](#). Altogether, the data suggest that

376 leaching entirely removed the metasomatic carbonates from the WR samples.

377 [Ionov et al. \(2002a\)](#) outlined two types of PM-normalized ([McDonough and Sun,](#)
378 [1995](#)) trace element patterns in WR Spitsbergen xenoliths. Our data ([Fig. 2](#)) show that
379 the patterns for Type-1 peridotites are nearly flat for heavy to medium REE
380 (HREE-MREE) with steep La-Ce-Pr inflections, while Type-2 peridotites show a
381 continuous decrease in normalized REE from Ce to Ho ([Fig. 2a and c](#)). As a result,
382 Type-1 peridotites have lower MREE/HREE and higher La/Ce ratios than Type-2
383 peridotites.

384 Both types have strong negative Nb and Ta anomalies; all WR Type-1 peridotites
385 and the majority of Type-2 peridotites show positive Sr anomalies ([Fig. 2b and d](#)).
386 Because of the high MREE levels, Type-2 peridotites seem to have larger negative Zr,
387 Hf and Ti anomalies ([Fig. 2d](#)) even though the abundances of these elements are
388 similar to those in Type-1 peridotites. Three samples cannot be grouped with either
389 Type-1 or Type-2 ([Fig. 2e, f](#)). Among the leached samples with mainly Ca-rich
390 carbonates, one (4-36-90) is of Type 1 while the other three are of Type 2.

391 Trace element abundances and patterns for leaching residues and WR samples in
392 this study ([Fig. 3](#)) are similar to those for two samples reported by [Ionov et al. \(1993\)](#).
393 The concentrations of incompatible trace elements in the leachates in this study,
394 calculated relative to the mass of leached materials, are lower than those reported by
395 [Ionov et al. \(1993\)](#) when plotted relative to 1% of mass of WR samples. The leaching
396 with 10% HNO₃ in the previous work may have dissolved more material than the
397 leaching with 10% HAc in this study. The leachates contain more REE and large ion
398 lithophile elements (Cs, Rb, Ba), but less HFSE than leaching residues and bulk rocks
399 ([Figs. 3–5](#)). Besides, the leachates and the residues display the same Type-1 and
400 Type-2 REE patterns, but the leachates have the deepest HFSE anomalies ([Fig. 5](#)).

401

402 **4.2 Sr-Nd isotope compositions**

403 The WR Spitsbergen xenoliths in this study show a broad overall ⁸⁷Sr/⁸⁶Sr range

404 (0.7030–0.7112; Fig. 6a), with $^{87}\text{Sr}/^{86}\text{Sr}$ values in four samples (0.708–0.711) much
405 higher than in the other eleven samples (~0.703–0.704). Three out of seven leached
406 samples have the most radiogenic Sr, the highest Sr (and Ca) concentrations in the
407 leachates and also contain large, least altered carbonate pockets. In general, the WR
408 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in this study are higher than those for pure clinopyroxene and
409 amphibole separates from the same samples reported by Ionov et al. (2002b) (Fig. 7b
410 and S-Fig. 2a). Our WR data show no apparent differences in $^{87}\text{Sr}/^{86}\text{Sr}$ between
411 Type-1 and Type-2 peridotites, unlike data of Ionov et al. (2002b) who found that
412 clinopyroxene has less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ in Type-1 than in Type-2 peridotites. Few
413 samples were measured for Nd isotopes here because of low Nd abundances. The WR
414 $^{143}\text{Nd}/^{144}\text{Nd}$ range in this study (0.51218–0.51295; Fig. 6b) is narrower than for pure
415 amphibole and clinopyroxene reported by Ionov et al. (2002b) (S-Fig. 2b).

416 The leachates, leaching residues and WR samples for each xenolith have distinct Sr
417 isotopic compositions (Fig. 7b). The $^{87}\text{Sr}/^{86}\text{Sr}$ in the leachates (0.7049–0.7141) have a
418 wider range and are generally higher than in the residues (0.7036–0.7055). For a
419 given xenolith, the WR sample has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in-between those for leachates and
420 residues.

421 Unlike for Sr isotope ratios, the leachates, residues and WR samples have similar
422 Nd isotopic compositions (Fig. 7c), consistent with low Nd in the carbonates (Ionov,
423 1998). The leachates contain only 1–7 wt.% of the total Nd in the bulk rocks (Table 3).
424 The Sr and Nd isotope ratios in the leachates and the residues are positively correlated
425 (Fig. 8b, c).

426

427 4.3 Calcium isotopic compositions

428 The $\delta^{44/40}\text{Ca}$ values in the WR Spitsbergen peridotites range from 0.73 to 0.89‰
429 (Fig. 6a), i.e. are slightly lower than the BSE estimate ($0.94 \pm 0.05\%$; Kang et al.
430 (2017)). There is no obvious difference between Type-1 and Type-2 xenoliths with
431 $\delta^{44/40}\text{Ca}$ ranges of 0.78–0.89‰ and 0.73–0.87‰, respectively and between two

432 groups of leached samples based on Ca-Mg-Fe proportions in the leachates. The
433 $\delta^{44/40}\text{Ca}$ range for leaching residues (0.78–1.00‰) extends to slightly higher values
434 than for the WR samples, but the WR-residue differences do not exceed ~0.2‰ in
435 individual xenoliths (Fig. 7a) and are principally within analytical uncertainty.

436 The leachates in six out of seven samples have significantly lower, and more
437 variable, $\delta^{44/40}\text{Ca}$ (0.17–0.68‰) than the WR samples and residues (Fig. 7a). The
438 averages for the CaO-rich and Mg,Fe-rich leachates are very close (0.41‰ vs. 0.49‰).
439 A single outlier is leachate from sample 43-86 that yielded anomalously high $\delta^{44/40}\text{Ca}$,
440 $1.47 \pm 0.03\text{‰}$ (2sd, n = 3) and $1.46 \pm 0.08\text{‰}$ (2sd, n = 3) for two duplicates (Table 3),
441 much higher than for the residue and WR sample. The Ca isotopic data for the
442 leachate appear to be robust based on good reproducibility of the duplicated analyses,
443 but the reasons for the anomalous values are not clear and are not further discussed
444 below.

445 As shown in Table 3, the leached fractions account for only 3–12 wt.% Ca in each
446 xenolith, such that the carbonates (with highly variable $\delta^{44/40}\text{Ca}$ values) appear to have
447 limited influence on $\delta^{44/40}\text{Ca}$ of the WR samples. Like Sr and Nd isotope ratios, the
448 $\delta^{44/40}\text{Ca}$ of the residues are negatively correlated with those of the leachates (Fig. 8a).

449

450

5. DISCUSSION

451

5.1 Major element composition and origin of leached carbonate materials

453 Electron probe analyses of carbonates in our samples (Ionov et al., 1996) show that
454 the dolomite contains 28–40 wt.% CaO, 13–24 wt.% MgO and 0.3–5.0 wt.% FeO
455 while the Mg-calcite contains 44–53 wt.% CaO, 3–11 wt.% MgO and 0.3–2.7 wt.%
456 FeO. The leachates from three xenoliths that host large mosaic carbonate aggregates
457 (4-36-90, 4-90-9 and 21-6) contain 21–33 wt.% CaO, 12–20% MgO and 2.2–3.4%
458 FeO, with higher CaO than for MgO in each case. The leachates from these xenoliths
459 appear to be derived essentially from the dolomite and Mg-calcite in such aggregates.

460 The leachate from sample 43-86 (that also has large pockets of mosaic Mg-calcite
461 and dolomite) has less CaO (20 wt.%) than MgO (27 wt.%) and thus contains inputs
462 from other carbonate materials. Leachates from the other three xenoliths (63-90-18,
463 SB-4 and 28B) contain even less CaO (9–15 wt.%) and two to four times more MgO
464 (34–37 wt.%) as well as 11–14 wt.% FeO. These ranges correspond to mixtures of
465 dolomite and Mg-calcite with magnesite, ankerite $[\text{Ca}(\text{Fe},\text{Mg})(\text{CO}_3)_2]$ and amorphous
466 carbonate materials at margins of primary carbonate aggregates (Ionov et al., 1993).

467 Two formation modes could be envisaged for these materials. (1) Reaction of
468 carbonate-rich melts with host peridotites at conditions (e.g. temperature increase
469 related to basaltic magmatism) that do not allow precipitation of coarse Ca-rich
470 carbonates. (2) Recrystallisation and alteration at margins of granular carbonate
471 pockets. While they do not appear to be contaminated by host basalt or post-eruption
472 alteration (that precipitates pure calcite), their composition may not be identical to
473 that of granular metasomatic carbonates.

474

475 **5.2 ‘Carbonatite’ signatures and residence of Ca, Sr and Nd in WR peridotites**

476 Substantial differences between trace element patterns of leachates and bulk-rocks
477 are seen in Figs. 3–5. The leachates show much greater enrichments of highly
478 incompatible relative to moderately incompatible elements and negative HFSE
479 anomalies, i.e. show essential features inferred for carbonatite metasomatism (e.g.
480 Hauri et al., 1993; Rudnick et al., 1993) that are absent in the bulk-rocks. In particular,
481 WR Type-1 peridotites and residues show no significant Ti-Zr-Hf anomalies and no
482 fractionated Zr/Hf ratios while LREE/HREE ratios are much lower than in the
483 leachates. These results reinforce the conjecture of Ionov et al. (2002a) that element
484 patterns of Spitsbergen peridotites produced by percolation of volatile-bearing mafic
485 melts are not as fractionated as in inferred media of carbonatite metasomatism.

486 In a more general sense this study suggests that enrichments by volatile-bearing
487 silicate melts, on their own, are not likely to yield chemical signatures typical of

488 carbonatite metasomatism that require inputs from particular, carbonate-rich liquids.
489 Further, the metasomatic effects of carbonate-rich liquids are less apparent in fertile
490 lherzolites and previously enriched mantle than in highly melt-depleted protoliths
491 (harzburgites, dunites) low in incompatible elements (e.g. Yaxley et al., 1998). The
492 latter is the case for the Spitsbergen samples in which the patterns of bulk-rocks and
493 leached residues are not very different in spite of the presence of carbonates.

494 The contribution of carbonates to the WR balance of Ca, Sr and Nd and their
495 isotopic ratios in Spitsbergen xenoliths is evaluated here quantitatively from leaching
496 data. Table 3 presents WR Ca-Sr-Nd isotopic compositions calculated from mass
497 proportions of acid-leached material and residues in WR xenoliths, their Ca-Sr-Nd
498 abundances, and $\delta^{44/40}\text{Ca}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values (see also S-Tables 1-2 and
499 Fig. 7). The measured WR compositions are similar to the estimates for the majority
500 of the samples suggesting that the procedure is robust. The only outlier is sample
501 4-36-90, with the calculated WR $^{87}\text{Sr}/^{86}\text{Sr}$ value lower than the measured (Fig. 7b).
502 This may be due to irregular carbonate distribution in the rocks, hence different
503 carbonate mass fractions in the WR powder and sample duplicate used for leaching.

504 Significant differences in $\delta^{44/40}\text{Ca}$ were found between the leachates (dissolved
505 carbonates) and leaching residues (silicates), with $\Delta^{44/40}\text{Ca}_{\text{leachate-residue}}$ from -0.83 to
506 -0.17‰ for six xenoliths, and 0.69‰ for anomalous sample 43-86 (Fig. 7a). By
507 contrast, the WR $\delta^{44/40}\text{Ca}$ values are within analytical uncertainty ($\sim 0.1\text{‰}$) of those in
508 the residues, indicating small effects of carbonates on $\delta^{44/40}\text{Ca}$ of the WR xenoliths
509 because of low Ca mass fractions hosted by the carbonates (3–12%; Table 3).

510 The relations between WR samples, leachates and residues are different for Sr and
511 its isotope ratios. The leachates contain much more Sr than the residues (277–2923 vs.
512 16–60 ppm; S-Table 2) and have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in all the xenoliths. As a result,
513 $^{87}\text{Sr}/^{86}\text{Sr}$ in the WR samples are significantly higher than in the residues, in particular
514 for samples 4-36-90, 4-90-9 and 21-6 (cf. Fig. 7b). The leachates from these samples,
515 with carbonates dominated by dolomite and Mg-calcite, have 2337–2923 ppm Sr

516 (35–51% of Sr mass in WR samples) with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7136–0.7141.
517 Therefore, in spite of the low mass fractions of the leached carbonates in the xenoliths
518 (0.6–1.4%), they host a large share of Sr (8–51 wt.%) and greatly influence $^{87}\text{Sr}/^{86}\text{Sr}$
519 ratios in WR peridotites.

520 The limited Nd isotope data from leaching experiments show that $^{143}\text{Nd}/^{144}\text{Nd}$ in
521 leachates are close to, or slightly lower, than in residues and WR samples (Fig. 7c), in
522 line with low Nd fractions hosted by carbonates (1–7 wt.%).

523 To sum up, the role of carbonates is very different in the WR balance of Ca, Sr and
524 Nd abundances and isotopic compositions of Spitsbergen xenoliths. The metasomatic
525 carbonates have very high Sr content and moderate to high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and thus
526 may greatly affect the WR [Sr] and $^{87}\text{Sr}/^{86}\text{Sr}$ values of mantle peridotites even at low
527 mass fractions. These effects are the greatest for xenoliths with large, unaltered
528 aggregates of dolomite and Mg-calcite.

529 These observations may help to trace metasomatic history also of some
530 carbonate-free rocks. Carbonates are not stable in the uppermost mantle, and are
531 transient phases rapidly consumed by reaction with orthopyroxene and spinel to form
532 clinopyroxene and olivine (Brey et al., 1983; Dalton and Wood, 1995). This is why
533 carbonates are very rare in mantle xenoliths. As the carbonates react out, Sr
534 enrichments with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, initially residing in carbonates, may ultimately
535 be hosted by clinopyroxene, amphibole, silicate glass, alkali feldspar, phosphates etc.;
536 minerals replacing the carbonates may be zoned and/or include different generations
537 (e.g. Aulbach et al., 2011; Coltorti et al., 1999; Deng et al., 2017; Guo et al., 2020;
538 Ionov et al., 2006; Liu et al., 2012). As a result, unusually high Sr content and isotope
539 ratios in carbonate-free peridotites and their minerals can be seen as indices of
540 metasomatism by carbonate-rich melts that lost CO_2 due to reaction with host mantle.
541 Such reasoning was used by Hauri et al. (1993) to infer hotspot-related carbonatite
542 metasomatism in the oceanic upper mantle based on clinopyroxene analyses. This
543 study provides direct evidence for enrichment of the mantle in radiogenic Sr by

544 carbonate-rich media.

545

546 **5.3 Sr isotope evidence for distinct silicate and carbonatite metasomatic media**

547 The Sr isotope data on carbonates in the Spitsbergen xenoliths allow to elucidate
548 the nature of their parental media. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonate-bearing xenoliths,
549 and in particular of leachates (i.e. carbonates) from these samples, are higher than
550 those for leached residues as well as for silicate minerals separated from Spitsbergen
551 xenoliths reported by [Ionov et al. \(2002b\)](#). The differences between the leachates and
552 the silicates are the greatest for three xenoliths with large aggregates of dolomite and
553 Mg-calcite ([Fig. 7b](#); [S-Fig. 2a](#)), i.e. the samples apparently most affected by putative
554 carbonate-rich media and least affected by carbonate alteration during eruption. The
555 $^{87}\text{Sr}/^{86}\text{Sr}$ range (0.7136–0.7141) in the leachates from these samples may be close to
556 $^{87}\text{Sr}/^{86}\text{Sr}$ in these media. This unequivocally demonstrates the lack of Sr isotope
557 equilibrium between the carbonates on the one hand, and coarse silicates in these
558 xenoliths on the other hand. This further implies that the carbonates could not be
559 formed from the liquids that metasomatized the silicate minerals because in such a
560 case the carbonates and the silicates would have very similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. We see
561 this is as a definitive proof that the carbonates were formed from a distinct
562 carbonate-rich liquid unrelated to silicate metasomatism.

563 High $^{87}\text{Sr}/^{86}\text{Sr}$ (~0.714) in metasomatic media require high long-term Rb/Sr ratios
564 in their sources, e.g. due to high modal phlogopite or K-amphibole. High $^{87}\text{Sr}/^{86}\text{Sr}$
565 were reported for clinopyroxene and amphibole from MARID xenoliths (0.705–0.936
566 [Fitzpayne et al., 2019](#); [Kramers et al., 1983](#)), carbonate mantle xenoliths (~0.709
567 [Howarth et al., 2019](#)) and pyroxenites from North China (up to 0.715 [Dai et al., 2020](#)).
568 Such domains may form in the mantle by fractionation of melts, e.g. at the top of a
569 mantle plume, or more likely by incorporation of (a) blocks delaminated from the
570 base of mantle lithosphere or (b) subducted crustal materials. For instance, [Hauri et al.](#)
571 [\(1993\)](#) attributed high $^{87}\text{Sr}/^{86}\text{Sr}$ (up to 0.713) in clinopyroxene in mantle xenoliths

572 from the Pacific to ‘carbonatite’ metasomatism by melts derived from recycled crustal
573 components in the convecting mantle. Our data do not allow to distinguish mantle vs.
574 crustal origins for the radiogenic Sr in the xenoliths in this study.

575 The very broad $^{87}\text{Sr}/^{86}\text{Sr}$ range (0.7049–0.7141) of the leachates (i.e. carbonates),
576 along with covariation of $^{87}\text{Sr}/^{86}\text{Sr}$ in the leachates and the residues (Fig. 8b) indicate
577 some limited isotope exchange between the carbonate-rich melt and host peridotites.
578 The exchange may have continued during or after the formation of the carbonates, in
579 particular for interstitial carbonate aggregates with greater surface relative to mass
580 (S-Fig. 1b-c, EA2). This may be the reason why the carbonate-rich melts (and/or
581 initially deposited dolomite and Mg-calcite in such pockets) reacted to form late-stage,
582 Mg-Fe-rich carbonates common in many xenoliths in this study (S-Fig. 1G).

583 To sum up, we posit that granular dolomite and Mg-calcite formed from a parental
584 carbonate-rich liquid that had $^{87}\text{Sr}/^{86}\text{Sr}$ of ~ 0.714 . The liquid, and possibly the initial
585 carbonates, reacted with the host peridotites ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7025\text{--}0.7041$; Ionov et al.
586 (2002b)) to form late-stage Mg-Fe carbonates. Sr-isotope exchange between the
587 carbonate-rich melt and host rocks increased the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in host peridotites, the
588 more so in the samples with more carbonates, and produced the positive correlation of
589 $^{87}\text{Sr}/^{86}\text{Sr}$ in leachates and residues, i.e. coexisting silicates and carbonates (Fig. 8b).

590 The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the residues of leaching that removed carbonates from the
591 Spitsbergen xenoliths (0.7036–0.7055) are higher than in the depleted MORB mantle
592 (DMM, ~ 0.7025 ; Fig. 6a) (e.g. Carlson and Ionov, 2019; Stracke, 2012). This can be
593 best explained by an earlier episode of ‘silicate’ metasomatism and possibly later
594 exchanges with evolving carbonate-rich melts (see above).

595 Late-stage metasomatism taking place shortly before volcanic eruptions that bring
596 mantle fragments to the surface has been documented in many xenolith suites.
597 Remarkable examples of this phenomenon are xenoliths containing pockets and veins
598 of silicate glass (e.g. Coltorti et al., 1999; Ionov et al., 1994), usually attributed to
599 pre-eruption intrusion of carbonate-rich media, as well as sheared cratonic peridotites

600 with deformation accompanying melt metasomatism (e.g. [Agashev et al., 2013](#); [Ionov](#)
601 [et al., 2017](#); [Katayama et al., 2009](#); [van der Meer et al., 2013](#)). Geophysical and
602 experimental data (e.g. [Xu et al., 2020](#)) suggest that low-volume carbonate-rich melts
603 can be pervasively present in the deep upper mantle. Such melts may trail upwelling
604 mantle that generates xenolith-bearing magmas and react with their wall-rocks.

605

606 **5.4 Ca isotope fractionation in the Spitsbergen mantle**

607 Radiogenic ^{40}Ca enrichment from ^{40}K decay can decrease $\delta^{44/40}\text{Ca}$ values in rocks
608 with old ages and high K/Ca ratios ([Fantle and Tipper, 2014](#)). The lithospheric mantle
609 beneath Spitsbergen apparently formed in early Paleoproterozoic, most likely between
610 1.7 and 2.7 Ga based on Lu-Hf and Re-Os isotope data ([Choi et al., 2010](#)). However,
611 WR samples and residues in this study have low K/Ca ratios (<0.03 ; [S-Table 1](#)) such
612 that ^{40}K decay could decrease $\delta^{44/40}\text{Ca}$ of any of these samples only by $<0.02\%$, i.e.
613 within analytical uncertainties, and thus could not affect the observed $\delta^{44/40}\text{Ca}$ range.

614 As noted in Section 2, the Al_2O_3 range in the Spitsbergen xenoliths indicates that
615 their protoliths were residues of melt extraction ([Ionov et al., 2002a](#)) because Al_2O_3 in
616 mantle rocks is a robust melting index, little affected by metasomatism ([Pearson et al.,](#)
617 [2014](#)). Peridotites formed by melt extraction from fertile mantle and unaffected by
618 posterior metasomatism, like those from Tariat in Mongolia ([Carlson and Ionov, 2019](#);
619 [Ionov and Hofmann, 2007](#)), define linear co-variation on CaO vs. Al_2O_3 plots ([Fig.](#)
620 [1a](#)), that overlaps the primitive mantle (PM) ([McDonough and Sun, 1995](#)). Some
621 Spitsbergen peridotites plot close to this trend, but many have higher CaO and Ca/Al
622 ratios at given Al_2O_3 ([Fig. 1a, b](#)) indicating post-melting Ca enrichments. These
623 enrichments are partly hosted by carbonates, but the fact that six out of seven leached
624 residues show higher CaO and Ca/Al ratios than the melt-extraction trend ([Fig. 1a, b](#))
625 suggest that metasomatic Ca additions may be mainly hosted by silicates. Overall, the
626 Ca budget in the Spitsbergen xenoliths records the combined effects of melt extraction
627 and enrichments by silicate and carbonatite media.

628

629 5.4.1 $\delta^{44/40}\text{Ca}$ in products of melting and silicate metasomatism

630 Recent studies found that large degrees of partial melting may induce small, but
631 conspicuous Ca isotopic fractionation, with higher $\delta^{44/40}\text{Ca}$ in refractory melting
632 residues than in coexisting melts. This inference is supported, first, by data on fertile
633 to refractory mantle peridotites that show: (a) co-variation of $\delta^{44/40}\text{Ca}$ with Al_2O_3 and
634 CaO (Fig. 9a-b); (b) higher (by $\sim 0.1\text{‰}$) than in the BSE estimate $\delta^{44/40}\text{Ca}$ values for
635 melt-depleted (and non-metasomatized, i.e. LREE-depleted) low-Ca-Al lherzolites
636 and harzburgites (e.g. Ionov et al., 2019; Kang et al., 2017). Furthermore, oceanic
637 basalts show $\delta^{44/40}\text{Ca}$ values that are consistently lower than in the BSE, e.g. $0.83 \pm$
638 0.11‰ (2sd, $n = 21$) for MORB and $0.80 \pm 0.08\text{‰}$ (2sd, $n = 21$) for back-arc basin
639 basalts (Chen et al., 2020; Zhu et al., 2020; Zhu et al., 2018b).

640 Chen et al. (2019) obtained average $\delta^{44/40}\text{Ca}$ of $0.94 \pm 0.11\text{‰}$ (2sd, $n = 22$) for
641 melt-depleted (2.0–3.4 wt.% Al_2O_3) lherzolites from two tectonically emplaced
642 massifs in the Alps. They failed to establish correlations of $\delta^{44/40}\text{Ca}$ with Al_2O_3 (i.e.
643 melting degrees), apparently because of the lack of fertile lherzolites and complex
644 melt impregnation in their samples. Furthermore, they reported $\delta^{44/40}\text{Ca}$ below the
645 BSE estimate both in residual harzburgites ($0.89 \pm 0.09\text{‰}$; 2sd, $n = 3$) and magmatic
646 pyroxenites ($0.86 \pm 0.10\text{‰}$; 2sd, $n = 14$). We find confusing that Chen et al. (2019)
647 used their data to define the $\delta^{44/40}\text{Ca}$ range, alternately, for “Earth’s mantle”, “upper
648 mantle” or “fertile mantle rocks” as $0.94 \pm 0.10\text{‰}$ (2sd, $n = 47$). The Earth’s mantle
649 is heterogeneous, with $\delta^{44/40}\text{Ca}$ well beyond the above range reported both for
650 xenoliths of the lithospheric mantle (e.g. Chen et al., 2018; Ionov et al., 2019; Kang et
651 al., 2019; Kang et al., 2020) and asthenosphere-derived magmatic rocks (see above).
652 Further, the above range cannot refer to “fertile mantle” because Chen et al. (2019)
653 reported data on melt-depleted peridotites overprinted by melt infiltration (without
654 trace element data to evaluate possible metasomatic inputs).

655 The Al_2O_3 content in leached residues in this study is much lower than in the BSE

656 (1.30–2.45 vs. 4.45 wt.%; [McDonough and Sun \(1995\)](#)) indicating that they
657 experienced ~10–25% of partial melting ([Herzberg, 2004](#)). The $\delta^{44/40}\text{Ca}$ values of
658 melting residues with this Al_2O_3 range should be ~0.12–0.04‰ higher than in the
659 BSE based on equilibrium fractionation modeling (Fig. 9a-b [Chen et al., 2019](#); [Kang](#)
660 [et al., 2017](#)). By contrast, the $\delta^{44/40}\text{Ca}$ values for six out of seven leached samples
661 (0.78–0.90‰, av. $0.83 \pm 0.09\%$, 2sd) and 16 out of 17 WR Spitsbergen samples
662 (0.73–0.89‰, av. $0.83 \pm 0.10\%$, 2sd) are lower than the BSE estimate ($0.94 \pm 0.05\%$;
663 [Kang et al. \(2017\)](#)) and for non-metasomatized (from trace element data) fertile and
664 melt-depleted peridotites in the literature ([Fig. 9](#)). The $\delta^{44/40}\text{Ca}$ values in the majority
665 of the Spitsbergen samples are below the BSE range also if the uncertainty of
666 individual analyses is considered ([Fig. 9](#)). We conclude that the silicate metasomatism
667 decreased $\delta^{44/40}\text{Ca}$ values in the Spitsbergen lithospheric mantle by 0.1–0.2‰ relative
668 to the likely range of ~1.0–1.1‰ in the initial melting residues (e.g. [Kang et al.,](#)
669 2017).

670 Earlier xenolith studies inferred that metasomatism by silicate melts may decrease
671 $\delta^{44/40}\text{Ca}$ in fertile or melt-depleted peridotites (e.g. [Kang et al., 2017](#)), but its effects
672 on Ca isotopes continue to be debated. [Kang et al. \(2019\)](#) reported low $\delta^{44/40}\text{Ca}$ values
673 (0.65–0.87‰), correlated with $(\text{Gd}/\text{Yb})_{\text{N}}$, for Ca-Fe-rich lherzolites and wehrlites
674 from Tok in the SE Siberian craton formed by reaction of lherzolites and harzburgites
675 with silica-undersaturated partial melts. [Kang et al. \(2019\)](#) used equilibrium isotope
676 fractionation modeling to infer that the Tok mantle was metasomatized by low-
677 $\delta^{44/40}\text{Ca}$ liquids generated from eclogites. The $\delta^{44/40}\text{Ca}$ values of leached Spitsbergen
678 xenoliths are not correlated with $(\text{Gd}/\text{Yb})_{\text{N}}$, which argues against metasomatism by
679 silicate melts from eclogite-rich sources. We see no reason to link these values to
680 kinetic fractionation (e.g. [Zhao et al., 2017](#)) either because our samples show no
681 modal or chemical (e.g. Fe enrichments) heterogeneities indicative of such a process.

682 Overall, the $\delta^{44/40}\text{Ca}$ range in the leaching residues, hence in the Spitsbergen mantle
683 before the most recent enrichment event, can be explained by a combination of melt

684 extraction, that moderately increased $\delta^{44/40}\text{Ca}$ values, and subsequent silicate-melt
685 metasomatism that brought $\delta^{44/40}\text{Ca}$ in the melting residues below the BSE range.

686

687 *5.4.2 Carbonatite Metasomatism*

688 The effects of carbonatite metasomatism on $\delta^{44/40}\text{Ca}$ of mantle peridotites can be
689 directly evaluated using data on carbonate-bearing xenoliths. [Ionov et al. \(2019\)](#)
690 reported leaching data on xenoliths from the Obnazhennaya (Obn) kimberlite on the
691 NE Siberian craton that contain carbonates texturally equilibrated with silicates. The
692 $\delta^{44/40}\text{Ca}$ values in leachates from these samples (0.82–0.84‰) are similar to those for
693 leached residues (0.70–0.84‰) within analytical uncertainty, which [Ionov et al. \(2019\)](#)
694 attributed to Ca isotope equilibration of the carbonates with silicates ([Fig. 8a](#)).

695 By contrast, the carbonates in the Spitsbergen xenoliths mainly occur in texturally
696 discordant pockets and veins, and differ strongly in Ca and Sr isotopic compositions
697 from the leached silicate residues ([Fig. 7](#)). These carbonates are usually enclosed in
698 Na,Al-rich silicate glass and fine-grained aggregates of silicates and spinel formed by
699 reaction of carbonate-rich melts with host mantle ([Ionov, 1998; Ionov et al., 1996](#)), i.e.
700 are out of chemical equilibrium with coarse silicates and have little direct contact with
701 them. This, together with the short duration of the melt-rock reaction, may explain
702 why the parental carbonate-rich melts did not attain Ca-Sr isotope equilibrium with
703 the host mantle. The broad ranges of $\delta^{44/40}\text{Ca}$ (0.17–0.68‰) and $^{87}\text{Sr}/^{86}\text{Sr}$
704 (0.7049–0.7141) in the leachates may be related to different amounts of the
705 carbonate-rich melts and extents of isotopic exchange with host peridotites.

706 The differences between $\delta^{44/40}\text{Ca}$ values of bulk (0.73–0.95‰) and leached
707 (0.78–1.00‰) Spitsbergen xenoliths ([Figs. 6a and 7a](#)) are minor and imply limited
708 bulk contributions from carbonatite metasomatism. This observation is consistent with
709 Ca-isotope data on relevant mantle rocks from the literature. The $\delta^{44/40}\text{Ca}$ values in the
710 majority of carbonate-bearing Obn xenoliths are only 0.10–0.15‰ lower than the
711 BSE estimate ([Fig. 9; Ionov et al. \(2019\)](#)). Few mantle xenoliths presumably affected

712 by carbonatite metasomatism reported in [Ionov et al. \(2019\)](#) and [Kang et al. \(2017\)](#)
713 deviate by $>0.3\%$ from the BSE estimate. The greatest metasomatism-induced Ca
714 isotope effects are found in rocks with low pre-metasomatic Ca content that had high
715 Ca additions and developed high Ca/Al ratios. Mass balance estimates show that the
716 carbonates only account for 3–12% of Ca in the WR Spitsbergen xenoliths ([Table 3](#)),
717 in line with the relatively low Ca/Al ratios (<2) in these xenoliths ([Fig. 9c](#)).

718 To sum up, both carbonatite and silicate metasomatism reduced $\delta^{44/40}\text{Ca}$ values of
719 Spitsbergen peridotites and thus contributed to Ca isotope mantle heterogeneity. Both
720 processes may result in lower $\delta^{44/40}\text{Ca}$ values in mantle peridotites than in the BSE or
721 melting residues such that Ca isotopes cannot robustly distinguish between these two
722 types of mantle metasomatism ([Ionov et al., 2019](#)). On the other hand, the very low
723 $\delta^{44/40}\text{Ca}$ in acid-leached materials from some carbonate-bearing Spitsbergen xenoliths,
724 together with literature data on refractory peridotites with high Ca/Al, indicate that
725 carbonatite metasomatism has a potential to yield the lowest $\delta^{44/40}\text{Ca}$ in the mantle.

726

727 **5.5 Sources of carbonatites and carbonate-rich media of mantle metasomatism**

728 The isotopic signatures of metasomatism in the lithospheric mantle are related to
729 the nature and sources of its media. An important issue is the share of carbonates in
730 such media. Early experimental data and studies of mantle xenoliths evoked sodic
731 dolomitic carbonate melts (e.g. [Yaxley et al., 1991](#)) while studies of CO_2 -rich magmas
732 (carbonatites and kimberlites) suggest that near-solidus melts of carbonated peridotite
733 must be silicate-dominated with only dilute carbonate contents (e.g. [Tappe et al.,](#)
734 [2017](#)). Furthermore, discrete CO_2 -rich magma batches with different $\delta^{44/40}\text{Ca}$ ratios
735 may be derived from mixed sources in the convecting upper mantle ([Tappe et al.,](#)
736 [2020](#)). The common association of carbonates in the Spitsbergen xenoliths with
737 silicate glass and fine-grained silicates suggest that their parental liquids contain
738 silicate components, but their share cannot be constrained from our data.

739 Carbonate-rich liquids generated both from ‘juvenile’ carbonated mantle and

740 sources containing subducted carbonates were recently evoked to explain the origin of
741 carbonatites and kimberlites (e.g. [Banerjee and Chakrabarti, 2019](#); [Tappe et al., 2017](#)).
742 [Ionov et al. \(2019\)](#) argued that recycling of carbonates, that show a broad $\delta^{44/40}\text{Ca}$
743 range, may not always alter the Ca isotopic composition in global mantle. [Banerjee](#)
744 [and Chakrabarti \(2019\)](#) reported a $\delta^{44/40}\text{Ca}$ range of 0.6–1.1‰, that overlaps the BSE
745 estimate, for seven carbonatites from India and explained it by mixing of the plume
746 end-member with recycled carbonates. [Amsellem et al. \(2020\)](#) obtained a much lower
747 average $\delta^{44/40}\text{Ca} = 0.26 \pm 0.25\text{‰}$ (2 sd, n = 50) for Ca-Mg-Fe carbonatites and argued
748 that it reflects the incorporation of isotopically light marine carbonates into their
749 mantle sources. By contrast, [Sun et al. \(2021\)](#) reported primary carbonatite and
750 associated silicate rocks that are rather homogeneous in Ca isotope compositions that
751 are comparable to those of basalts, which implies that the carbonatites are generated
752 from a ‘juvenile’ mantle source without requiring the involvement of recycled
753 carbonates. [Banerjee et al. \(2021\)](#) found BSE-like $\delta^{44/40}\text{Ca}$ values in carbonatites older
754 than 0.3 Ga, but low $\delta^{44/40}\text{Ca}$ values (0.63‰, n=29) in younger carbonatites. While the
755 topic may require further investigation, it is evident that carbonate-rich mantle melts
756 may have both BSE-like and low $\delta^{44/40}\text{Ca}$ values. This is consistent with inferences in
757 this study that Ca isotope data cannot robustly distinguish carbonate and silicate
758 mantle metasomatism (see the previous section).

759 This study found lower $\delta^{44/40}\text{Ca}$ than for the BSE in the carbonates of mantle origin
760 in Spitsbergen xenoliths. It appears that carbonatite metasomatism generally lowers
761 $\delta^{44/40}\text{Ca}$ in mantle rocks, likely including basalt source regions ([Huang et al., 2011](#);
762 [Ionov et al., 2019](#); [Kang et al., 2017](#); [Kang et al., 2016](#); [Liu et al., 2017a](#)). However,
763 the limited available data also suggest that carbonatite metasomatism may not change
764 $\delta^{44/40}\text{Ca}$ in the lithospheric mantle very much, except for rare highly refractory
765 peridotites ([Ionov et al., 2019](#)), the latter are insignificant in mantle magma sources.

766

767

6. SUMMARY OF CONCLUSIONS

768

769 Leaching of peridotite xenoliths from Spitsbergen with acetic acid extracted
770 carbonates formed in the latest metasomatic event and thus allowed to distinguish
771 chemical and Ca-Sr-isotope imprints of their parental carbonate-rich melts from the
772 combined effects of melt extraction and silicate metasomatism in leaching residues.

773 PM-normalized trace element patterns of the leached carbonates, unlike silicate
774 residues, show distinctive indices (LREE-enrichments, HFSE-depletions) of
775 carbonatite mantle metasomatism, suggesting that it necessitates specific
776 carbonate-rich liquids rather than fractionation products of volatile-bearing silicate
777 melts.

778 The carbonates are out of Ca-Sr isotope equilibrium with the silicates in the
779 Spitsbergen peridotites implying that the silicate and carbonatite metasomatism are
780 produced by different parental melts from distinct sources. This proves the existence
781 of distinctive carbonate-rich metasomatic media in the lithospheric mantle.

782 The Spitsbergen carbonates are rich in Sr (277–2923 ppm) and have high $^{87}\text{Sr}/^{86}\text{Sr}$
783 (0.7049–0.7141). These signatures are retained in host peridotites when the transient
784 carbonates react out to form Ca-rich silicates. High [Sr] and $^{87}\text{Sr}/^{86}\text{Sr}$ may be indices
785 (though not definitive proofs) of carbonatite metasomatism in mantle rocks.

786 The ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7136–0.7141) and $\delta^{44/40}\text{Ca}$ (0.35–0.45‰) in leachates
787 from three peridotites with large aggregates of dolomite and Mg-calcite constrain
788 their values in sources of putative carbonate-rich media that either had high long-term
789 Rb/Sr ratios or included recycled materials.

790 Both carbonatite and silicate metasomatism may produce $\delta^{44/40}\text{Ca}$ values lower than
791 the BSE, such that that Ca-isotope data cannot robustly tell apart these two
792 enrichment types, yet carbonatite metasomatism may yield the lowest $\delta^{44/40}\text{Ca}$.

793

794

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802

803 **Figure Captions**

804 **Fig. 1.** Co-variation plots for (a) CaO (wt.%), (b) Ca/Al ratios and (c) Sr (ppm)
805 versus Al₂O₃ (wt.%) in whole rock (WR) peridotite xenoliths from Spitsbergen (Spi)
806 (Ionov et al., 2002a) and in acid-leached samples of the same xenoliths (this study).
807 Also shown are the primitive mantle (PM, [McDonough and Sun, 1995](#)) and WR
808 peridotite xenoliths from Tariat (Tar) in Mongolia ([Ionov, 2007](#); [Ionov and Hofmann,](#)
809 [2007](#)) that define a regular melt extraction trend (grey area in (a)), experienced no or
810 little metasomatism after melting, and are similar in composition to depleted MORB
811 mantle ([Carlson and Ionov, 2019](#)). Some Spitsbergen peridotites plot above the fields
812 of the Tariat xenoliths due to metasomatic enrichments in Ca and Sr. Both leached and
813 non-leached Spitsbergen xenoliths are enriched in Ca suggesting that much Ca resides
814 in silicates. By contrast, non-leached bulk-rocks contain more Sr than acid-leached
815 xenoliths because the carbonates may host more Sr than silicates.

816 **Fig. 2.** Primitive mantle-normalized ([McDonough and Sun, 1995](#)) REE (left
817 column) and multi-element abundance patterns for whole-rock Spitsbergen peridotites.
818 Data and rock types are after [Ionov et al. \(2002a\)](#).

819 **Fig. 3.** Comparison of trace element concentrations of leachates (Leach), leached
820 residues (Res) and whole rocks (WR) for samples SB-4 and 43-86 in this study with
821 leaching data of the same samples from [Ionov et al. \(1993\)](#) assuming that leached
822 materials make up 1 wt.% of bulk rocks. The inferred element concentrations in the
823 leached materials after [Ionov et al. \(1993\)](#) are much higher because they employed
824 diluted HNO₃, which dissolved not only carbonates as in this study, but also extracted
825 trace elements from silicates.

826 **Fig. 4.** Primitive mantle-normalized ([McDonough and Sun, 1995](#)) REE patterns

827 for leachates (Leach) , residues (Res) and whole-rocks (WR) of carbonate-bearing
828 peridotites.

829 **Fig. 5.** PM-normalized (McDonough and Sun, 1995) multi-element abundance
830 patterns for leachates, residues and whole-rocks of carbonate-bearing peridotites.

831 **Fig. 6.** Plots of $\delta^{44/40}\text{Ca}$ vs. (a) $^{87}\text{Sr}/^{86}\text{Sr}$ and (b) $^{143}\text{Nd}/^{144}\text{Nd}$ for leachates (Leach),
832 residues (Res) and whole-rocks (WR) of Spitsbergen xenoliths. The blue horizontal
833 line and grey bar represent the $\delta^{44/40}\text{Ca}$ estimate for the BSE (Kang et al., 2017). The
834 vertical dashed lines represent $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ for three types of the depleted
835 MORB mantle (DMM): D-DMM, DMM and E-DMM after Workman and Hart
836 (2005).

837 **Fig. 7.** Comparisons of (a) $\delta^{44/40}\text{Ca}$, (b) $^{87}\text{Sr}/^{86}\text{Sr}$ and (c) $^{143}\text{Nd}/^{144}\text{Nd}$ in leachates
838 (Leach), residues (Res) and whole-rocks (WR) for seven carbonate-bearing
839 Spitsbergen xenoliths as well as Sr and Nd isotopic ratios of cpx (Ionov et al., 2002b).

840 **Fig. 8.** Co-variation plots of $\delta^{44/40}\text{Ca}$ (a), $^{87}\text{Sr}/^{86}\text{Sr}$ (b) and $^{143}\text{Nd}/^{144}\text{Nd}$ (c) for
841 leachates and leaching residues in individual xenoliths. from Spitsbergen (Spi). Also
842 shown are leachates and leaching residues in metasomatized, carbonate-bearing
843 Obnazhennaya (Obn) peridotites (Ionov et al., 2019). Thick grey lines represent equal
844 Ca-Sr-Nd isotopic values in leachates and leaching residues.

845 **Fig. 9.** Co-variation plots of $\delta^{44/40}\text{Ca}$ versus wt.% Al_2O_3 (a), wt.% CaO (b) and
846 Ca/Al (c) in WR xenoliths and leaching residues (Res) of Spitsbergen (Spi) xenoliths.
847 Also shown are melt-depleted peridotites from Tariat (Mongolia), and metasomatized,
848 carbonate-bearing Obnazhennaya peridotites (Ionov et al., 2019; Kang et al., 2017).
849 The blue horizontal line and gray bar represent estimated $\delta^{44/40}\text{Ca}$ of the BSE and 2sd
850 of the BSE estimate (Kang et al., 2017). The $\delta^{44/40}\text{Ca}$ in the melt-depleted peridotites
851 from Tariat and Obnazhennaya are negatively correlated with Al_2O_3 and CaO. The
852 leached Spitsbergen xenoliths display a negative $\delta^{44/40}\text{Ca}$ vs. Al_2O_3 correlation, but
853 their $\delta^{44/40}\text{Ca}$ values are lower than those for non-metasomatized melting residues
854 from the literature.

855

856

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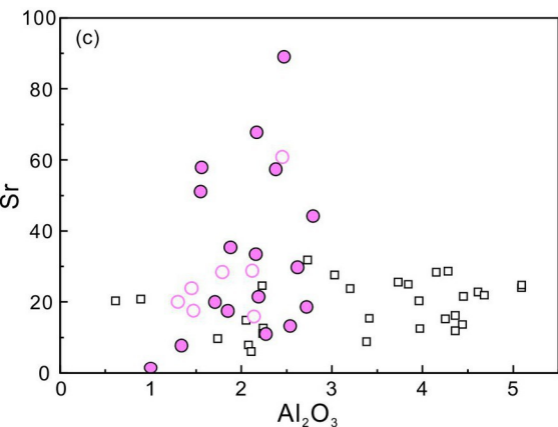
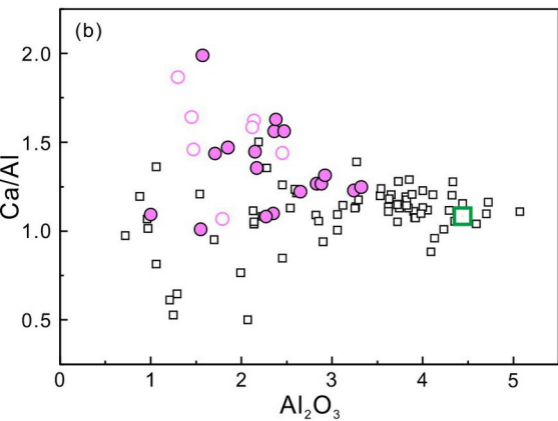
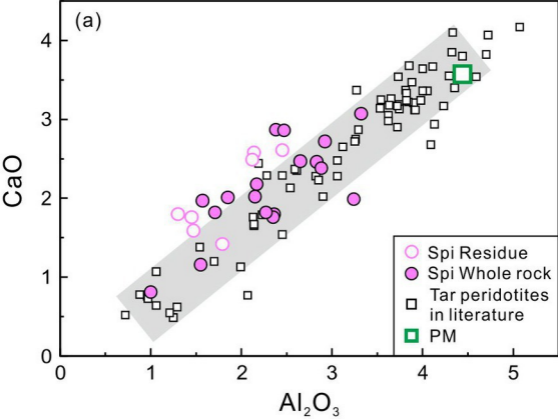
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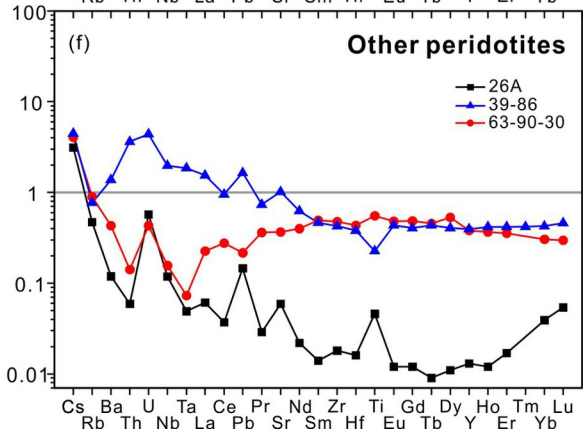
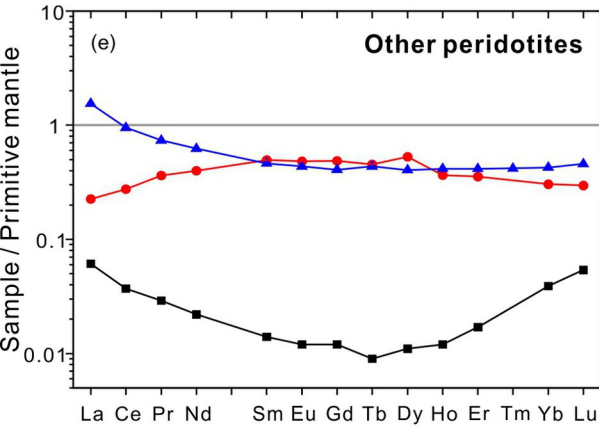
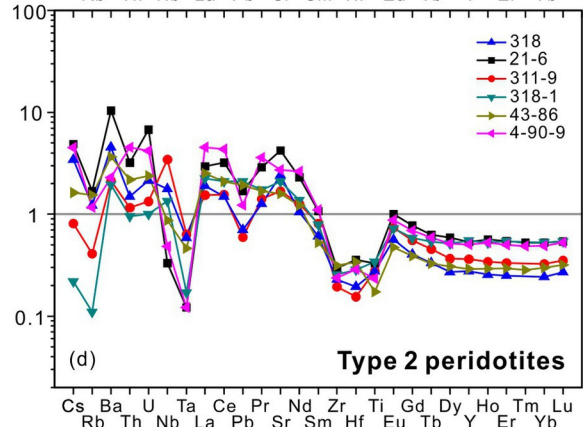
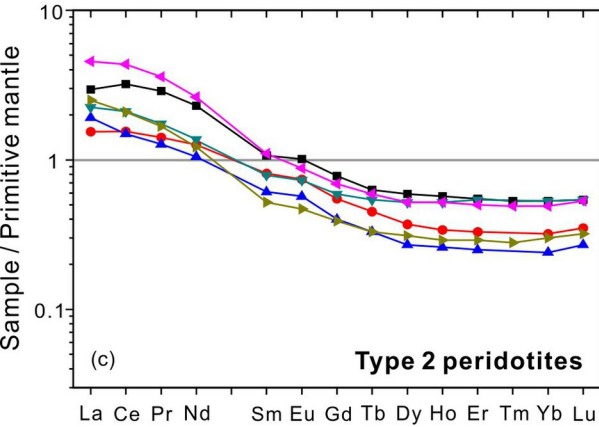
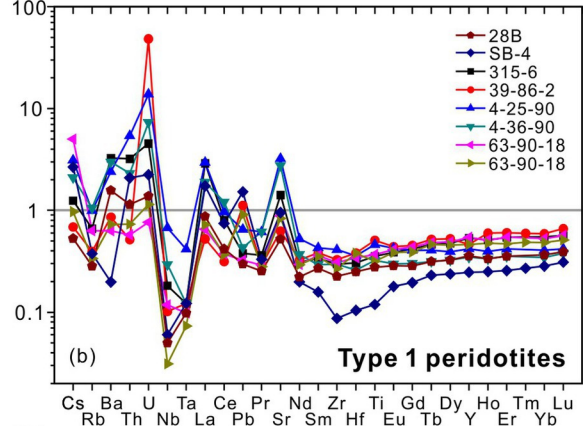
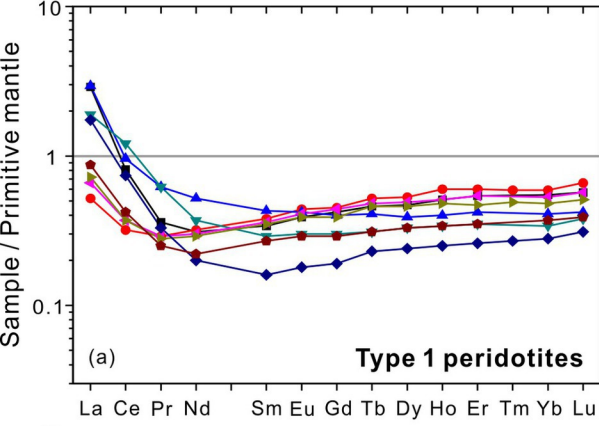
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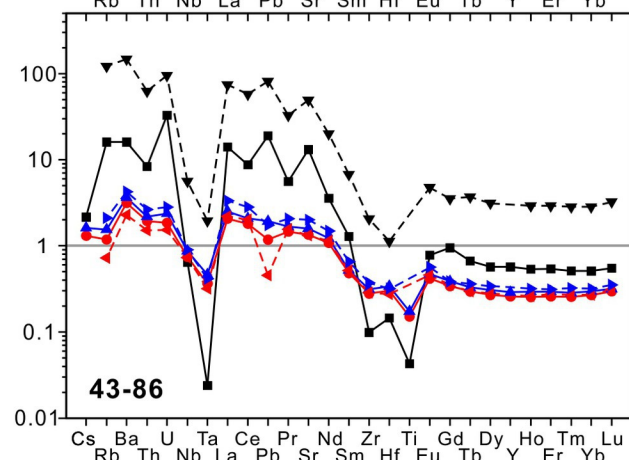
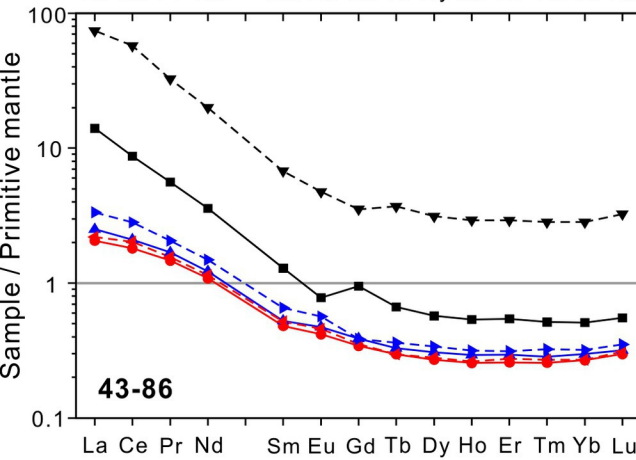
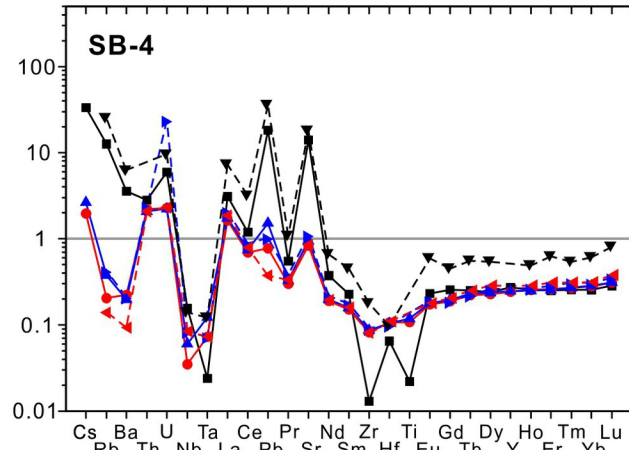
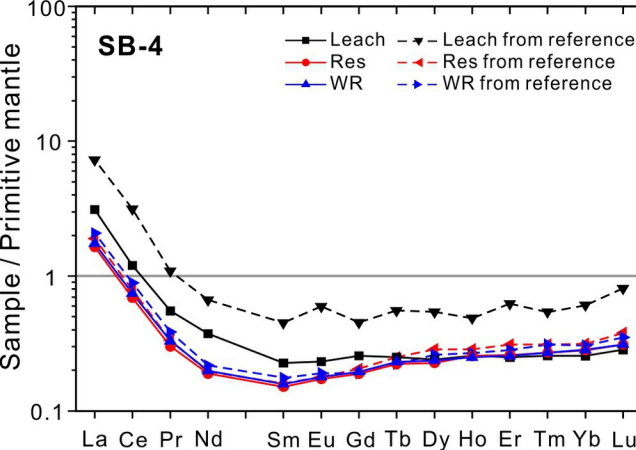
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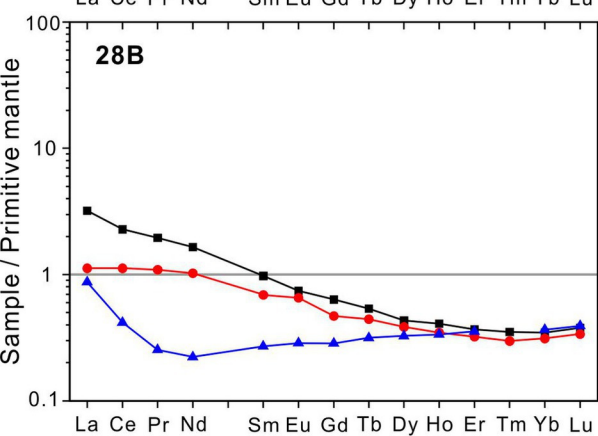
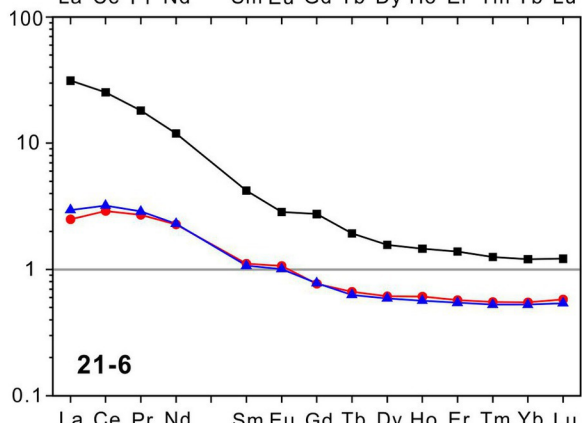
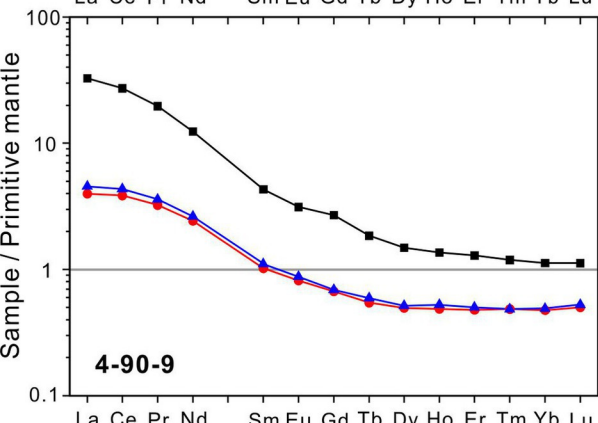
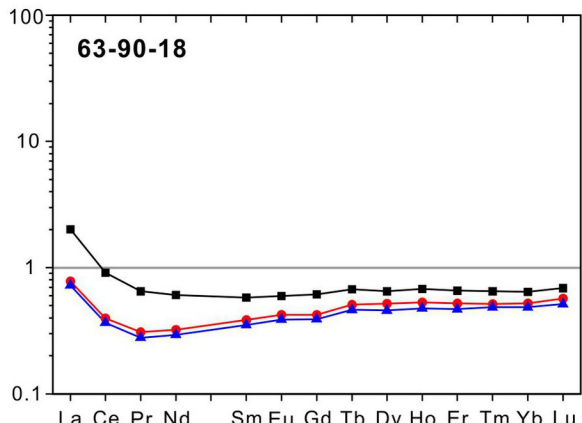
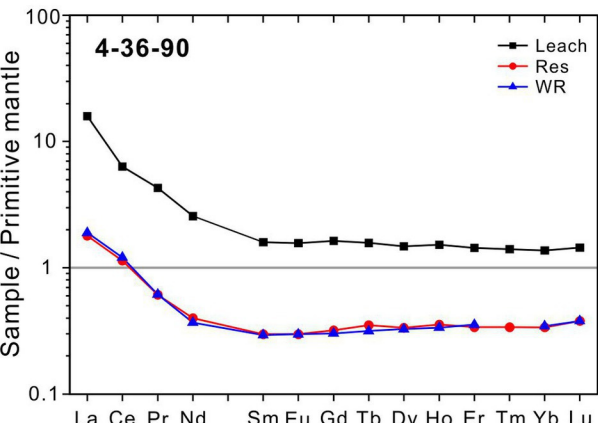
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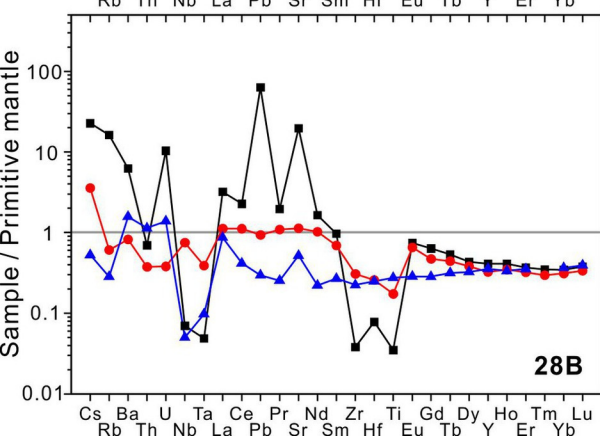
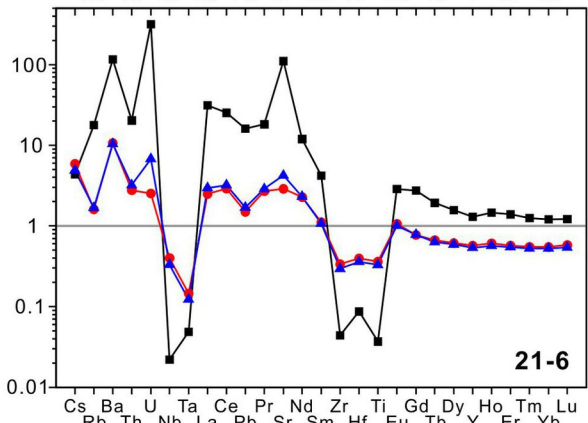
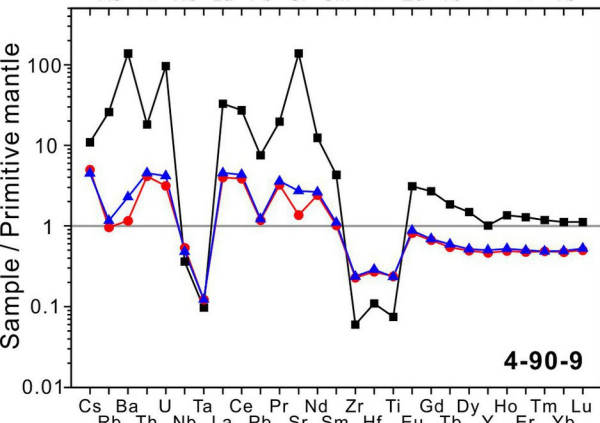
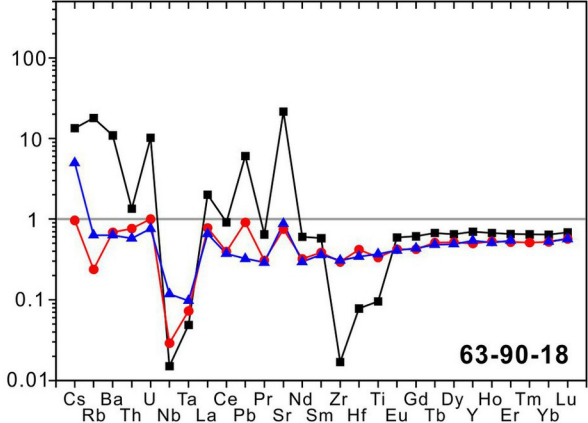
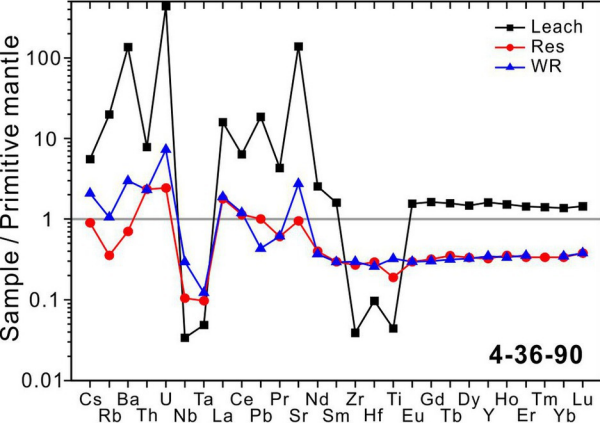
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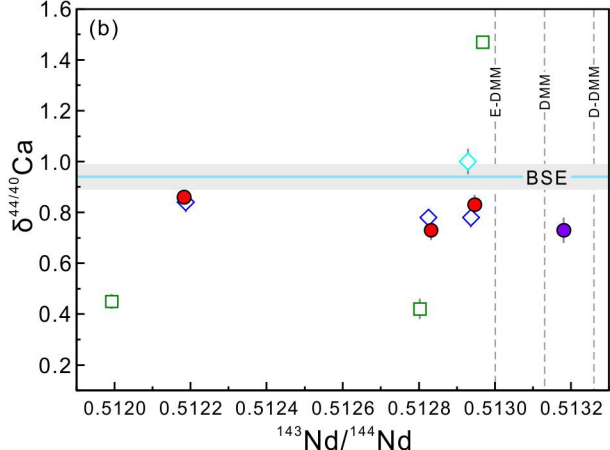
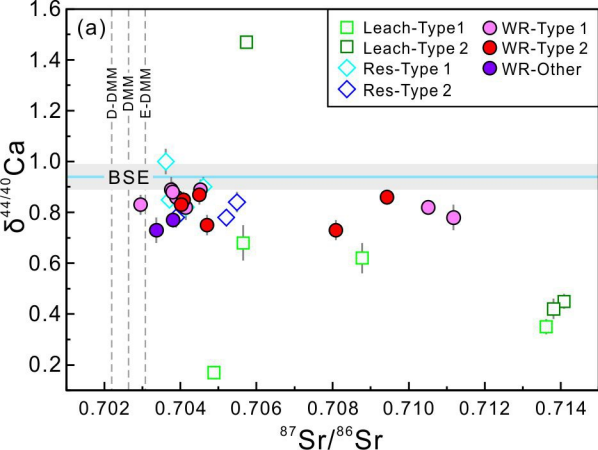


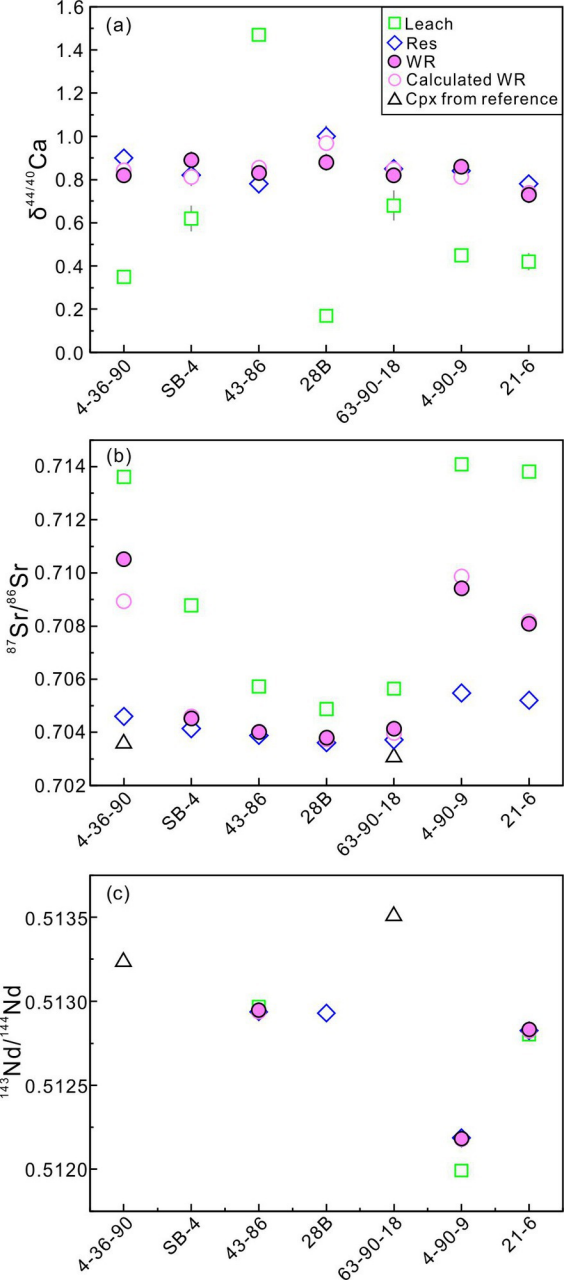


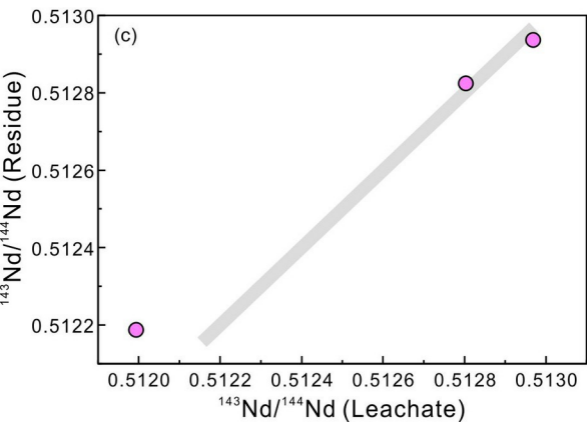
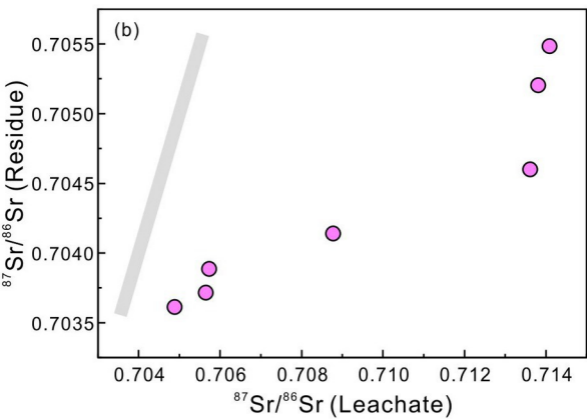
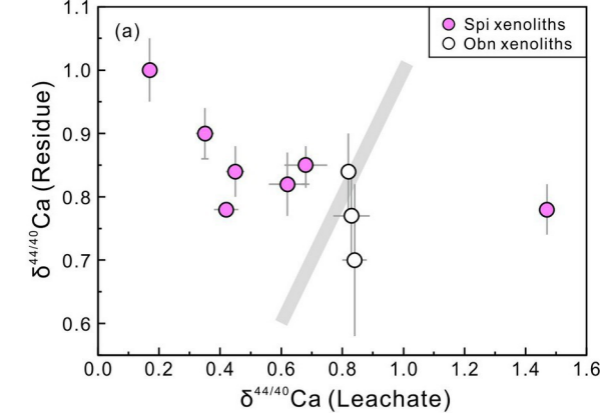












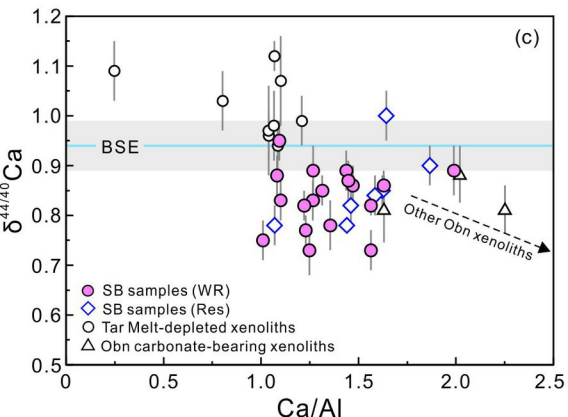
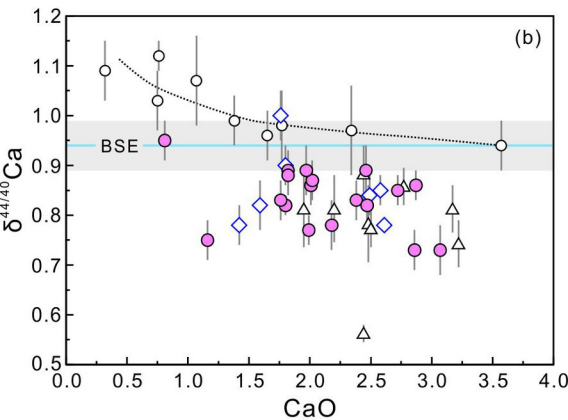
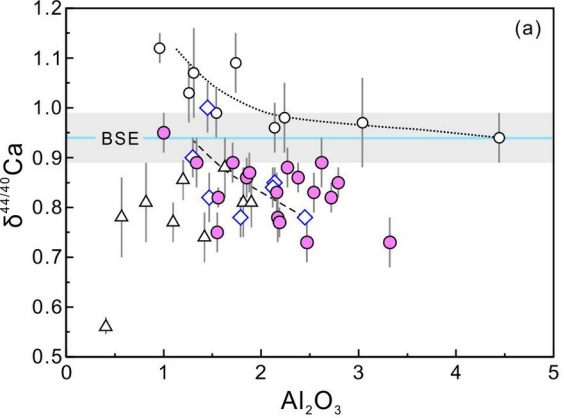


Table 1. Sample list and information summary for the Spitsbergen xenoliths.

Sample	Location	Rock type ^a	Leaching	Data source ^b														
				Major elements			Trace elements			Sr isotopes			Nd isotopes			Ca isotopes		
				WR	Res	Leach	WR	Res	Leach	WR	Res	Leach	WR	Res	Leach	WR	Res	Leach
4-36-90*	Halvdan	Spl Lh	×	×	×	×	(2)	×	×	×	×	×	×		×	×	×	
4-90-9*	Halvdan	Spl Lh	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	
21-6*	Halvdan	Spl Lh	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	
43-86*	Sverre	Spl Lh	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	
28B	Sverre	Spl Lh	×	(3)	×	×	(2)	×	×	×	×	×	×	×		×	×	
63-90-18	Sverre	Spl Lh	×	×	×	×	(2)	×	×	×	×	×	×	×		×	×	
SB-4	Halvdan	Spl Lh	×	×	×	×	×	×	×	×	×	×	×		×	×	×	
315-6	Halvdan	Spl Lh		×			(2)			×						×		
39-86-2	Sverre	Spl Lh		×			(2)			×						×		
4-25-90	Halvdan	Spl Lh		(2)			(2)			×						×		
63-90-18-1	Sverre	Spl Lh		×			×			×						×		
311-9	Halvdan	Spl Lh		×			(2)			×						×		
318	Halvdan	H _z		(2)			(2)			×						×		
318-1	Halvdan	Spl Lh		×			(2)			×						×		
26A	Sverre	H _z		(2)			(2)									×		
63-90-30	Sverre	Spl Lh		×			(2)									×		
39-86	Sverre	Spl Lh		×			×			×						×		
4A-90-1-Cpx	Sigurd	Amph Wh								(4)			(4)			×		
4A-90-1-Amph	Sigurd	Amph Wh								(4)			(4)			×		

^a Abbreviations: Spl Lh, spinel lherzolite; H_z, harzburgite; Wh, wehrlite; Cpx, clinopyroxene; Amph, amphibole; WR, whole-rock; Res, residues; Leach, leachates. *Samples that contain the largest and most abundant carbonate aggregates.

^b Data sources: ×, this study; (1) [Ionov et al. \(1993\)](#); (2) [Ionov et al. \(2002a\)](#); (3) [Ionov et al. \(1996\)](#); (4) [Ionov et al. \(2002b\)](#).

Table 2. Ca-Sr-Nd isotopic compositions of reference samples.

		$\delta^{44/40}\text{Ca}$	2SD ^a	n ^b	$^{87}\text{Sr}/^{86}\text{Sr}$	2SD	n	$^{143}\text{Nd}/^{144}\text{Nd}$	2SD	n
NIST SRM 915a	This study	-0.02	0.12	21						
	Huang et al. (2010)	0.04	0.13	45						
	Valdes et al. (2014)	0.00	0.17	74						
IAPSO seawater	This study	1.82	0.10	10						
	Farkaš et al. (2007)	1.86	0.20	5						
	He et al. (2017)	1.89	0.18	147						
DTS-1	This study	1.61	0.09	3						
	Huang et al. (2010)	1.59	0.16	3						
	Feng et al. (2017)	1.51	0.13	7						
DTS-2	This study	1.10	0.11	3						
	Feng et al. (2017)	1.20	0.11	9						
PCC-1	This study	1.10	0.08	3						
	Amini et al. (2009)	1.15	0.09	13						
BHVO-2	This study	0.84	0.09	5	0.703503		1			
	Valdes et al. (2014)	0.87	0.16	10						
	He et al. (2017)	0.79	0.09	7						
	Weis et al. (2006)				0.703487	0.000019	12			
NBS-987	This study				0.710254	0.000014	12			
	Thirlwall (1991)				0.710248	0.000011	427			
	Charlier et al. (2006)				0.710255	0.000018	222			
JNdi-1	This study							0.512111	0.000013	14
	Tanaka et al. (2000)							0.512115	0.000007	
	Li et al. (2012)							0.512113	0.000012	5
W-2	This study							0.512512		1
	Li et al. (2012)							0.512518	0.000006	2

^a 2SD: two standard deviations.

^b n: number of replicate Ca-Sr-Nd isotope analyses.

Table 3. Ca-Sr-Nd isotopic compositions of leachates, residues, whole-rocks (WR) and calculated WR for carbonate-bearing xenoliths.

Sample		Mass fraction	Ca fraction	$\delta^{44/40}\text{Ca}$	2SD	2SE ^a	n	Sr fraction	$^{87}\text{Sr}/^{86}\text{Sr}^c$	Nd fraction	$^{143}\text{Nd}/^{144}\text{Nd}^c$
4-36-90	Leachate	0.006	0.10	0.35	0.05	0.03	3	0.48	0.713612	0.04	
	Residue	0.994	0.90	0.90	0.07	0.04	3	0.52	0.704601	0.96	
	Whole Rock	1.000	1.00	0.82	0.03	0.02	3	1.00	0.710515	1.00	
	Calculated WR			0.84					0.708932		
4-90-9	Leachate	0.010	0.08	0.45	0.05	0.03	3	0.51	0.714085	0.05	0.511993
	Residue	0.990	0.92	0.84	0.08	0.04	3	0.49	0.705484	0.95	0.512187
	Whole Rock	1.000	1.00	0.86	0.06	0.03	3	1.00	0.709426	1.00	0.512183
	Calculated WR			0.81					0.709869		0.512178
21-6	Leachate	0.014	0.12	0.42	0.07	0.04	3	0.35	0.713810	0.07	0.512803
	Residue	0.986	0.88	0.78	0.02	0.01	3	0.65	0.705203	0.93	0.512825
	Whole Rock	1.000	1.00	0.73	0.06	0.04	3	1.00	0.708086	1.00	0.512832
	Calculated WR			0.74					0.708175		0.512823
43-86	Leachate	0.009	0.11	1.47	0.03	0.02	3	0.08	0.705733	0.03	0.512968
	Leachate-R ^b			1.46	0.08	0.05	3				
	Residue	0.991	0.89	0.78	0.09	0.04	4	0.92	0.703886	0.97	0.512937
	Whole Rock	1.000	1.00	0.85	0.13	0.07	3	1.00	0.704016	1.00	0.512938
	Whole Rock-R ^b			0.82			2		0.704023		0.512956
Calculated WR			0.86					0.704029		0.512938	
SB-4	Leachate	0.007	0.03	0.62	0.10	0.06	3	0.10	0.708775	0.01	
	Residue	0.993	0.97	0.82	0.09	0.05	3	0.90	0.704142	0.99	
	Whole Rock	1.000	1.00	0.89	0.06	0.04	3	1.00	0.704527	1.00	
	Calculated WR			0.81					0.704604		
28B	Leachate	0.006	0.04	0.17	0.02	0.01	3	0.10	0.704880	0.01	
	Residue	0.994	0.96	1.00	0.09	0.05	3	0.90	0.703615	0.99	0.512929
	Whole Rock	1.000	1.00	0.88	0.06	0.04	3	1.00	0.703799	1.00	
	Calculated WR			0.97					0.703742		
63-90-18	Leachate	0.006	0.03	0.68	0.11	0.07	3	0.14	0.705647	0.01	
	Residue	0.994	0.97	0.85	0.05	0.03	3	0.86	0.703716	0.99	
	Whole Rock	1.000	1.00	0.83	0.05	0.03	3	1.00	0.704138	1.00	
	Whole Rock-R ^b			0.80			1		0.704133		
	Calculated WR			0.85					0.703980		

^a 2SE: two standard deviations of the mean. $2SE = 2SD/\text{sqrt}(n)$.

^b R: repeated dissolution and analysis for two whole rocks and a repeated analysis for one leachate.

^c Sr-Nd isotopes of leachate, residue and whole rock of carbonate-bearing xenoliths are measured once.

Table 4. Ca-Sr-Nd isotopic compositions of non-leached whole-rock Spitsbergen xenoliths and minerals.

Sample		$\delta^{44/40}\text{Ca}$	2SD	2SE	n	$^{87}\text{Sr}/^{86}\text{Sr}^{\text{a}}$	$^{143}\text{Nd}/^{144}\text{Nd}$
315-6	Whole rock	0.89	0.09	0.05	3	0.703760	
39-86-2	Whole rock	0.83	0.07	0.04	3	0.702950	
4-25-90	Whole rock	0.78	0.12	0.05	7	0.711183	
63-90-18-1	Whole rock	0.86	0.08	0.04	3	0.703893	
311-9	Whole rock	0.87	0.06	0.04	3	0.704491	
318	Whole rock	0.75	0.06	0.04	3	0.704696	
318-1	Whole rock	0.85	0.05	0.03	3	0.704079	
26A	Whole rock	0.95	0.07	0.04	3		
63-90-30	Whole rock	0.89	0.08	0.05	3		
39-86	Whole rock	0.77	0.06	0.03	3	0.703805	
4A-90-1-Cpx ^b	Cpx mineral	1.05	0.09	0.05	3	0.703950 ^c	0.512904 ^c
4A-90-1-Amph ^b	Amph mineral	0.97	0.09	0.05	3	0.704000 ^c	0.512894 ^c

^a Single Sr isotope analyses for non-leached whole-rock xenoliths.

^b Mineral abbreviations: cpx, clinopyroxene; amph, amphibole.

^c Sr and Nd isotopic compositions of cpx and amph in sample 4A-90-1 are from [Ionov et al. \(2002b\)](#).