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1 Calcium isotopic signatures of carbonatite and silicate metasomatism,  
2 melt percolation and crustal recycling in the lithospheric mantle

3  
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22 *5260 words in the main text*

23

24 **Abstract** (316 words)

25 Ca isotopes can be strongly fractionated at the Earth's surface and thus may be tracers of  
26 subducted carbonates and other Ca-rich surface materials in mantle rocks, magmas and fluids.  
27 However, the  $\delta^{44/40}\text{Ca}$  range in the mantle and the scope of intra-mantle isotope fractionation  
28 are poorly constrained. We report Ca isotope analyses for 22 mantle xenoliths: four basalt-  
29 hosted refractory peridotites from Tariat in Mongolia and 18 samples from the Obnazhennaya  
30 (Obn) kimberlite on the NE Siberian craton. Obn peridotites are Paleoproterozoic to Archean  
31 melting residues metasomatised by carbonate-rich and/or silicate melts including unique  
32 xenoliths that contain texturally equilibrated carbonates.  $\delta^{44/40}\text{Ca}$  in 15 Obn xenoliths shows  
33 limited variation (0.74–0.97‰) that overlaps the value ( $0.94 \pm 0.05\%$ ) inferred for the bulk  
34 silicate Earth from data on fertile lherzolites, but is lower than  $\delta^{44/40}\text{Ca}$  for non-metasomatised  
35 refractory peridotites from Mongolia ( $1.10 \pm 0.03\%$ ). Bulk  $\delta^{44/40}\text{Ca}$  in four Obn peridotites  
36 containing metasomatic carbonates ranges from  $0.81 \pm 0.08\%$  to  $0.83 \pm 0.06\%$ , with similar  
37 values in acid-leachates and leaching residues, indicating isotopic equilibration of the  
38 carbonates with host rocks.

39 We infer that (a) metasomatism tends to decrease  $\delta^{44/40}\text{Ca}$  values of the mantle, but its  
40 effects are usually limited ( $\leq 0.3\%$ ); (b) Ca isotopes cannot distinguish “carbonatite” and  
41 “silicate” types of mantle metasomatism. The lowest  $\delta^{44/40}\text{Ca}$  value (0.56‰) was obtained for  
42 a phlogopite-bearing Obn peridotite with a very high Ca/Al of 8 suggesting that the greatest  
43 metasomatism-induced Ca isotope shifts may be seen in rocks initially low in Ca that  
44 experienced significant Ca input leading to high Ca/Al. Two Obn peridotites, a dunite (melt  
45 channel material) and a veined spinel wehrlite, have high  $\delta^{44/40}\text{Ca}$  values (1.22‰ and 1.38‰),  
46 which may be due to isotope fractionation by diffusion during silicate melt intrusion and  
47 percolation in the host mantle. Overall, we find no evidence that recycling of crustal  
48 carbonates may greatly affect Ca isotope values in the global mantle or on a regional scale.

49

50 *Keywords:* Ca isotopes; Isotope fractionation; Lithospheric mantle; Carbonate; Metasomatism; Crustal

51 recycling

## 1. INTRODUCTION

Two most abundant Ca isotopes,  $^{40}\text{Ca}$  (96.94%) and  $^{44}\text{Ca}$  (2.09%), have a mass difference of about 10% (Heuser et al., 2002) and thus can experience significant fractionation at low temperatures near the Earth's surface. The Ca isotope compositions, expressed as  $\delta^{44/40}\text{Ca}$  relative to the NIST SRM 915a reference material, range by up to several permil in Ca-rich sedimentary and other rocks formed or altered near the surface (Amini et al., 2009; Blättler and Higgins, 2017; Fantle and Tipper, 2014; Feng et al., 2016). In contrast, high temperature equilibrium isotope fractionation in the mantle should be at least an order of magnitude lower (e.g. Huang et al., 2010; Wang et al., 2017; Zhu et al., 2018). This difference may make it possible to use Ca isotopes to trace recycling of Ca-rich surface materials because mantle rocks contaminated by surface materials may have unusual isotope ratios. Hence, Ca isotopes may shed more light on the long-lasting debate on the role of crustal components in the mantle (e.g. Xu, 2002) along with other non-conventional stable isotopes (e.g. Huang et al., 2011; Wang et al., 2016). Ca isotopes are particularly promising to explore the role of subducted Ca-rich sediments in the sources of mantle metasomatism and mantle-derived magmas (e.g. Chen et al., 2018; Huang S. et al., 2011; Zeng et al., 2010), and in carbon cycling (e.g. Tappe et al., 2017).

The application of Ca isotopes to these topics necessitates a good knowledge of, first, the range of Ca isotope compositions in pristine mantle rocks that contain no crustal additions, and second, the extent of intra-mantle isotope differentiation by melting and metasomatism including non-equilibrium processes like diffusion (e.g. Zhao et al., 2017) and inter-mineral fractionation (Huang et al., 2010; Kang et al., 2016; Wang et al., 2017). Recently, Kang et al. (2017) reported Ca isotope compositions for mantle peridotites ranging from fertile lherzolites to harzburgites, and constrained the Ca isotope composition of the bulk silicate Earth (BSE)

77 and pristine melting residues. They also found that  $\delta^{44/40}\text{Ca}$  in metasomatized peridotites  
78 spans a range from the BSE to considerably lower values.

79 Here we report  $\delta^{44/40}\text{Ca}$  for a suite of strongly metasomatized, Ca-enriched mantle rocks to  
80 better define the Ca isotope range in the lithospheric mantle, primarily to constrain the role of  
81 metasomatism by carbonate-rich and silicate melts. We provide whole rock (WR) data for 16  
82 peridotite and two pyroxenite xenoliths from the Obnazhennaya (Obn) kimberlite in the NE  
83 Siberian craton (Ionov et al., 2015; Ionov et al., 2018b) as well as for acid leachates and  
84 leaching residues of three Obn peridotites that contain metasomatic carbonate. We also report  
85 WR data for four refractory non-metasomatised peridotite xenoliths from Tariat in Mongolia  
86 (Ionov and Hofmann, 2007) to better define the Ca isotope range in pristine melting residues.

87

88

## 2. LOCALITIES AND SAMPLES

89

### 2.1. Obnazhennaya and its mantle xenoliths

90  
91 The ~160 Ma Obnazhennaya kimberlite (70°15' N, 121°35'E) is located in the NE  
92 Siberian craton (Fig. 1). It is one of only two kimberlites in Siberia that contain peridotite  
93 xenoliths sufficiently large and fresh for WR petro-geochemical studies. Re-Os isotope data  
94 suggest that their sources experienced partial melting at ~1.9 and 2.8 Gy ago (Ionov et al.,  
95 2015; Ionov et al., 2018a). Petrographic and chemical data (Ionov et al., 2018b /and  
96 references therein) suggest that the Obn xenolith suite is unusual for cratons, with common  
97 peridotites rich in clinopyroxene (cpx) and garnet but low in orthopyroxene (opx), no sheared  
98 rocks, and low P-T values suggesting a very thin mantle lithosphere ( $\leq 100$  km). Some  
99 samples contain alteration products (mainly serpentine at grain boundaries and veins in  
100 olivine), but they are less common than in most cratonic suites elsewhere.

101 The Obn peridotites have protogranular to mosaic-equigranular microstructures and are  
102 grouped into four series (Table 1): (1) low-cpx spinel harzburgites and dunites; (2)  
103 phlogopite- and carbonate-bearing, Ca-rich rocks with low to moderate Al; (3) peridotites  
104 with low to moderate Al, rich in Ca and cpx; (4) Ca-Al-rich lherzolites rich in pyroxenes ±  
105 garnet. They are distinguished from typical cratonic xenolith suites by the rarity of  
106 harzburgites and by gradual modal variations of olivine, pyroxenes and garnet between  
107 peridotites and pyroxenites. In some of these rocks opx is replaced with late-stage cpx ±  
108 phlogopite (Fig. 2a). Three peridotites contain pockets of carbonate (Mn-Mg-bearing calcite)  
109 texturally equilibrated with garnet and olivine (Fig. 2c, d); these rocks are unique because  
110 peridotite xenoliths containing carbonates of mantle origin are extremely rare (e.g., Ionov et  
111 al., 1993). Pyroxenites (websterites) occur as discrete xenoliths (O-1080) and veins in  
112 peridotites (Obn 58-13 and 68-13; Fig. 2b).

113 The majority of the Obn xenoliths have low Al<sub>2</sub>O<sub>3</sub> (≤1.9 wt.%) and high MgO (>42%),  
114 consistent with an origin as residues of high-degree partial melting because these oxides are  
115 considered to be robust melt extraction indices, and because they plot on the Al-Mg trend  
116 defined by experimental and natural (Tariat) melting residues (Fig. 3a). Yet the Obn xenoliths  
117 also show petrographic and chemical features that cannot be explained by melt extraction  
118 alone, in particular anomalously high CaO at given Al<sub>2</sub>O<sub>3</sub> (Fig. 3b). As a result, the Ca/Al  
119 ratios of nearly all Obn peridotites in this study are much higher than in the primitive mantle  
120 (McDonough and Sun, 1995) and in residual mantle peridotites (Ionov and Hofmann, 2007;  
121 Palme and Nickel, 1985) (1.6–8.0 vs. 1.0–1.5; Fig. 3c). These and other data suggest that the  
122 Obn xenoliths initially formed as refractory melting residues, but were reworked by silicate  
123 and/or carbonatite metasomatism with significant Ca input. The Ca-Al-rich rocks formed by  
124 reaction and mingling with large amounts of silicate melts. The three Series 1 peridotites low  
125 in both Ca and Al are melt-channel materials (Ionov et al., 2018b).

126 Another four peridotite xenoliths are from late Cenozoic (~0.5 Ma) alkali basaltic breccia  
127 at Shavaryn-Tsaram in the Tariat district of central Mongolia (Ionov 2007) within the Central  
128 Asian orogenic belt. The samples are cpx-poor lherzolites or cpx-bearing spinel harzburgites  
129 with modal and major oxide compositions typical for refractory melting residues, and no  
130 evidence for metasomatism (Ionov and Hofmann, 2007). Their Al<sub>2</sub>O<sub>3</sub> range (1.0–2.1 wt.%;  
131 Table 1) is similar to that for the Obn peridotites, but the Tariat peridotites show no Ca  
132 enrichments and no anomalous Ca/Al ratios (Fig. 3).

133

## 134 2.2. Sample selection and treatment

135 The samples (aliquots of those reported by Ionov et al., 2018b and Ionov and Hofmann,  
136 2007) are listed in Table 1 that provides a summary of essential petrologic and chemical data.  
137 The xenoliths are 10–30 cm in size. Their rinds were removed by sawing. Slabs of fresh  
138 material from xenolith cores were inspected to make sure they contain no host lava, veins or  
139 modal gradations. A large amount of fresh material (normally >100 g) was taken to provide  
140 representative WR samples and crushed to <5–10 mm in a steel jaw crusher carefully cleaned  
141 to avoid cross-contamination. Splits of crushed material (50–100 g) were ground to fine  
142 powder in agate.

143 Three carbonate-bearing Obn peridotites (8-13, 22-13 and 39-13) were acid-leached to  
144 dissolve metasomatic calcite and analyze the resulting solution and the residue after leaching.  
145 Aliquots of crushed ( $\leq 2$  mm) rocks were treated with 5 ml of 10% HNO<sub>3</sub> for 2 minutes at  
146 room temperature, which produced CO<sub>2</sub> bubbles for less than a minute. The solution was  
147 extracted, the residue washed with 2 ml milli-Q water four times, and the wash water was  
148 added to the acid-leach solution for analysis. The residues were dissolved using the same  
149 procedure as for WR powders (described below). Previous work showed that leaching of  
150 silicate minerals (including phlogopite and amphibole) and glass from mantle xenoliths with

151 diluted cold HNO<sub>3</sub> for a few minutes does not destroy these phases nor affect their surfaces  
152 (e.g., [Ionov and Hofmann, 1995](#); [Ionov et al., 1993](#)).

153

### 154 3. ANALYTICAL PROCEDURES AND DATA QUALITY

155

156 Sample dissolution, chemical purification and mass spectrometric analysis of Ca were  
157 done at Arizona State University (ASU) following procedures defined by [Romaniello et al.](#)  
158 [\(2015\)](#). Briefly, 10–60 mg of rock powder was digested using a mixture of concentrated HF  
159 and HNO<sub>3</sub> (5:1) in a 7 mL Savillex<sup>TM</sup> PFA beaker on hot plate at 110°C for 2–3 days. After  
160 the digestion, the samples were dried at 80°C and refluxed with 6M (mol/L) HCl several  
161 times to remove precipitated CaF<sub>2</sub> until completely dissolved, then evaporated to dryness. The  
162 dried material was dissolved in 2M HNO<sub>3</sub> for column chemistry.

163 Separation of Ca from sample matrix was performed automatically using the prepFAST  
164 MC (ESI, Omaha, NE, USA) and the supplied 1 mL Sr-Ca column (part number CF-MC-  
165 SrCa-1000) following the method of [Romaniello et al. \(2015\)](#). Elution uses 2M HNO<sub>3</sub> + 1  
166 wt.% H<sub>2</sub>O<sub>2</sub> to remove most major and trace matrix elements. Sr is eluted in 6M HNO<sub>3</sub> and Ca  
167 with 12M HNO<sub>3</sub>. In the final step, 10 mL of 1M HF is used to remove all remaining elements  
168 from the resin (REE, Hf, Cd and U). The Ca yield of the column chemistry, calculated by  
169 comparing the amount of Ca before and after the column procedure, ranged from 90% to  
170 93%. [Romaniello et al. \(2015\)](#) found no detectable Ca isotope fractionation at Ca yields as  
171 low as 75%. The concentrations of Ca and other elements were measured using an ICAP-Q  
172 quadrupole inductively-coupled plasma mass spectrometer (ICP-MS: Thermo Scientific,  
173 Bremen, Germany) at ASU following the method of [Romaniello et al. \(2015\)](#).

174 Calcium isotope compositions were measured on a Neptune multi-collector (MC) ICP-MS  
175 (Thermo Scientific, Bremen, Germany) at ASU equipped with a Jet sample cone, an H-

176 skimmer cone, and an Apex-Q desolvating nebulizer (ESI, Omaha, NE, USA). Measurements  
177 were done using the double spike method with sample-standard bracketing. The Ca double  
178 spike was prepared from two isotopically enriched CaCO<sub>3</sub> powders (Isoflex USA)  
179 containing <sup>43</sup>Ca (62.20 atom %) and <sup>46</sup>Ca (15.90 atom %), respectively. The isotope  
180 compositions of the double spike and the in-house natural isotope standard (“ICP1” NIST  
181 10000 ppm ICP Ca standard, lot #X-10-39A) were calibrated using MC-ICP-MS. The double-  
182 spike solution was added as 2% of the total Ca concentration in samples ≥24 hours before the  
183 isotope analysis to allow full spike-sample equilibration.

184 The samples and standards were measured in high-resolution mode with a mass resolution  
185 of ≥8000 (measured as  $M/\Delta M$ , where  $\Delta M$  is the mass difference at 5% and 95% peak height).  
186 Optimized instrument operating parameters were: sample gas, 0.9 L min<sup>-1</sup>; auxiliary gas, 0.9  
187 L min<sup>-1</sup>; cooling gas, 14.50 L min<sup>-1</sup>, and N<sub>2</sub> of 2–5 mL min<sup>-1</sup>. Ca samples were introduced at a  
188 concentration of 3 µg/g and flow rate of 200 mL min<sup>-1</sup> yielding a sensitivity of ~3.3 V <sup>44</sup>Ca<sup>+</sup>  
189 per µg/g Ca. Faraday cups were positioned to measure <sup>42</sup>Ca<sup>+</sup>, <sup>43</sup>Ca<sup>+</sup>, <sup>44</sup>Ca<sup>+</sup>, <sup>45</sup>Sc<sup>+</sup>, <sup>46</sup>Ca<sup>+</sup>, <sup>47</sup>Ti<sup>+</sup>,  
190 and <sup>48</sup>Ca<sup>+</sup>. <sup>45</sup>Sc was measured to align the uninterfered low-mass shoulder of the Ca and Ti  
191 isotopes with its peak center. Once aligned, the center cup was set to measure an optimal  
192 position on the uninterfered low-mass peak shoulder of Ca isotopes. <sup>47</sup>Ti was monitored to  
193 correct for the isobaric interference of <sup>48</sup>Ti on <sup>48</sup>Ca. Doubly charged Sr<sup>2+</sup>, which is a common  
194 isobaric interference for Ca isotopes, was monitored for all samples and standards using a  
195 sub-configuration of Faraday cups. Details of the cup configuration and interference  
196 corrections are given in [Romaniello et al. \(2015\)](#). Double-spiked Ca samples were run in  
197 sequence with every two samples bracketed by the equivalently spiked ICP1 in-house  
198 standard. Mass bias and corrected isotopic ratios were calculated using the Newton-Rhapson  
199 procedure ([Albarède and Beard, 2004](#)).

200 Three purified and double-spiked secondary Ca standards (international reference

201 materials NIST SRM 915a, NIST SRM 915b, and IAPSO: [http://www.ciaaw.org/calcium-](http://www.ciaaw.org/calcium-references.htm)  
202 [references.htm](http://www.ciaaw.org/calcium-references.htm)) were measured every 10–14 samples in each analytical session to check if the  
203 method consistently produces accurate and precise values. NIST SRM915a and SRM915b are  
204 carbonate reference materials, and IAPSO is seawater; all secondary standards were purified  
205 using the same procedure as the samples. The Ca isotope ratios are calculated in delta notation  
206 ( $\delta^{44/42}\text{Ca}_{\text{SRM915a}}$ ,  $\delta^{44/42}\text{Ca}$  (‰) =  $[(^{44}\text{Ca}/^{42}\text{Ca})_{\text{sample}}/(^{44}\text{Ca}/^{42}\text{Ca})_{\text{NIST SRM 915a}} - 1]$ ). Final data are  
207 reported as  $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$  ( $\delta^{44/40}\text{Ca}$  (‰) =  $[(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}}/(^{44}\text{Ca}/^{40}\text{Ca})_{\text{NIST SRM 915a}} - 1]$ )  
208 obtained by multiplying  $\delta^{44/42}\text{Ca}_{\text{SRM915a}}$  by a scaling factor of 2.049 based on kinetic mass  
209 dependent fractionation (Young et al., 2002) (Table 2).

210 All samples were measured at least 3 times; the analytical error is reported as 2 standard  
211 deviations (2SD) of replicate measurements. Long-term external precision (2SD of  $\delta^{44/42}\text{Ca}$  in  
212 SRM915a) during this study was 0.08‰ (n=24), and the precision for  $\delta^{44/40}\text{Ca}$  can be  
213 propagated as  $0.08 \times 2.049 \approx \pm 0.16\%$ . Mean  $\delta^{44/40}\text{Ca}$  values (relative to SRM915a) for  
214 reference samples run in the same session (Table 2) are: SRM915a,  $0.00 \pm 0.16\%$  (n=24);  
215 SRM915b,  $0.70 \pm 0.16\%$  (n=20); IAPSO Seawater,  $1.82 \pm 0.16\%$  (n=17); BHVO-2,  
216  $0.82 \pm 0.10\%$  (n=3); PCC-1,  $1.29 \pm 0.02\%$  (n=3). These values agree with data in the literature,  
217 for example He et al. (2017) reported  $0.79 \pm 0.09\%$  (n=7) for in BHVO-2 and Liu et al. (2017)  
218 reported  $1.15 \pm 0.09\%$  (n=7) for peridotite PCC-1 (see also Feng et al., 2016; Valdes et al.,  
219 2014; Amsellem et al., 2017) confirming the robustness of our analytical procedure. In  
220 addition, full duplicates of sample Obn 8-13 obtained by digestion of two batches of powder  
221 reproduced within the analytical error (Table 2).

222

223

## 4. RESULTS

224

### 225 4.1. Ca isotopes in whole-rock xenoliths

226 The  $\delta^{44/40}\text{Ca}$  values in the WR xenoliths from the Obn suite (Table 2) range from 0.56 to  
227 1.38‰, but the range is much more narrow (0.74–0.97‰) for 15 out of 18 samples analyzed  
228 (Fig. 4). These 15 samples are mainly harzburgites, but also include spinel and garnet  
229 lherzolites, wehrlites and pyroxenites, i.e. all main rock types in the Obn suite (Ionov et al.,  
230 2018b). The three outliers are xenoliths with unusual rock types or major oxide compositions.  
231 The highest  $\delta^{44/40}\text{Ca}$  ( $1.38 \pm 0.04\text{‰}$ ) is in Obn 68-13, the only peridotite sample  
232 in the suite taken close to contact with a pyroxenite vein (Fig. 2b). The other sample with  
233 high  $\delta^{44/40}\text{Ca}$  ( $1.22 \pm 0.07\text{‰}$ ) is a spinel dunite (melt channel material  
234 consisting of olivine and accessory chromite) with the lowest  $\text{Al}_2\text{O}_3$  (0.14 wt.%)  
235 among our samples. The lowest  $\delta^{44/40}\text{Ca}$  value ( $0.56 \pm 0.03\text{‰}$ ) is for peridotite Obn 24-  
236 13, in which coarse opx is replaced with fine-grained pockets of cpx, phlogopite  
237 and chromite (Fig. 2a). Four peridotite xenoliths from Tariat in Mongolia (harzburgites to low-cpx  
238 lherzolites) have  $\delta^{44/40}\text{Ca}$  values from 0.96 to 1.12‰. Their range overlaps the highest  $\delta^{44/40}\text{Ca}$   
239 values found in four out of 15 “conventional” Obn xenoliths (0.96–0.97‰), but is  
240 considerably higher than  $\delta^{44/40}\text{Ca}$  in the remaining 11 Obn samples (0.74–0.88‰) (Fig. 4).

241

#### 242 4.2. Ca isotope data from acid-leaching experiments

243 Leaching by diluted  $\text{HNO}_3$  done on crushed (but not ground) aliquots of three xenoliths  
244 should dissolve metasomatic calcite, but leave intact the silicate and oxide minerals. For one  
245 sample (Obn 8-13, Fig. 2c) the WR powder was analyzed in duplicate. The additional  $\delta^{44/40}\text{Ca}$   
246 values determined for the leachate and residue, as well as bulk  $\delta^{44/40}\text{Ca}$  values calculated  
247 using the Ca proportions in the leachate and residue for each sample, are given in Table 3.

248 All four analyses obtained on sample Obn 8-13 are within analytical uncertainty, with  
249  $\delta^{44/40}\text{Ca}$  values of  $0.88 \pm 0.04\text{‰}$  and  $0.83 \pm 0.12\text{‰}$  for the WR duplicates,  $0.82 \pm 0.01\text{‰}$  for  
250 the leachate and  $0.84 \pm 0.06\text{‰}$  in the residue. The differences between the leachate and

251 residue for two other samples are insignificant as well:  $0.84 \pm 0.04\%$  for the leachate and  
252  $0.70 \pm 0.12\%$  for the residue of Obn 22-13, and  $0.83 \pm 0.06\%$  for the leachate and  $0.81 \pm$   
253  $0.08\%$  for the residue of Obn 39-13. To sum up, the  $\delta^{44/40}\text{Ca}$  values of the leachates and  
254 residues are essentially the same within analytical uncertainty suggesting that the metasomatic  
255 carbonates do not differ significantly in  $\delta^{44/40}\text{Ca}$  from the host rock.

256

257

## 5. DISCUSSION

258

### 259 5.1 $\delta^{44/40}\text{Ca}$ in refractory, melt-depleted peridotite mantle

260 The Obn and Tariat peridotite xenoliths are fragments of the lithospheric mantle, which is  
261 believed to form from the asthenosphere either by conductive cooling or, most commonly, by  
262 additions of solidified melt extraction residues. Kang et al. (2017) estimated the  $\delta^{44/40}\text{Ca}$   
263 value in the bulk silicate Earth (BSE;  $0.94 \pm 0.05\%$ ) from data for fertile off-craton lherzolite  
264 xenoliths, which experienced no or only very low degrees of partial melting, and have major  
265 oxide compositions (MgO,  $\text{Al}_2\text{O}_3$ , CaO etc.) similar to those of the primitive mantle (PM).  
266 They further argued that  $\delta^{44/40}\text{Ca}$  values for refractory peridotites (formed by high degrees of  
267 melt extraction from fertile mantle) are somewhat higher ( $1.06 \pm 0.04\%$ ) if they are not  
268 significantly affected by post-melting metasomatism (Fig. 4).

269 The  $\delta^{44/40}\text{Ca}$  values of the four melt-depleted peridotites from Mongolia ( $0.96\text{--}1.12\%$ )  
270 follow the trends defined by the samples reported by Kang et al. (2017) in plots vs.  $\text{Al}_2\text{O}_3$  and  
271 CaO (Fig. 4a, b). Their averages ( $1.04 \pm 0.08\%$  for all four, and  $1.10 \pm 0.03\%$  for two most  
272 refractory samples with the lowest Al and Ca) are consistent with the conclusion of Kang et  
273 al. (2017) on the effects of melting on  $\delta^{44/40}\text{Ca}$  in residues. Combining the data on peridotites  
274 with  $\text{Al}_2\text{O}_3 < 2$  wt.% from the study of Kang et al. (2017) and this work yields an average of  
275  $1.08 \pm 0.03\%$  for refractory mantle, i.e.  $\sim 0.14\%$  heavier than the BSE estimate.

276 The Obn peridotites studied here, however, are neither fertile mantle samples, nor pristine  
277 melting residues because their modal and chemical compositions have been strongly affected  
278 by melt metasomatism (Ionov et al., 2018b). The dunites (low-Ca-Al peridotites) appear to be  
279 melt channel materials formed by reaction of peridotites with mafic melts, while the  
280 ubiquitously high CaO and Ca/Al (Fig. 3b, c), as well as occasional carbonates and late-stage  
281 cpx, in the remainder of the peridotite suite suggest important Ca input, most likely by  
282 carbonate-rich melts. The effects of melt extraction on Ca isotope ratios in these samples must  
283 have been obscured by the later processes.

284

## 285 **5.2 Ca-isotope signatures of mantle metasomatism**

### 286 *5.2.1 $\delta^{44/40}\text{Ca}$ in carbonate-bearing xenoliths*

287 The effects of carbonatite metasomatism on  $\delta^{44/40}\text{Ca}$  of mantle peridotites are examined  
288 here directly using analyses of natural carbonate-bearing xenoliths, which are very rare  
289 worldwide (e.g. Ionov et al., 1993). The precursors of Ca-rich, low-Al (0.4–1.9 wt.%  $\text{Al}_2\text{O}_3$ )  
290 Obn peridotites were refractory melting residues, possibly akin to melt-depleted Tariat  
291 peridotites (*section 5.1*), assuming that Al concentrations are not affected by the  
292 metasomatism. The  $\delta^{44/40}\text{Ca}$  values of WR Obn xenoliths containing metasomatic carbonates  
293 (0.74–0.88‰) are consistently lower (by 0.2–0.3‰) than for their likely residual protoliths  
294 ( $1.08 \pm 0.03\%$  as discussed in the previous section). It follows that the metasomatism of the  
295 Obn peridotites by carbonate-rich media reduced  $\delta^{44/40}\text{Ca}$  values, but the Ca isotope change is  
296 moderate.

297 Mass balance estimates using modal abundances (Table 1) and observed Ca concentrations  
298 in minerals (Ionov et al., 2018b) show that calcite hosts 75–85% of Ca in these rocks. The  
299 fact that  $\delta^{44/40}\text{Ca}$  values are similar for acid-leachates (i.e. dissolved carbonates) and leaching  
300 residues (silicates) for all the samples may indicate that the carbonates are close to isotope

301 equilibrium with Ca-bearing silicates (mainly garnet and cpx) in the host peridotites. This  
302 must be the case for garnet, which is texturally equilibrated with calcite in pockets formed by  
303 reaction of metasomatic liquids with opx and spinel (Fig. 2c, d). In contrast, cpx in these  
304 rocks only occurs outside the calcite- and garnet-bearing pockets and may have existed before  
305 their formation. Trace element data (Ionov et al., 2018b) suggest that the cpx may not be fully  
306 equilibrated with the garnet in the metasomatic pockets.

307 Another xenolith strongly reworked by the carbonatite-type metasomatism is Obn 24-13,  
308 in which much of the opx is replaced with cpx-phlogopite pockets (Fig. 2a; Ionov et al.,  
309 2018b). This sample has the lowest  $\delta^{44/40}\text{Ca}$  (0.56‰) for this study, i.e.  $\geq 0.2\%$  lower than for  
310 the carbonate-bearing Obn peridotites and  $\sim 0.5\%$  lower than for unmetasomatized Tariat  
311 peridotites. This peridotite contains very little  $\text{Al}_2\text{O}_3$  (0.41 wt.%) and has a very high Ca/Al of  
312 8, suggesting that its Ca budget is dominated by metasomatic Ca input (Fig. 3c).

313 It appears that, in general, the greatest metasomatism-induced Ca isotope offsets in the  
314 Obn suite are for rocks initially very low in Ca that experienced high Ca additions relative to  
315 their Ca contents before the metasomatism, and developed high Ca/Al ratios. The Obn suite  
316 defines a negative Ca/Al vs.  $\delta^{44/40}\text{Ca}$  trend (Fig. 4c), which remains significant (linear  
317 correlation coefficients of 0.4–0.7) also without the two samples with the highest Ca/Al (5.9  
318 and 8.0). Thus, assuming that all the Ca-rich, low-Al Obn peridotites were metasomatized by  
319 the same liquid the  $\delta^{44/40}\text{Ca}$  of such a liquid could be close to 0.5‰, like in Obn 24-13.  
320 Alternatively, xenolith Obn 24-13 may have been metasomatized by a batch of Ca-rich liquid  
321 with lower  $\delta^{44/40}\text{Ca}$  than for other Obn peridotites. It is also likely that the  $\delta^{44/40}\text{Ca}$  in the  
322 metasomatic media evolved as they percolated through the residual mantle with higher  
323  $\delta^{44/40}\text{Ca}$ .

324 We infer that the metasomatism of the type that produced the carbonate-bearing Obn  
325 xenoliths tends to decrease the  $\delta^{44/40}\text{Ca}$  values of residual mantle rocks, but its effects are

326 usually limited ( $\leq 0.3\%$ ) even in cases of strong Ca enrichments and apparent Ca isotope  
327 equilibration between the metasomatic media and the reworked peridotites.

328

### 329 5.2.2 Ca isotope signatures of “carbonatite” vs. “silicate” metasomatism

330 Kang et al. (2017) reported  $\delta^{44/40}\text{Ca}$  ranging from 0.25 to 0.96‰ for six harzburgites and  
331 low-cpx lherzolites with “carbonatite-type” metasomatism (inferred from WR and cpx REE  
332 patterns) from the Udachnaya kimberlite in the central Siberian craton and from Tariat (Fig.  
333 1; Doucet et al., 2012; Ionov et al., 2010). They found the lowest  $\delta^{44/40}\text{Ca}$  of 0.25‰ in a single  
334 sample extremely low in  $\text{Al}_2\text{O}_3$  (0.09 wt.%) and with high Ca/Al (3.9), but other low- $\delta^{44/40}\text{Ca}$   
335 (0.55–0.79‰) xenoliths from Kang et al. (2017) have both low CaO and low Ca/Al (Fig. 4b,  
336 c), unlike those in this study. Furthermore, Kang et al. (2017) reported  $\delta^{44/40}\text{Ca}$  of 0.83 to  
337 0.89‰ for three Ca-Al-rich lherzolites affected by “silicate-melt” metasomatism (Fig. 4),  
338 which overlap the  $\delta^{44/40}\text{Ca}$  range for the carbonate-bearing Obn xenoliths.

339 The  $\delta^{44/40}\text{Ca}$  range for eight out of nine metasomatized xenoliths from Kang et al. (2017)  
340 (0.55–0.96‰) is nearly the same as for the Obn xenoliths studied here apart from two unusual  
341 Obn peridotites (see next section) with high  $\delta^{44/40}\text{Ca}$  (Fig. 4). In particular, the  $\delta^{44/40}\text{Ca}$  range  
342 in the Udachnaya and Tariat xenoliths presumably affected by the silicate-melt metasomatism  
343 (0.83–0.89‰) overlaps the  $\delta^{44/40}\text{Ca}$  range in the carbonate-bearing and other Ca-rich Obn  
344 xenoliths of this study. We conclude that  $\delta^{44/40}\text{Ca}$  cannot be used to robustly distinguish  
345 between “carbonatite” and “silicate” metasomatism. It appears, however, that the lowest  
346  $\delta^{44/40}\text{Ca}$  in the lithospheric mantle may be found mainly in the most refractory, low-Al  
347 peridotites.

348

### 349 5.3 Peridotites with high $\delta^{44/40}\text{Ca}$

350 The  $\delta^{44/40}\text{Ca}$  of 1.22 and 1.38‰ in two Obn xenoliths are enigmatic because they are too  
351 high to be attributed either to melt extraction from fertile mantle (*section 5.1*) or to reaction  
352 with the same Ca-rich metasomatic media that affected the other Obn xenoliths (which have  
353 lower  $\delta^{44/40}\text{Ca}$ ). Metasomatized Tariat xenoliths have lower  $\delta^{44/40}\text{Ca}$  as well (*section 5.2.2*).  
354 Alternative explanations could take into account the evidence that both anomalous Obn  
355 samples were affected by silicate melt percolation. [Figure 2b](#) shows that peridotite Obn 68-13  
356 was sampled close (1–2 cm) to a websterite vein, composed of opx and cpx with minor  
357 olivine and spinel. Fine-grained spinel websterite veins with gradational contacts in this and  
358 other Obn xenoliths formed shortly before the kimberlite eruption because long residence in  
359 the mantle leads to recrystallization to more coarse and texturally equilibrated rocks ([Ionov et](#)  
360 [al., 2018b](#)). Furthermore, the absence of sharp contacts with host peridotites excludes an  
361 origin by intrusion of the kimberlite magma that carried the xenoliths.

362 It is conceivable that the silicate liquid, which formed the pyroxenite vein, had a high  
363  $\delta^{44/40}\text{Ca}$  and conveyed this Ca-isotope signature to the host peridotite by infiltration. This  
364 hypothesis cannot be tested directly because we have no Ca-isotope data on the vein, but it  
365 does not appear likely. First,  $\delta^{44/40}\text{Ca}$  values for erupted continental and oceanic basaltic  
366 magmas are <1.2‰ (e.g. [Zhu et al., 2018](#)). Second, the WR trace element pattern of Obn 68-  
367 13 is very similar to that of other Obn peridotites in this study ([Ionov et al., 2018b](#)) that show  
368 much lower  $\delta^{44/40}\text{Ca}$ . Finally, two pyroxenites analyzed in this study, including another fine-  
369 grained websterite, show lower  $\delta^{44/40}\text{Ca}$  (0.74–0.93‰; [Table 2](#)) further arguing against a  
370 source liquid with an anomalously high  $\delta^{44/40}\text{Ca}$ .

371 A detailed study, with analyses of the vein and of the host peridotites at different distances  
372 from the vein, is needed to examine the high  $\delta^{44/40}\text{Ca}$  in Obn 68-13. However, a viable  
373 alternative could be diffusion-driven kinetic fractionation of Ca isotopes at the melt-rock  
374 boundary, similar to that invoked to explain experimentally produced  $\delta^{44/40}\text{Ca}$  fractionation of

375 6‰ at the interface of molten basalt and rhyolite (Richter et al., 2003) or anomalous Cr  
376 isotope ratios in veined Tariat xenoliths (Xia et al., 2017). A diffusion-controlled process may  
377 have also enriched dunite Obn 59-13 (likely of melt-channel origin) in heavy Ca isotopes.

378 Kinetic fractionation of metal stable isotopes during melt-rock reaction and melt  
379 percolation was earlier invoked for Li, Fe, Mg (Foden et al., 2018; Pogge von Strandmann et  
380 al., 2011; Teng et al., 2011; Weyer and Ionov, 2007; Wu et al., 2018; Xiao et al., 2013) and  
381 other elements. Evidence for diffusion-controlled Ca isotope fractionation has been  
382 previously reported for a suite of peridotite xenoliths from North China that show  
383 anomalously low  $\delta^{44/40}\text{Ca}$  (−0.08 to 0.92‰) and  $\delta^{57/54}\text{Fe}$  (Zhao et al., 2017). Variable, but  
384 generally low, Mg# in those xenoliths are attributed to percolation of evolved basaltic liquids  
385 and possibly compositional effects of Ca isotopic fractionation between co-existing cpx and  
386 opx, supported by numeric modeling (Huang et al., 2010; Wang et al., 2017). Mass balance  
387 considerations suggest that if such a process produces a low- $\delta^{44/40}\text{Ca}$  component, it should  
388 also produce a complementary high- $\delta^{44/40}\text{Ca}$  component, which might explain the high-  
389  $\delta^{44/40}\text{Ca}$  values in the two Obn samples.

390

#### 391 **5.4 Ca isotopes as tracers of Ca recycling**

392 Mantle metasomatism by carbonatite and carbonate-rich silicate liquids extracted from  
393 subducted slabs that contain sedimentary carbonates has been repeatedly invoked for  
394 lithospheric erosion and reworking of the mantle lithosphere, in particular beneath the North  
395 China craton (e.g. Chen et al., 2018). Our study, however, finds no coherent and significant  
396 Ca isotope variations in mantle xenoliths that could be seen as robust evidence either for  
397 carbonatite metasomatism or links to subduction-related materials and tectonic settings.

398 Kang et al. (2017) speculated that low  $\delta^{44/40}\text{Ca}$  values in metasomatized mantle xenoliths  
399 may be linked to recycled crustal materials because the Ca isotope compositions of

400 sedimentary carbonates are highly heterogeneous and many of these rocks have lower  $\delta^{44/40}\text{Ca}$   
401 than BSE estimates (e.g. [Fantle and Tipper, 2014](#); [Farkaš et al., 2016](#); [Griffith et al., 2015](#);  
402 [Husson et al., 2015](#)). In particular, [Fantle and Tipper \(2014\)](#) reported a  $\delta^{44/40}\text{Ca}$  range from -  
403 1.1 to 1.8‰ for 1301 carbonate rocks (with 95% of data from -0.2 to +1.3‰) and a mean of  
404  $0.60 \pm 0.02\text{‰}$ , which is lower than the mean ( $0.94 \pm 0.04\text{‰}$ ) they obtained for 153 silicate  
405 rocks and minerals. Earlier, [Huang S. et al. \(2011\)](#) attributed  $\sim 0.3\text{‰}$  variation in  $\delta^{44/40}\text{Ca}$  for  
406 11 Hawaiian tholeiites (0.75–1.05‰) to addition of up to 4% of hypothetical recycled marine  
407 carbonates with  $\delta^{44/40}\text{Ca}$  of 0.2‰ to a plume component with  $\delta^{44/40}\text{Ca}$  of 1.05‰.

408 In contrast, a more recent data compilation for 505 Precambrian (0.54–3.0 Ga) carbonates  
409 ([Blättler and Higgins, 2017](#)) yielded an average  $\delta^{44/40}\text{Ca}$  of 0.94‰ and showed that the means  
410 for samples from 12 time intervals with >10 analyses did not exhibit a persistent temporal  
411 trend. [Blättler and Higgins \(2017\)](#) argued that the mean of the available carbonate sediment  
412 dataset is indistinguishable from  $\delta^{44/40}\text{Ca}$  estimates for the BSE within uncertainty. [Blättler](#)  
413 [and Higgins \(2017\)](#) also reported a  $\delta^{44/40}\text{Ca}$  range of 0.5–1.3‰ for carbonate veins from a  
414 drilled section of 170 Ma altered oceanic crust, with the majority of the data between 0.88 and  
415 1.28‰. They noted that the average for veins from this and the majority of other drilled sites  
416 are higher than BSE estimates, which implies that alteration of oceanic crust may not produce  
417 low  $\delta^{44/40}\text{Ca}$  values in subducted slabs.

418 Two aspects of the data in this study are consistent with the contention that sediment  
419 recycling and subduction of oceanic crust may not produce significant bulk changes in the Ca  
420 isotope composition of the mantle. The first is that metasomatism does not appear to produce  
421 considerable  $\delta^{44/40}\text{Ca}$  shifts from the BSE value in the majority of studied mantle peridotites.  
422 This is expected if the mean  $\delta^{44/40}\text{Ca}$  of recycled crustal materials is similar to that of the  
423 convecting mantle. The second argument is the lack of clear differences in the  $\delta^{44/40}\text{Ca}$  values  
424 of mantle xenoliths affected by “carbonatite” vs. “silicate” mantle metasomatism (*section*

425 5.2.2). The opposite should be observed if carbonatite liquids are derived from the recycling  
426 of sedimentary carbonates with  $\delta^{44/40}\text{Ca}$  distinct from those of mafic silicate melts, which are  
427 thought to be derived by low-degree melting and fractionation in upwelling deep mantle.

428 It is difficult, however, to assess how spatially heterogeneous and extreme could be the  
429  $\delta^{44/40}\text{Ca}$  values of subducted carbonate sediments and their derivatives on a local or a regional  
430 scale. [Blättler and Higgins \(2017\)](#) reported standard deviations ranging from 0.03 to 0.27‰  
431 for mean  $\delta^{44/40}\text{Ca}$  values of individual sections/formations (with  $\geq 10$  analyses) of their  
432 carbonate dataset, which may reflect Ca isotope variability within the formations. Mingling of  
433 fluids expelled from different parts of subducted slab (e.g. various sediments and altered  
434 oceanic crust) may further reduce Ca isotope variability in the metasomatic media injected to  
435 the mantle. Although one cannot rule out that recycling of sedimentary units with anomalous  
436  $\delta^{44/40}\text{Ca}$  values could locally introduce to the mantle carbonate-rich fluids or liquids that differ  
437 from the BSE estimate ( $0.94 \pm 0.05\text{‰}$ ) by  $>0.5\text{‰}$  (highest 2SD values for individual  
438 formations reported by [Blättler and Higgins, 2017](#)), such cases may be rare.

439 This contention is supported by the limited currently available Ca-isotope data on mantle  
440 rocks. The  $\delta^{44/40}\text{Ca}$  values in carbonate-bearing Obn xenoliths are just 0.10–0.15‰ lower than  
441 the BSE estimate. Only one out of 50 samples from six eruption centers reported here and by  
442 [Kang et al. \(2017\)](#) deviates by  $>0.5\text{‰}$  from the BSE value. This speaks for limited Ca isotope  
443 variability in liquids expelled from subducted slabs, and/or effective homogenization of their  
444 compositions on the way to the mantle domains studied so far. Stronger  $\delta^{44/40}\text{Ca}$  deviations by  
445 metasomatism cannot be ruled out at present, but may be rare; in some cases they may be due  
446 to kinetic isotope fractionation rather than exotic source compositions (*section 5.3*). Overall, it  
447 appears that Ca isotopes have little use as a tracer of carbonate recycling.

448 [Chen et al. \(2018\)](#) reported a  $\delta^{44/40}\text{Ca}$  range of 0.8–1.2‰ in pyroxenes (cpx and opx)  
449 from metasomatized peridotite xenoliths at Fanshi in NE China. This range extends to higher

450 values than for the peridotites reported in this study and the literature (Kang et al., 2017; Zhao  
451 et al., 2017). Chen et al. (2018) contended that the heavy Ca isotope compositions are  
452 inconsistent with low  $\delta^{44/40}\text{Ca}$  in carbonated sediments from the Paleo-Asian ocean and  
453 attributed the high  $\delta^{44/40}\text{Ca}$  to Ca isotope fractionation during subduction of carbonated  
454 sediments. The latter argument, however, may be at odds with their conclusion that Ca  
455 isotopes can be used to detect recycled crustal materials in the mantle.

456 To sum up, our data show no clear evidence that subduction and recycling of surface  
457 carbonates were responsible for mantle metasomatism and lithospheric erosion beneath  
458 Obnazhennaya. Overall, we see no evidence that Ca isotopes are robust and unequivocal  
459 tracers of recycling of surface carbonates to the mantle. It appears that although the Ca  
460 isotope range in some sedimentary carbonate suites is broad, their global, regional and  
461 temporal averages may not be very different from  $\delta^{44/40}\text{Ca}$  in the BSE (Blättler and Higgins,  
462 2017) and the most common mantle peridotites. It is also possible that local Ca  
463 isotope heterogeneities in subducted rocks are leveled out during the extraction of carbonate-  
464 rich fluids from the slab, and mingling and transport of the fluids/melts to the mantle  
465 lithosphere. Finally, while fluids released from subducted slabs impact the mantle wedge, the  
466 subducted sediments are ultimately stored in the deep mantle where they contribute to plume  
467 sources (e.g. Zeng et al., 2010). In such a case, Ca isotope signatures of melts and fluids  
468 generated by recent subduction events may be similar to those of plume-related magmatism.

469

470

## 6. SUMMARY OF CONCLUSIONS

471 The scope and the origin of Ca isotope variations in the lithospheric mantle are examined  
472 using analyses of 22 mantle xenoliths, including the first data on carbonate-bearing mantle  
473 rocks, as well as literature results. The  $\delta^{44/40}\text{Ca}$  range of  $1.10 \pm 0.03\%$  determined for  
474 refractory, non-metasomatized off-craton peridotites is higher than the BSE estimate ( $0.94 \pm$

475 0.05‰) based on fertile lherzolites (Kang et al., 2017) due to isotope fractionation during  
476 melt extraction.

477 The  $\delta^{44/40}\text{Ca}$  range for the majority of metasomatized peridotites from the Obnazhennaya  
478 kimberlite on the SE Siberian craton is narrow (0.74–0.97‰) and overlaps the BSE value.  
479 Bulk  $\delta^{44/40}\text{Ca}$  in Obn peridotites containing metasomatic calcite ranges from 0.81 to 0.83‰,  
480 with similar values in acid-leachates (carbonates) and leaching residues. Metasomatism tends  
481 to decrease the  $\delta^{44/40}\text{Ca}$  values of the affected mantle rocks, but the effects are usually limited  
482 ( $\leq 0.3\%$ ). Peridotites that were refractory and Ca-poor before the metasomatism, and which  
483 received the greatest relative Ca input (seen as high Ca/Al) usually have the lowest  $\delta^{44/40}\text{Ca}$ .

484 We find no evidence that  $\delta^{44/40}\text{Ca}$  can robustly distinguish between “carbonatite” and  
485 “silicate” metasomatism, or that recycling of crustal carbonates may greatly affect Ca isotope  
486 compositions in the global mantle. The latter may not be very different from the global mean  
487  $\delta^{44/40}\text{Ca}$  of subducted sedimentary carbonates implying that Ca isotopes have little use as a  
488 tracer of carbonate recycling. It is conceivable, however, that anomalous  $\delta^{44/40}\text{Ca}$  values are  
489 produced locally by kinetic isotope fractionation during intrusion and percolation of melts in  
490 channels and host peridotites. Ca isotope signatures of melts and fluids generated by recent  
491 subduction events may be similar to those of plume-related magmatism containing sediments  
492 subducted long time ago.

493

494

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501

502

## APPENDIX. SUPPLEMENTARY MATERIAL

503 Supplementary data associated with this article can be found, in the online version, at

504 <http://dx.doi.org/...>

505

### 506 **Figure captions**

507 **Fig. 1.** Locality map for the Obnazhennaya (Obn) and Udachnaya (Ud) kimberlite pipes on  
508 the Siberian craton, and the Cenozoic Tariat (Tar) volcanic field in central Mongolia.

509 **Fig. 2.** Photomicrographs in transmitted plane-polarized light (a-c), and a back-scattered  
510 electron (BSE) image (d) of Obnazhennaya peridotite xenoliths. Abbreviations: Carb,  
511 carbonate; Cpx, clinopyroxene; Phl, phlogopite; Spl, spinel; Gar, garnet; Ol, olivine. (a)  
512 Pocket of Cpx, Phl and Cr-spinel in Obn 24-13, likely formed by reaction of carbonate-rich  
513 media with orthopyroxene. (b) Websterite vein in fine-grained, mosaic, spinel peridotite Obn  
514 68-13; thin dark veinlet in the peridotite is chlorite, a Ca-free alteration mineral. (c) Carb-Gar-  
515 Ol-Spl pocket similar to that shown in detail in d. (d) Carbonate (Mg-Fe-Mn-bearing calcite)  
516 texturally equilibrated (straight grain boundaries) with garnet and olivine.

517 **Fig. 3.** Co-variation plots of MgO (a), CaO (b) and Ca/Al (c) vs. Al<sub>2</sub>O<sub>3</sub> (wt.%) in whole-  
518 rock (WR) peridotite xenoliths from Obnazhennaya (Obn, large circles; Obn 21-13 with ~8  
519 wt.% Al<sub>2</sub>O<sub>3</sub> is beyond the scale) and Tariat (“Tar”, triangles). Also shown (small rhombs) are  
520 additional Tariat samples from the literature (Ionov (2007); Ionov and Hofmann (2007)),  
521 which were not analyzed for Ca isotopes, and primitive mantle (PM) after McDonough and  
522 Sun (1995); PM is a term used in studies of chemical composition of mantle xenoliths, which  
523 is essentially equivalent to BSE commonly used in isotope studies. The Obn peridotites plot  
524 close to the melt extraction trend defined by the literature data for Tariat xenoliths on the Al-  
525 Mg diagram (a); this is because both Al and Mg are robust melt extraction indices and are

526 little affected by metasomatism. In contrast, the majority of the Obn peridotites have much  
527 higher CaO and Ca/Al due to post-melting Ca enrichments. The highest Ca/Al ratios are in  
528 low-Al<sub>2</sub>O<sub>3</sub> (<1.5 wt.%) rocks, i.e. residues of high degrees of melt extraction initially strongly  
529 depleted in Ca, for which the metasomatic input dominates the WR Ca budget.

530 **Fig. 4.** Co-variation plots of  $\delta^{44/40}\text{Ca}$  vs. (a) Al<sub>2</sub>O<sub>3</sub>, (b) CaO and (c) Ca/Al (wt.%) in whole-  
531 rock peridotite xenoliths from Obnazhennaya and Tariat. Large filled symbols, data from this  
532 study (circles, non-metasomatized melt-depleted Tariat peridotites; rhombs, metasomatized  
533 Obn xenoliths; triangle, Obn peridotite next to a vein); small empty symbols, data from [Kang](#)  
534 [et al. \(2017\)](#) for residual (KangRes, circles) and metasomatized (KangMet) peridotite  
535 xenoliths. Abbreviations: L, low (<2 wt.%); H, high; BSE, bulk silicate Earth (primitive  
536 mantle). Also shown are co-variation trends (best-fit lines: exponential in a-b and linear in c)  
537 and coefficients ( $R^2$ ) for residual, non-metasomatized Tariat peridotites from this study  
538 combined with those from [Kang et al. \(2017\)](#). The metasomatized peridotites tend to have  
539 lower  $\delta^{44/40}\text{Ca}$  than pristine melting residues, but the difference is small except for some  
540 samples with very low CaO and Al<sub>2</sub>O<sub>3</sub> ( $\leq 1$  wt.%). The  $\delta^{44/40}\text{Ca}$  are correlated with Ca/Al in  
541 the Obn suite, but not for xenoliths from the Udachnaya kimberlite (small rhombs, [Kang et](#)  
542 [al., 2017](#)).

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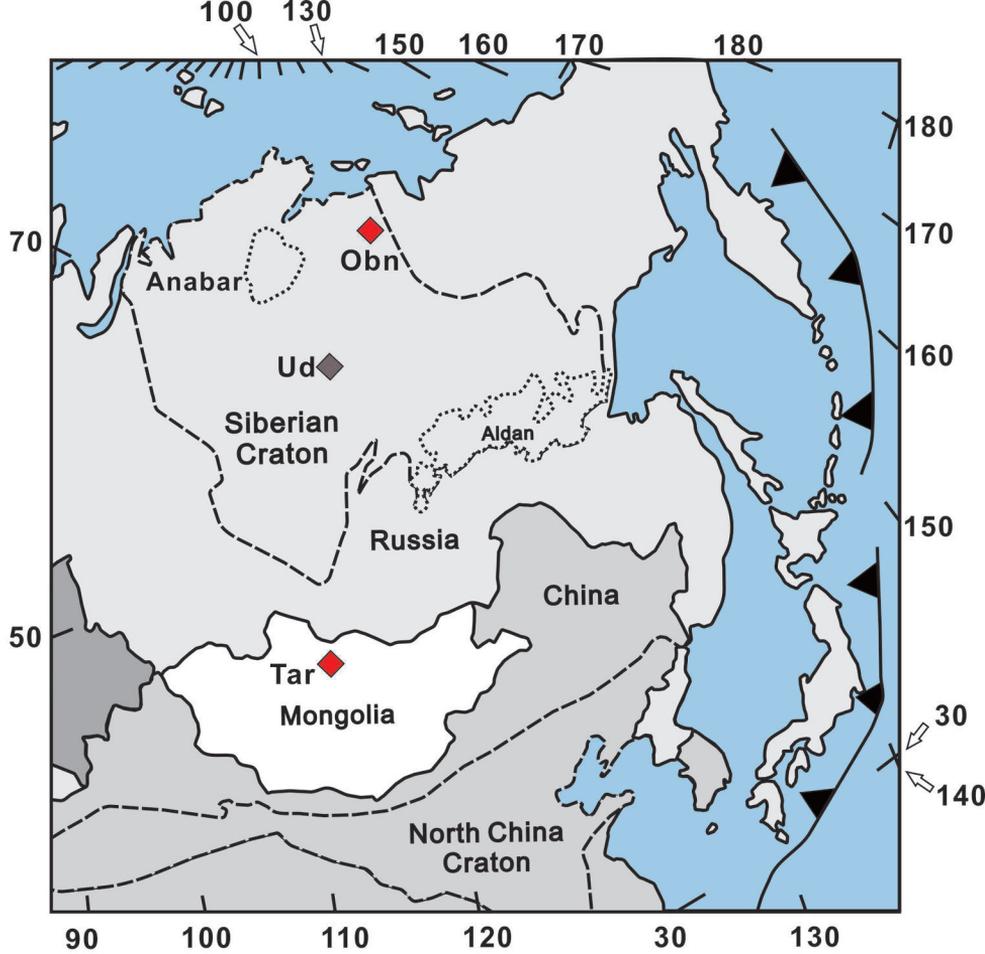
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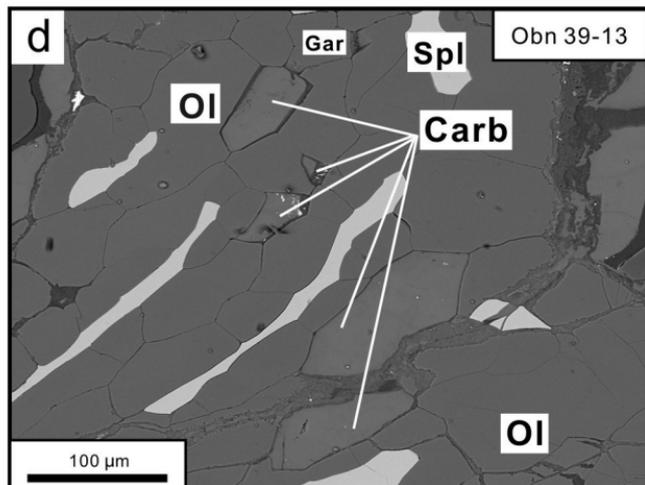
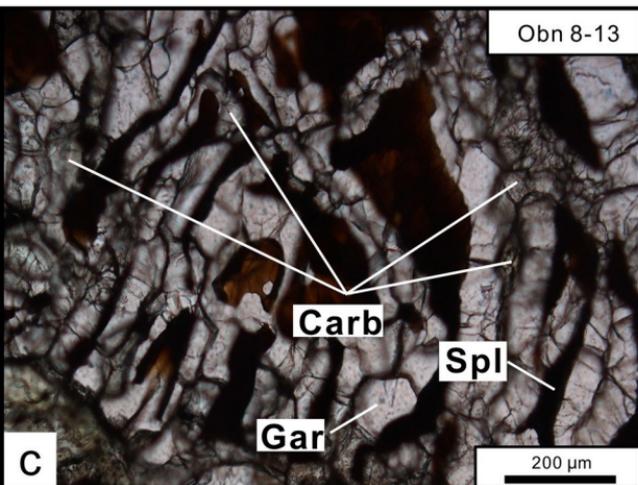
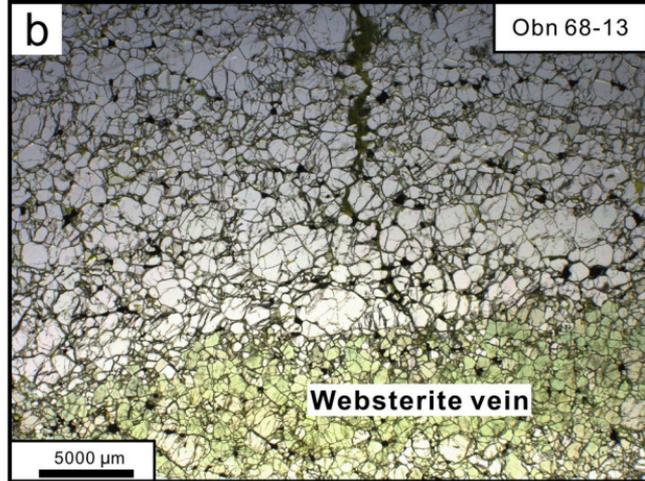
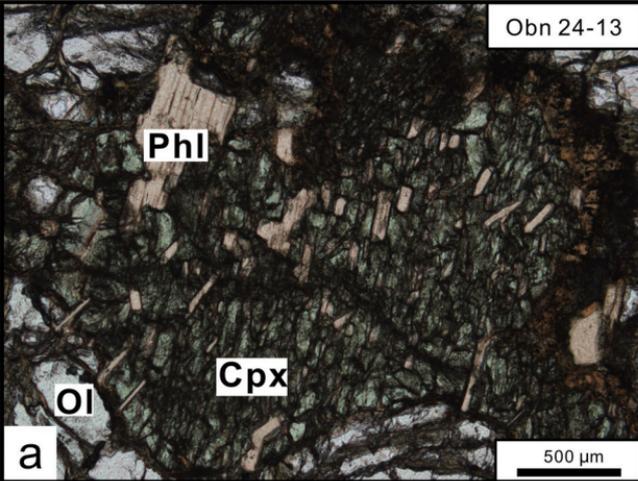
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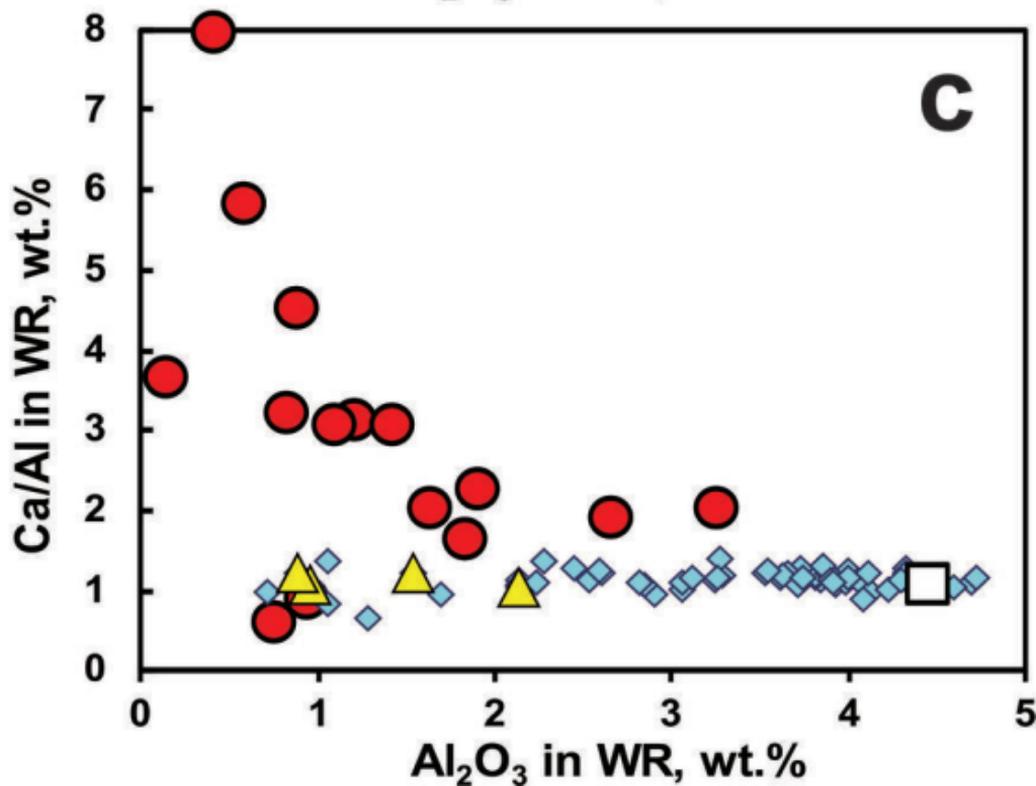
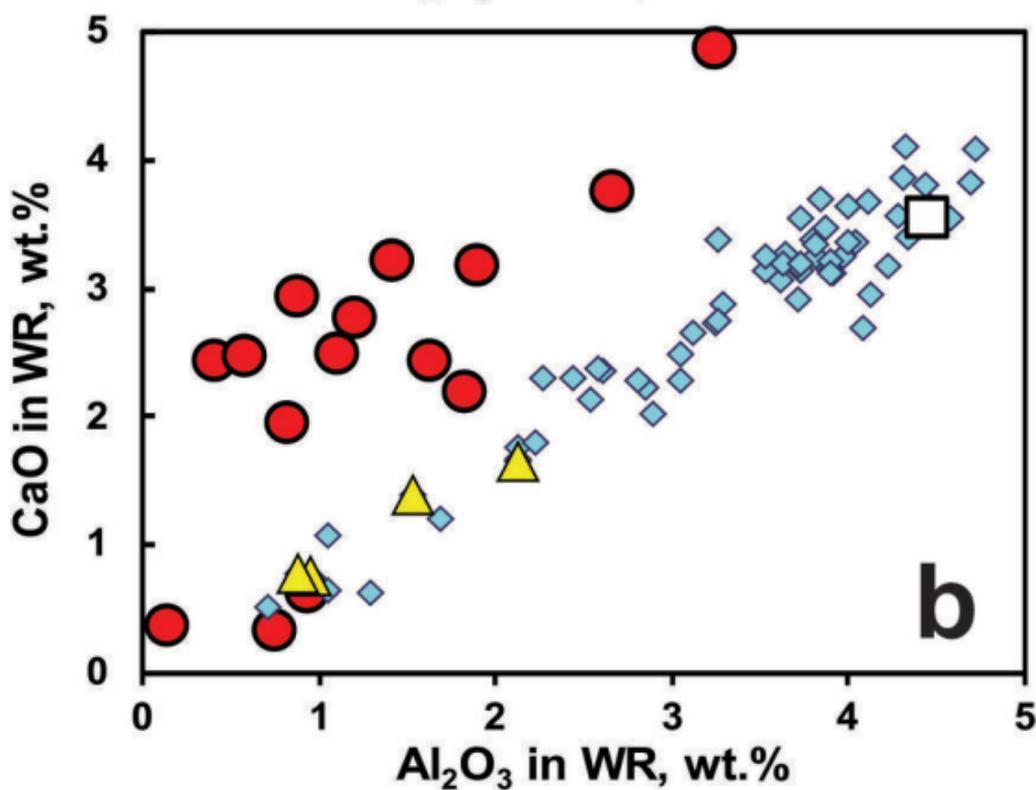
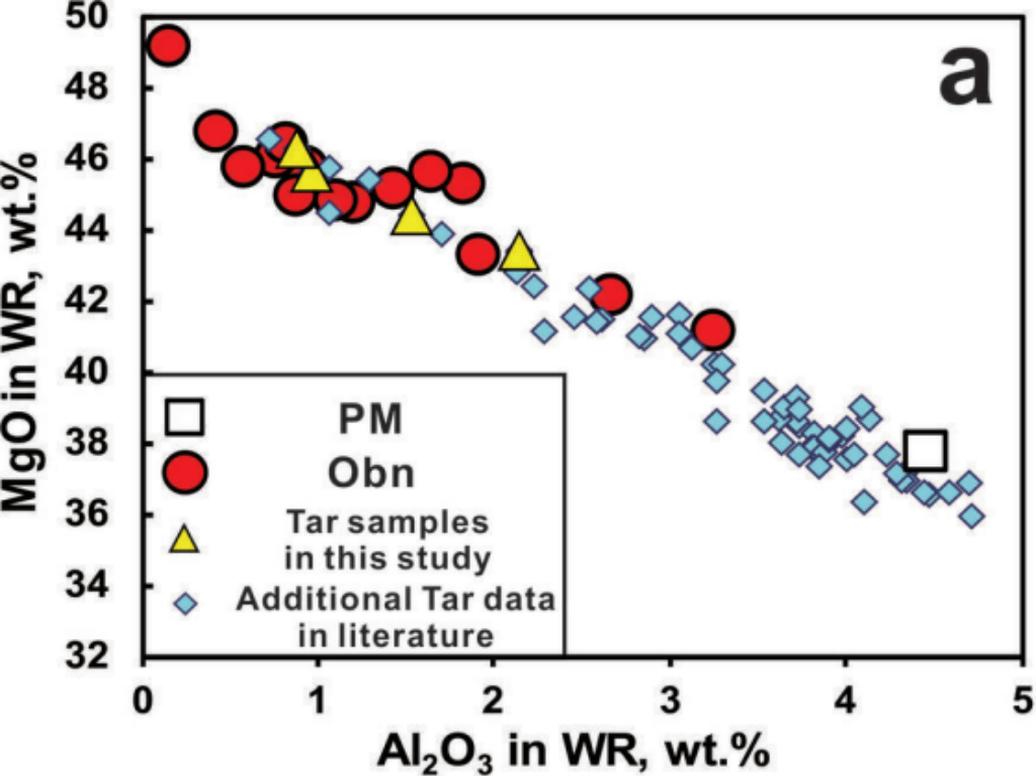
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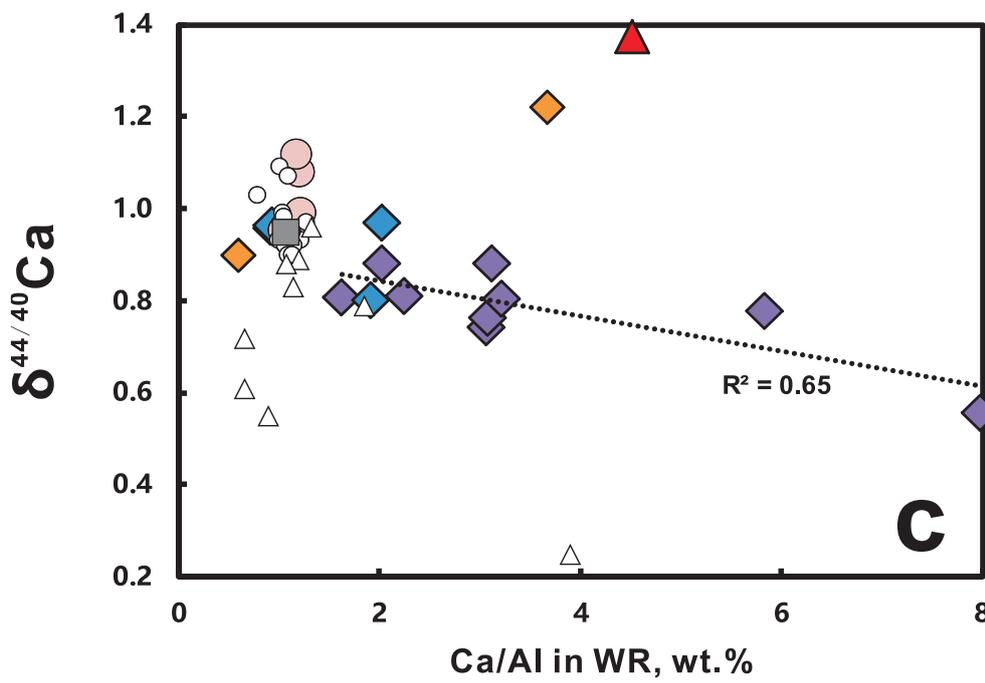
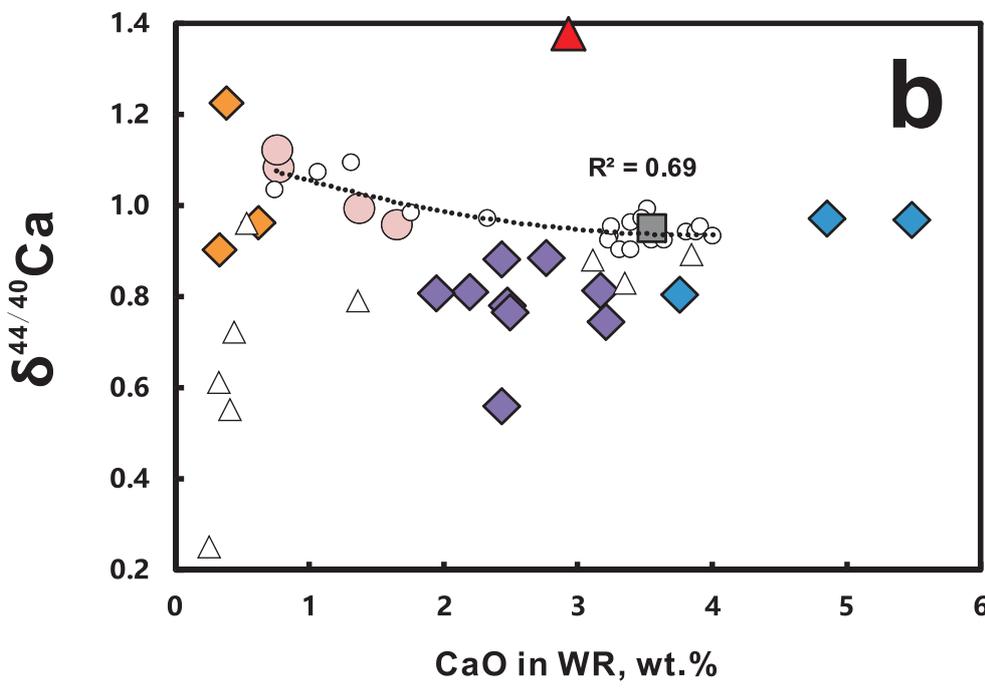
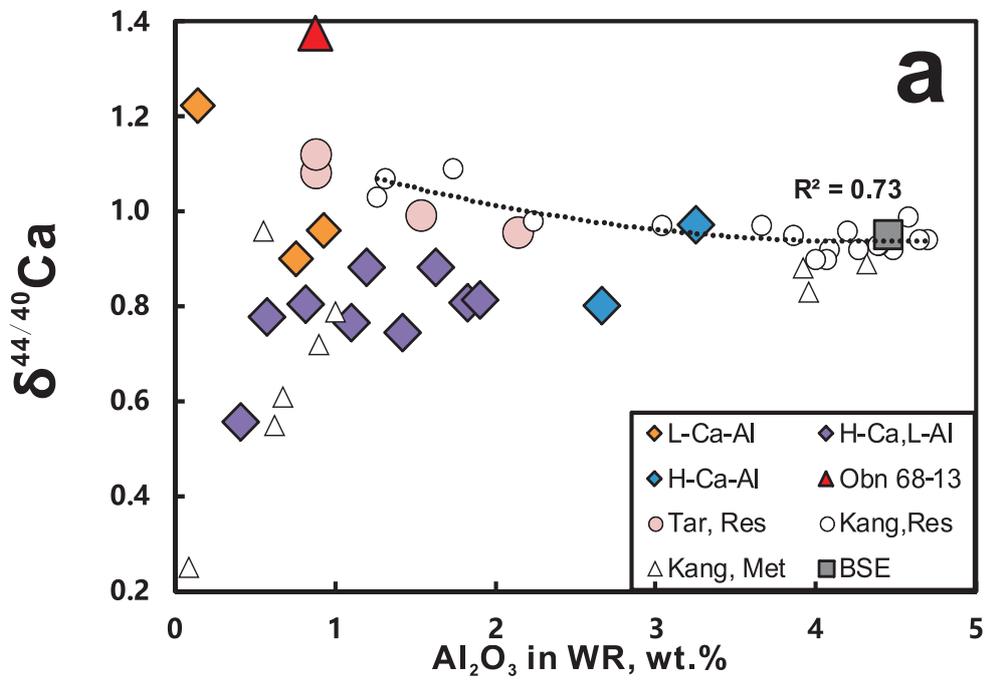


Table 1. Summary of essential data on xenoliths

Sa. N°	Rock type	$\delta^{44/40}\text{Ca}$	T°C	P, GPa	Whole-rock composition, wt.%				Ol Mg#	Modal composition, %							
		SRM 915a			Ca-opx	Al-opx	Al <sub>2</sub> O <sub>3</sub>	CaO		Ca/Al	Mg#	Ol	Opx	Cpx	Sp	Gar	Phl
<i>Low-Ca-Al dunites and harzburgites</i>																	
Obn 59-13	Sp Dunite	1.22	n.a.	n.a.	0.14	0.38	3.7	0.915	0.916	98.2	-	1.5	0.4	-	-	-	-
Obn 60-13	Sp-rich Dunite	0.96	n.a.	n.a.	0.93	0.63	0.9	0.888	0.892	94.4	-	2.2	3.3	-	-	-	-
Obn 69-13	Sp Hz	0.90	923	/1.5/	0.76	0.33	0.6	0.918	0.921	74.8	23.8	0.7	0.7	-	-	-	-
<i>Phl-bearing, mainly carbonate bearing, Ca-rich peridotites with low to moderate Al</i>																	
Obn 08-13	Gar-Sp-Phl Hz	0.85	729	2.1	1.20	2.77	3.1	0.919	0.921	69.9	20.4	0.8	0.5	2.3	1.6	4.4	-
Obn 22-13	Sp Hz	0.81	1027	/1.5/	1.82	2.20	1.6	0.917	0.920	76.1	15.8	1.9	2.6	-	0.5	3.1	-
Obn 24-13	Sp-Phl Lh	0.56	784	/1.5/	0.41	2.44	8.0	0.918	0.920	84.2	6.6	3.6	0.1	-	2.4	3.1*	-
Obn 39-13	Gar-Sp Hz	0.81	711	1.6	1.90	3.17	2.3	0.918	0.920	66.4	20.7	2.1	1.3	4.0	1.1	4.5	-
Obn 53-13	Gar-Sp-Phl Hz	0.74	767	2.6	1.42	3.22	3.1	0.919	0.924	75.7	12.0	0.5	1.7	2.9	1.8	5.4	-
<i>Ca-rich peridotites with low to moderate Al</i>																	
Obn 12-13	Sp Lh-Wh	0.88	1047	/1.5/	1.63	2.44	2.0	0.920	0.921	84.0	2.6	10.7	2.6	-	-	-	-
Obn 37-13	Sp Lh-Wh	0.78	685	/1.5/	0.57	2.48	5.9	0.915	0.918	85.2	3.9	10.5	0.4	-	-	-	-
Obn 68-13	Sp Wh	1.38	891	/1.5/	0.88	2.94	4.5	0.909	0.912	84.0	2.5	12.4	1.2	-	-	-	-
O-1017	Sp Lh	0.77	706	/1.5/	1.10	2.50	3.1	0.917	0.923	74.8	13.0	11.2	1.0	-	-	-	-
O-1061	Gar-Sp Hz	0.81	716	/1.5/	0.82	1.95	3.2	0.916	0.919	87.7	2.6	4.2	1.3	4.2	-	-	-
<i>Ca,Al-rich lherzolites</i>																	
Obn 06-13	Sp Lh	0.97	668	/1.5/	3.25	4.86	2.0	0.924	0.924	68.7	5.7	21.7	4.0	-	-	-	-
Obn 21-13	Gar-Sp Lh	0.97	698	2.0	7.98	5.49	0.9	0.900	0.922	44.7	7.0	17.4	1.1	29.8	-	-	-
O-47	Sp Lh	0.80	n.a.	n.a.	2.66	3.76	1.9	0.909	0.908	61.8	22.0	16.2	n.a.	-	-	-	-
<i>Garnet and plagioclase pyroxenites</i>																	
Obn 58-13	Sp-Pl Wbst vein	0.74	n.a.	n.a.	11.08	3.22	0.4	0.919	-	-	28.9	59.1	7.6	-	-	-	4.5
O-1080	Ol-Gar-Sp Wbst	0.93	729	2.1	7.18	8.02	1.5	0.909	0.922	30.1	12.6	38.1	1.3	17.9	-	-	-
<i>Refractory Tariat peridotites</i>																	
Mo4399-23	Sp Hz	1.08	876	/1.5/	0.88	0.78	1.2	0.912	0.913	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Mo-92	Low-cpx Sp Lh	0.96	898	/1.5/	2.14	1.65	1.0	0.912	0.913	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Mo-94a	Sp Hz	1.12	886	/1.5/	0.96	0.76	1.1	0.910	0.911	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Mo-95	Low-cpx Sp Lh	0.99	868	/1.5/	1.54	1.38	1.2	0.908	0.909	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

See Table 2 for details of Ca isotope data (reproducibility, accuracy, analyses of reference samples). Value for Obn 8-13 is an average of two full duplicates.

Data on the samples are from [Ionov et al. \(2018b\)](#). Sample 58-13 is a vein in a harzburgite.

Ol, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Sp, spinel; Gar, garnet; Carb, carbonate (calcite); Phl, phlogopite; Pl, plagioclase

Lh, lherzolite; Hz, harzburgite; Wh, wehrlite; Wbst, websterite; n.a., not available; -, absent.

See [Ionov et al. \(2018b\)](#) for opx-based methods used to obtain equilibration temperatures (T) and pressures (P); P=1.5 GPa is assumed for spinel peridotites.

Modal estimates obtained by least squares method from whole-rock and mineral analyses, and normalized to 100%.

\*Modal carbonate in sample 24-13 is an estimate for a hypothetical calcite component that could react with opx to yield metasomatic Cpx-Spl±Phl pockets

Table 2. Whole-rock Ca isotope compositions of xenoliths and reference samples

Sa. N°	Rock type	$\delta^{44/42}\text{Ca}$	2SD	$\delta^{44/40}\text{Ca}$	$\delta^{44/40}\text{Ca}$	2SD	n
		relative to ICP1		relative to SRM 915a	relative to SRM 915b		
<i>Obn low Ca-Al dunite and harzburgite</i>							
Obn-59/13	Sp Dunite	0.25	0.03	1.22	0.52	0.07	3
Obn-60/13	Sp-rich Dunite	0.12	0.02	0.96	0.26	0.04	3
Obn-69/13	Sp Hz	0.09	0.09	0.90	0.20	0.18	3
<i>Obn Phl-bearing, mainly carbonate bearing, Ca-rich peridotites with low to moderate Al</i>							
Obn-8/13	Gar-Spl-Phl Hz	0.08	0.02	0.88	0.18	0.04	3
<sup>a</sup> Obn-8/13 R		0.06	0.06	0.83	0.13	0.12	3
<sup>b</sup> Obn-22/13	Sp Hz, vermic.	0.04	0.06	0.81	0.11	0.12	3
Obn-24/13	Sp-Phl Lh	-0.08	0.01	0.56	-0.14	0.03	3
<sup>b</sup> Obn-39/13	Gar-Sp Hz	0.05	0.04	0.81	0.11	0.08	3
Obn-53/13	Gar-Sp-Phl Hz	0.01	0.04	0.74	0.04	0.09	3
<i>Obn Ca-rich peridotites with low to moderate Al</i>							
Obn-12/13	Sp Lh-Wh, vermic	0.08	0.05	0.88	0.18	0.11	3
Obn-37/13	Sp Lh-Wh	0.03	0.06	0.78	0.08	0.13	3
Obn-68/13	Sp Wh	0.32	0.02	1.38	0.68	0.04	3
O-1017	Sp Lh	0.02	0.04	0.77	0.07	0.07	3
O-1061	Gar-Sp Hz vermic	0.04	0.07	0.81	0.11	0.14	3
<i>Obn Ca, Al-rich lherzolites</i>							
Obn-6/13	Sp Lh, protogran	0.12	0.01	0.97	0.27	0.02	3
Obn-21/13	Gar-Sp Lh	0.12	0.03	0.97	0.27	0.06	3
O-47	Sp Lh	0.04	0.07	0.80	0.10	0.14	3
<i>Obn garnet and plagioclase pyroxenites</i>							
Obn-58/13	Sp-Pl Wbst vein	0.01	0.01	0.74	0.04	0.03	3
O-1080	Ol-Gar-Sp Wbst	0.11	0.07	0.93	0.23	0.14	3
<i>Refractory Tariat peridotites</i>							
Mo4399-23	Sp Hz	0.18	0.01	1.08	0.38	0.03	3
Mo-92	Low-cpx Sp Lh	0.12	0.02	0.96	0.26	0.05	3
Mo-94a	Sp Hz	0.20	0.01	1.12	0.42	0.03	3
Mo-95	Low-cpx Sp Lh	0.13	0.02	0.99	0.29	0.05	3
<i>International reference samples</i>							
SRM 915a	Carbonate	-0.35	0.08	0	-0.70	0.16	24
SRM 915b	Carbonate	-0.01	0.08	0.70	0	0.16	20
IAPSO	Seawater	0.54	0.08	1.82	1.13	0.16	17
PCC-1	Sp Lh	0.28	0.01	1.29	0.59	0.02	3
BHVO-2	Basalt	0.05	0.05	0.82	0.12	0.1	3

ICP1, in-house Ca isotope standard (see text). See Table 1 for other abbreviations.

<sup>a</sup>R denotes full procedural replicated sample.

<sup>b</sup>Calculated based on the analyses of residue and leachate given in Table 3.

n, number of repeated measurements of the same solution

Table 3. The Ca isotope composition of leachate, residue and calculated bulk rock.

Sa. N°		Ca fraction	$\delta^{44/42}\text{Ca}$ relative to ICP1	2SD	$\delta^{44/40}\text{Ca}$ relative to SRM 915a	$\delta^{44/40}\text{Ca}$ relative to SRM 915b	2SD	n
Obn-8/13	leachate	0.18	0.05	0.00	0.82	0.12	0.01	3
	residue	0.83	0.06	0.03	0.84	0.14	0.06	3
	calculated bulk	1.00			0.83	0.13	0.06	3
Obn-22/13	leachate	0.75	0.06	0.02	0.84	0.14	0.04	3
	residue	0.25	-0.01	0.06	0.70	0.00	0.12	3
	calculated bulk	1.00			0.81	0.11	0.12	3
Obn-39/13	leachate	0.75	0.05	0.03	0.83	0.13	0.06	3
	residue	0.25	0.02	0.03	0.77	0.07	0.06	3
	calculated bulk	1.00			0.81	0.11	0.08	3

ICP1, in-house Ca isotope standard (see text)