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1 **Rare Earth Elements in apatite: a proxy for unravelling carbonatite**
2 **melt compositions**

3

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12

13

14 **Abstract**

15 Carbonatites are fascinating magmatic rocks because of their anomalous compositions,
16 including the fact that some of these rocks host major rare earth element (REE) deposits.
17 Despite much recent work, our understanding of their genesis and the composition of
18 initial carbonatite melts is hindered by two major obstacles: most carbonatites we see
19 are intrusive rocks, and they are commonly affected by metasomatic overprint. Here,
20 we report experimental data in which we use apatite as a geochemical proxy to see back
21 through crystallization and metasomatic events, thus making it possible to decipher the
22 composition of carbonatite melts. We determined partition coefficients between apatite
23 and carbonatite melts for a broad range of elements. The Na-rich nature of carbonatite
24 melts plays an important role in apatite-melt partition coefficients, which are in the
25 range of 1-7 for Sr, Y and REE in carbonatite systems. Using our new experimental
26 data combined with >700 apatite composition data from carbonatites in various
27 geodynamic settings, we show that carbonatite melt REE contents vary by more than
28 two orders of magnitude. This variation cannot be solely produced by crystal-melt
29 fractionation, implying that some carbonatite melts must be REE-rich or REE-poor
30 initially, and that they mostly remain so during differentiation. We conclude that the
31 degree of REE enrichment reflects carbonatite melts produced by immiscibility from
32 variably differentiated alkaline magmas.

33

34 **1. Introduction**

35 Intrusive carbonatite complexes are rare magmatic rocks that occur in the Earth's crust,
36 which have attracted much attention within the geochemical community. The reason
37 for this particular interest is that carbonatites display several enigmatic geochemical
38 features: (i) in contrast to the majority of magmas, they are silica-depleted (Massuyeau
39 et al., 2020) and contains > 20 wt% CO₂, implying a strong link with the carbon
40 geodynamic cycle (Dasugpta, 2013); (ii) they are inferred to be rich in water, sulfur and
41 halogens (Keppler, 2003; de Moor et al., 2013); (iii) they can be strongly enriched in
42 REE and other rare metals, e.g., Nb, Ta, Zr, Th and U, and as a result, the global source
43 for certain critical metals resides in a few exposed carbonatites (Verplanck et al., 2016).
44 The unusual nature of carbonatites thus constitutes a geochemical anomaly, with both
45 environmental and societal importance. In spite of their importance and numerous
46 studies addressing the genesis and evolution of carbonatites, the mode of formation of
47 these rocks remains elusive. It has long been proposed that carbonatites may be
48 produced by (i) partial melting of a carbonated mantle (Sweeney, 1994; Foley et al.,
49 2009); (ii) fractional crystallization of carbonated silicate magma (Lee and Wyllie,
50 1994; Veksler et al., 1998) and/or (iii) liquid immiscibility (Halama et al., 2005;
51 Mitchell, 2009; Gittins and Mitchell, 2023). Is there a way to relate these general types
52 of formation to the enigmatic geochemical features identified above? In particular, why
53 do only few carbonatites contain economically-viable REE concentrations whereas
54 others contain much less REE (Fig. 1)? The latter question is critical for improving our
55 understanding of carbonatite genesis and REE ore deposit formation, and provides the
56 core motivation for numerous recent studies (Yaxley et al., 2022 and the reference
57 therein).

58 Carbonatite rocks contain substantial volatiles (e.g., F, Cl and S), as abundant apatite
59 (Ca₅(PO₄)₃(OH, Cl, F)), fluorite (CaF₂), barite (BaSO₄), carbonate (various minerals
60 with compositions (Ca,Mg,Fe)CO₃) and sulphide minerals (Le Bas, 1989; McLemore,
61 2018). The REE contents of carbonatites can be high, but are above all strikingly
62 variable (Smith et al., 2016), ranging from hundred ppm to several weight%, as shown
63 by the REE contents of more than 3500 natural carbonatite rocks from the GEOROC
64 database (Fig. 1, <http://georoc.mpch-mainz.gwdg.de/georoc/>). Establishing links
65 between these geochemical features has been difficult since almost all exposed
66 carbonatites are intrusions, consisting mainly of calcite or dolomite cumulates, which

67 certainly differ from the composition of their parental magmas (Xu et al., 2007;
68 Weidendorfer et al., 2017; Yaxley et al., 2022). Moreover, carbonatite rocks have
69 commonly experienced metasomatic processes, which can drastically change their
70 volatile element content and REE distribution (Le Bas, 1989; Anenburg et al., 2020).
71 As a consequence, our knowledge of the composition of carbonatite melts remains poor,
72 making it difficult to discriminate carbonatite rocks that preserve a magmatic signature
73 from those affected by hydrothermal processes.

74 Despite limited information regarding the precise composition and liquid line of
75 descent of carbonatite melts derived from the mantle, recent advancements have
76 informed our working hypotheses, such as studies on extrusive carbonatite rocks,
77 carbonatite melt inclusions and experimental petrology. (1) The unique occurrence of
78 extrusive carbonatites at Oldonyo Lengai, Tanzania, reveals Na-rich melt compositions
79 that differ from the majority of intrusive carbonatites and are highly differentiated
80 carbonatites (Weidendorfer et al., 2017). These extrusive rocks are, however, unlikely
81 to represent a universal proxy of carbonatite melts (De Moor et al., 2013; Gusmicz et
82 al., 2019; Berkesi et al., 2020; Yaxley et al., 2022). (2) The study of melt inclusions is
83 a powerful tool for determining initial melt compositions, and existing data point
84 towards Na-rich compositions (Guzmics et al., 2012; 2015; 2019). Nevertheless,
85 carbonatite melt inclusions are very scarce and their chemical compositions are difficult
86 to quantify due to post-entrapment processes and the fact that, in most cases, carbonate
87 and silicate melt inclusions are associated (Yaxley et al., 2022). (3) Experimental
88 petrology has been used to link Na-rich melts and the Ca-rich nature of intrusive
89 carbonatites (Weidendorfer et al., 2018), clearly demonstrating that all carbonatite
90 melts must contain a significant amount of Na. Yet, many unanswered questions remain
91 regarding the mechanisms underlying the wide range of REE found in carbonatite rocks
92 that crystallize from Na-rich and volatile-rich carbonatite systems (Anenburg et al.,
93 2021). In particular, possible links between REE abundance in carbonatite melts and
94 different genetic models for carbonatite melt generation remain highly debated.

95 We propose here to investigate the volatile and REE contents in carbonatite melts by
96 means of a suitable proxy mineral. Apatite is the obvious mineral, because it is
97 commonly found in carbonatite rocks (Chakhmouradian et al., 2017), and can
98 incorporate all of the major magmatic volatile species (F, S, Cl), as well as REE, into
99 its structure (Pan and Fleet, 2002). Knowledge of the partition coefficients between

100 apatite and carbonatite melt makes it possible to decipher the elusive geochemical
101 record of the early magmatic carbonatite history. There are three representative
102 experimental studies on the partitioning of trace elements between apatite and
103 carbonatite melts (Klemme and Dalpé, 2003; Hammouda et al., 2010; Sartori et al.,
104 2023), but the results for REE are not consistent. Klemme and Dalpé (2003) found REE
105 to be incompatible in apatite, with partition coefficients of less than 1 at 1 GPa and
106 1250 °C, whereas Hammouda et al. (2010) and Sartori et al., (2023) found them to be
107 compatible in apatite at 4-6 GPa and 1200-1380 °C. Besides, two studies used dry
108 calcite melts as the starting material at mantle conditions (Klemme and Dalpé, 2003;
109 Hammouda et al., 2010), whereas carbonatite magmas must contain significant
110 amounts of alkali and volatile elements (Guzmics et al., 2019; Weidendorfer et al.,
111 2017; Berkesi et al., 2020).

112 Here, we present new experiments defining partition coefficients between apatite and
113 an alkali-rich carbonatite melt (Table 1) with various volatile element (H, F, S, Cl)
114 concentrations. The experiments were performed at 800 °C, 200 MPa and over a range
115 of oxygen fugacities ($\log fO_2$ ranges from $\sim \Delta \text{FMQ} + 0$ to $\Delta \text{FMQ} + 3$; FMQ – fayalite-
116 magnetite-quartz buffer) using internally heated pressure vessels, IHPV (Table 2). We
117 also determined the apatite-melt partition coefficients for the piston cylinder (PC)
118 experiments of Nabyl et al. (2021), which were conducted over a broader range of
119 conditions from 850 to 1050 °C and at 800 MPa (Table 2). We found that the apatite-
120 melt REE partition coefficients in geologically realistic carbonatite melt compositions
121 vary within a narrow range, with values of 1-7. This implies that individual REE
122 partitioning between apatite and carbonatite melt are independent on pressure,
123 temperature and volatile activities. These new results are used to quantify the REE
124 abundances for natural carbonatite melts using apatite as a proxy. The calculated REE
125 abundances for carbonatite melts greatly vary, encompassing a range of concentration
126 consistent with the genesis of most carbonatite rocks by immiscibility with alkaline
127 melts.

128

129

130

131 **2. Methods**

132 *2.1. Anhydrous starting materials*

133 Several starting materials were investigated in this study (Table 1). The starting
134 materials used for the IHPV and PC experiments were prepared by mixing synthetic
135 carbonates, oxides, silicates and apatite, following the procedure of Nabyl et al. (2021).
136 The carbonatite powder was prepared from a mixture of high-purity synthetic powders
137 (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO_2 , CaCO_3 , Na_2CO_3 , K_2CO_3 , SrCO_3 , and BaCO_3) and
138 natural magnesite (MgCO_3). The bulk compositions of the starting carbonatite powders
139 are given in Table 1. The starting carbonatite materials were then doped with REE and
140 other trace elements in the form of oxides or fluorides (La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 ,
141 Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_4O_7 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Yb_2O_3 , Lu_2O_3 , Sc_2O_3 , Y_2O_3 ,
142 Nb_2O_5 , Ta_2O_5 , ZrO_2 , HfO_2 , PbO , NiO , CoO , MoO_3 and WO_3). The powders were first
143 mixed in an agate mortar by hand (for ~30 minutes) in a glove box to avoid atmospheric
144 water contamination, and then by an automatic grinder with an agate mortar and ball
145 mill (for ~30 minutes). For F-, Cl- and S-doped experiments in IHPV, NaF, NaCl and
146 Na_2SO_4 powders were further added to the starting carbonatite for IHPV runs (Table
147 1). For experiments in PC, the starting carbonatite runs were directly doped with
148 phonolite and P_2O_5 powders (Table 2) as described in Nabyl et al. (2021). Prior to and
149 between all experiments, the synthetic powders were stored in a dry oven at 120 °C.

150

151 *2.2. Sample preparation*

152 Sample preparation for IHPV and PC experiments followed the same protocol. The
153 starting material powders were taken out of the 120 °C oven directly prior to loading
154 into metal capsules to minimize hydration. Sample powder (~20-30 mg) was loaded
155 into gold capsules 10-25 mm in length with an outer diameter (O.D.) of 2.9 mm and an
156 inner diameter (I.D.) of 2.5 mm. The powder was tightly packed using a steel rod.
157 Deionized H_2O (resistivity higher than $180000 \Omega \cdot \text{m}$) was loaded into the capsules using
158 a 1-10 μL micropipette. In IHPV charges, 9-11 wt% H_2O was added to capsules,
159 whereas 3-6 wt% was added to capsules used in hydrated PC runs (Table 2). After
160 loading H_2O and starting material powders, the upper ends of the gold capsules were
161 crimped and then welded shut using a pulsed arc welder while being cooled with wet
162 tissue to avoid heating and thereby H_2O loss from the charge. Following, the gold

163 capsules were stored in a 120 °C oven overnight, and finally weighed again to check
164 for the presence of leaks. Any sample capsules that deviated by more than 0.0002 g
165 from their after-welding weight were discarded.

166

167 *2.3.High-temperature, high-pressure experiments*

168 The high-pressure charges were synthesized in the piston cylinders at the Institut des
169 Sciences de la Terre d'Orléans (ISTO), France. Experimental details are provided in
170 Nabyl et al. (2021). We specify that no particular attempt of controlling oxygen
171 fugacity, fO_2 , were conducted.

172 The low-pressure experiments were performed in a vertical internally heated pressure
173 vessel (IHPV) at 800 °C and 200 MPa at ISTO, France, and at 850-1050° C and 800
174 MPa in a PC press. For the IHPV experiments, the samples were pressurised using pure
175 Ar or Ar-H₂ mixtures (0.15–0.6 MPa H₂ total pressure) in order to vary fO_2 conditions
176 (cf. Scaillet et al., 1992). The more H₂ added, the more reduced, as defined by the water
177 dissociation constant (i.e. $H_2 + \frac{1}{2}O_2 = H_2O$, Gaillard et al., 2001). Given that we have
178 loaded high water contents (~9-11 wt%) into the capsules (table 2), and based on the
179 water solubility study of Keppeler (2003), we then assumed that the water activity in the
180 charges approached 1 to calculate the redox (fO_2) conditions. The calculated fO_2 values
181 for the IHPV experiments ranged from $\sim\Delta FMQ + 0$ to $\Delta FMQ + 3$ (Table 2).

182 The pressure was monitored by a transducer calibrated against a Heise Bourdon gauge
183 with an accuracy of ± 2 MPa (Gaillard et al., 2001; Andujar et al., 2013). The
184 experiments were performed in double-coiled Kanthal and molybdenum furnaces with
185 near-isothermal conditions (thermal gradient $<2-3^\circ C/cm$) in the 3 cm-long hotspot
186 (Andujar et al., 2013). Two S-type thermocouples (Pt₉₀Rh₁₀/Pt) were placed at the top
187 and bottom of the samples to monitor the temperature with an accuracy of at least ± 5
188 °C (Andujar et al., 2013). In order to ensure the growth of large apatite crystals suitable
189 for major- and trace-element analyses, all experiments were first brought up to 1000 °C
190 for 1-3 hours, followed by ramped cooling over 30 minutes to the experimental
191 temperature of 800 °C. For each experiment, 3 to 6 capsules were placed in an
192 aluminium tube fixed at the top of the furnace (hotspot), held by a thin
193 platinum/rhenium wire. To terminate each run, the platinum/rhenium wire was fused

194 electrically, which dropped the sample container into the cold part of the furnace,
195 ensuring fast isobaric quench (~ 100 °C/s). After the experiments, capsules were
196 checked for leaks by weighing their mass. Capsules with <0.0002 g weight difference
197 to the pre-experiment weight were considered successful. They were sliced open with
198 a low-speed saw along their length, and half of the run product was mounted in epoxy
199 resin. The sample surface was then polished using ethanol rather than water to limit the
200 dissolution of carbonatite material for optical observation and subsequent analyses.

201

202 *2.4. Imaging and analytical methods*

203 Run product preparation and all microchemical analyses were performed at the Institut
204 des Sciences de la Terre d'Orléans (ISTO). Back-scattered electron (BSE) images of
205 the run products were taken using a Merlin Compact ZEISS scanning electron
206 microscope (SEM), equipped with a micro-analyser system with a resolution of 129 eV
207 (EDS Bruker-QUANTAX-XFlash6). Energy dispersive spectroscopy (EDS) was
208 carried out to identify the phase assemblages using an accelerating voltage of 15 kV
209 and a working distance of 15 mm.

210 The major element compositions of apatite and the carbonatite run products were then
211 analysed using a Cameca SXFive electron microprobe equipped with five WDS
212 detectors. All analyses were performed with a 15 kV acceleration voltage, a 10 nA beam
213 current, and a beam size defocused to 10–50 μm , in order to reduce Na-loss during
214 analysis, and to sample the average composition of the quenched carbonatite melts. The
215 following standards were used to calibrate the instrument: albite for Na, apatite for P,
216 orthose for K, calcite for Ca, topaz for F, vanadinite for Cl, MgO for Mg, Al_2O_3 for Al,
217 Fe_2O_3 for Fe, MnTiO_3 for Mn and Ti, SrSO_4 for S and Sr. Measurement time was 10 s
218 on the peak and 5 s for the background for each element.

219 The trace element concentrations in apatite and the quenched carbonatite melts were
220 measured by LA-ICP-MS using a RESolution-SE 193 nm ArF excimer laser with a
221 S155 Laurin Technic sample cell attached to an Agilent 8900 QQQ quadrupole ICP-
222 MS. The laser was operated at a frequency of 5 Hz with energy densities from 2 to
223 about 5 J cm^{-2} on the sample surface. Spot analyses were performed using laser beam
224 diameters of 32–60 μm , depending on the size of the apatite crystals and quench-
225 crystallized melt pools. Measured isotopes were ^7Li , ^{23}Na , ^{24}Mg , ^{27}Al , ^{29}Si , ^{39}K , ^{44}Ca ,

226 ⁴⁷Ti, ⁵⁵Mn, ⁵⁷Fe, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁵⁹Co, ⁶⁰Ni, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ⁹⁵Mo, ¹³³Cs,
227 ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm,
228 ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ¹⁸²W, ²⁰⁸Pb, ²³²Th, and ²³⁸U, using dwell times of 10 ms per
229 isotope. Sample measurements were bracketed by analyses of NIST SRM reference
230 glasses to correct for time-dependent drift of sensitivity and mass discrimination.
231 Calibration was conducted using silicate glass standards (NIST SRM 610) with the
232 reference values of Jochum et al. (2011).

233 Apatite and the quench-crystallized carbonate melt from the piston cylinder samples
234 (Nabyl et al., 2021) were analysed using the same LA-ICP-MS machine as well as an
235 Agilent 7500 CS Quadrupole from the LMV laboratory (Clermont-Ferrand, France)
236 coupled to a 193 nm excimer laser ablation system (frequency of 2 Hz, ablation energy
237 of 1.5 to 3 mJ and beam size of 4 to 33 µm). Concentrations were obtained using the
238 same calibration and methodology (Nabyl et al., 2021). Reference materials NIST 612
239 and BCR-2G natural basaltic glass were analyzed as secondary standards to ensure the
240 accuracy of the results. The Ca contents of apatite and crystallized melt determined by
241 microprobe were used as the internal standard.

242 All melt and apatite experimental compositions are available in the supplementary table
243 S1.

244 *2.5. Geochemical criteria for magmatic apatite in carbonatite rocks*

245 More than 7000 apatite compositions from the GEOROC database (<https://georoc.eu/>)
246 and additional studies were examined (Table S2). The apatite compositions in this
247 database are from 240 localities and 35 countries worldwide. Their compositions reflect
248 a large variety of magmatic, hydrothermal and metamorphic processes and geological
249 environments. These apatites were formed in peralkaline magmatism, carbonatitic
250 magmatism, felsic magmatism, kimberlites, mafic to ultramafic magmatism; we also
251 reported metamorphic, hydrothermal and metasomatic apatites as defined in the source
252 papers. The database also includes apatite compositions from famous REE ore deposits
253 (Bayan Obo, Mountain Pass, and Mount Weld). Based on the source paper
254 interpretations and geochemical modelling of the REE content of apatite in equilibrium
255 with carbonatite melts, 745 natural apatite compositions from carbonatite rocks were
256 identified as being magmatic in origin (see section 4.2.1). For the discussion section of
257 this study, we combined interpretations from source papers with geochemical

258 modelling to determine the range in composition of magmatic apatite in carbonatite
259 rocks.

260 **3. Experimental Results**

261 All experimental conditions are listed in Table 2, apatite and melt compositions in Table
262 S1, and partition coefficients together with their uncertainties are given in Table 3. In
263 all experiments, the carbonatitic melt quenched to aggregates of sub-micrometer-size
264 elongated crystals (Fig. 2), with larger crystals in hydrous samples (Fig. 2b, c, d). The
265 size of apatite crystals varies from a few tens to a hundred micrometres, with no
266 observed zonation or inclusions (Fig. 2). Apatite crystals have variable morphology,
267 ranging from euhedral or subhedral (Fig. 2a, b, c) to anhedral (Fig. 2d).

268 Similar to the recent work of Sartori et al. (2023), we used Na-bearing starting materials
269 (Table 1). The melts produced were variably Na-rich and the chemical composition of
270 the run products was homogeneous (Table S1). Equilibrium conditions were obtained
271 between apatite and carbonatite melts at the investigated P-T conditions, as
272 demonstrated by the sharp geometry of the apatite-melt interfaces (Fig. 2), the
273 homogeneity of apatite compositions, and the homogeneous compositions measured in
274 carbonatite melts (Table S1). Partition coefficients were calculated using the Nernst
275 formula as a mass ratio of the element concentration in apatite relative to that in the
276 carbonatite melt: $D_{\text{Element}} = C^{\text{Apatite}}/C^{\text{Melt}}$ (Table 3). The partition coefficients of Sr, Y
277 and REE (D_{REE}) range from 1 to 7 (Fig. 3a). We found that the apatite-melt partition
278 coefficients do not correlate with the volatile contents (H_2O , F, Cl and S) of the
279 carbonatite melt or $f\text{O}_2$ (Table 2, Table 3, Fig. 3). Only two nominally dry experimental
280 charges appear to display D_{REE} slightly lower than the wet ones by ~30 %, but in
281 general, all measured REE partition data are in the range of 1-7 (Table 3) for the large
282 range of Cl, F, S contents and $f\text{O}_2$ conditions explored in our experiments (Table 2).
283 The variations observed for the partitioning of individual REE are within a factor of
284 two for the range of experimental conditions. No clear negative Eu anomalies are
285 observed for reduced or oxidized experiments. We also note that the REE partitioning
286 coefficients determined for the 200 and 800 MPa are indistinguishable.

287 Accordingly, no clear difference in partition coefficients for Sr, Y and REE (D) is
288 observed between our data and those of Hammouda et al. (2010) or Sartori et al. (2023),
289 despite significant differences in equilibration pressure, temperature, $f\text{O}_2$, halogen and

290 water contents (Fig. 3-4-5). However, our Sr, Y and REE partition coefficients and
291 those of Hammouda et al. (2010) and Sartori et al. (2023) are much higher than those
292 for the Na- and Si-poor carbonatite experiments of Klemme and Dalpé (2003), and
293 significantly lower than those for apatite-silicate melt partitioning (Waston and Green,
294 1981; Prowatke and Klemme, 2006) (Fig. 3-4). Figures 4a, b, and c show the partition
295 coefficients of La, Sm and Lu between apatite and melt as a function of SiO₂
296 concentration in the melt. All published experimental data are shown. For geologically
297 realistic carbonatite systems, i.e. Na-bearing melts with trace amounts of Si, the
298 partition coefficients of all REE are almost constant and lie within the limited range of
299 1 to 10. We note, however, that the partition coefficients increase dramatically once the
300 melt SiO₂ content exceeds 20 wt%. Most likely, a change must occur in a range of melt
301 SiO₂ contents between 10-30 wt%, where no data exists. This requires further
302 experimental investigations. All in all, these observations allow us to introduce the
303 notion of average partitioning coefficient data for individual RE-elements in carbonatite
304 systems (Table 3), since the carbonatite melts usually have less than 10 wt% SiO₂.

305 **4. Discussion**

307 *4.1. Factors controlling the partitioning of REE between apatite and carbonatite* 308 *melt*

309 Klemme and Dalpé (2003) found that REE were all incompatible in apatite at
310 equilibrium with a Ca-dominated carbonatitic melt at 1 GPa and 1250 °C. Hammouda
311 et al. (2010) found that REE were compatible in apatite in the Si-bearing CaCO₃-
312 Ca₅(PO₄)₃(F,OH) system at 4-6 GPa and 1200-1380 °C. Sartori et al. (2023) also
313 showed that REE were all compatible in apatite in the Si-bearing and Na-bearing
314 carbonatite system at 100-200 MPa and 750-1000°C. Similarly, we found that REE are
315 mostly compatible in apatite in Na-bearing systems (Fig. 3). We nevertheless note that
316 in their results, Hammouda et al. (2010) have one datapoint wherein REE appears to be
317 slightly incompatible in apatite (Fig.5). We have recalculated this datapoint from their
318 electron microprobe data, since there is no LA-ICPMS analysis for this experiment. For
319 the sake of transparency in our analysis, we decided to show it, but it is likely that this
320 datapoint is highly uncertain. The detected La content in the carbonatite melt of this
321 experiment is only 0.13 wt%, whereas the other samples of Hammouda et al (2010)

322 contained wt% of La. A content of 0.13wt% is only two times the average difference
323 between LA-ICPMS and EMP data for the two samples having both types of
324 measurements (and La-contents >1 wt%).

325 The most commonly considered factors controlling the partition coefficient between a
326 mineral and melt are temperature, pressure, oxygen fugacity, melt and mineral
327 compositions (Blundy and Wood, 2001). Based on the D_{REE} values (Fig. 3) for apatite-
328 melt, there appears to be no clear dependence on temperature, pressure, or oxygen
329 fugacity (Fig. 3; Figure S1). REE partition systematics between apatite and melt can,
330 however, be divided into two subdomains: small ranges of moderate D_{REE} values for
331 carbonatite systems, vs. high and highly variable D_{REE} values for silicate systems (Fig.
332 4a, b, c). For silicate systems, the inferred apatite substitution mechanism is $\text{Si}^{4+} +$
333 $\text{REE}^{3+} = \text{Ca}^{2+} + \text{P}^{5+}$ (Cherniak, 2000), hereafter the britholite substitution. Klemme and
334 Dalpé (2003) and Hammouda et al. (2010) suggested that this mechanism may also
335 prevail for carbonatite systems. In figure 5a, we plot the D_{REE} versus Si in apatite for
336 the available experimental data. It appears unclear whether silica incorporation in
337 apatite affects D_{REE} . All available data plot in the D_{La} range 1-7 for silica content in
338 apatite varying from 0.2 to 5 wt%, with the exception of the data of Klemme and Dalpé
339 (2003) and one datapoint from Hammouda et al. (2010), ie. the one analyzed by EMPA.
340 These lower values may rather indicate that the substitution mechanism $\text{Na}^{+} + \text{REE}^{3+}$
341 $= 2\text{Ca}^{2+}$ (Cherniak, 2000) is important for apatite in carbonatite systems. Klemme and
342 Dalpé (2003) and Hammouda et al. (2010) worked indeed on Na-free systems. We can
343 thus conclude that in systems containing trace amounts of Si and Na, as expected for
344 natural carbonatite, apatite-melt partitioning data are in the range 1-7.

345 Figure 5b shows a compilation of natural apatites in a plot REE vs. SiO_2 wt%. The data
346 have been sorted in order to visualize the role of the silica content of the bulk rocks on
347 putative Si-REE substitution in apatites. This is an extension of figure 4 toward natural
348 compositions but it is imperfect, given that the bulk SiO_2 contents of natural carbonated
349 rocks may not represent the silica content of the melt from which the apatites
350 crystallized. Nevertheless, this plot is useful as it shows a clear link between SiO_2 and
351 REE contents in apatites for silica-rich carbonated rocks ($\text{SiO}_2 > 10$ wt. %). This
352 relationship is less clear for carbonatite rocks with $<10\%$ bulk SiO_2 . For most of these
353 low Si-rocks, data are located in a cloud of points at <2 wt% SiO_2 and <2 wt% REE in
354 apatite. The experimental data reported in figure 4 are also plotted in figure 5b. Most

355 experimental data (Klemme and Dalpé 2003; Hammouda et al., 2010; Sartori et al.
356 2023; our data) plot in the cloud of points at low SiO₂ contents, where no Si-REE
357 substitution is visible. This is consistent with the D_{REE} data discussed in figure 4 and
358 5a. Some data by Hammouda et al. (2010), however, plot clearly in the high SiO₂ range
359 and show high REE contents (note that Hammouda et al. 2010 did not measure all REE;
360 ca. 1 wt% might be missing). These data are broadly in the trend indicated by the
361 crystallization of Si-rich carbonatites and consistent with a britholite substitution. Yet,
362 the D_{REE} measured by Hammouda et al. (2010) on high-Si apatites do not significantly
363 differ from others obtained on low-Si ones. This brings us to the surprising conclusion
364 that the britholite substitution does not significantly affect the apatite-melt D_{REE}.

365 An analysis of the natural and experimental data thus suggests that the partitioning of
366 REE between apatite and carbonatite melt remains in a narrow range for a large set of
367 P-T-fO₂-H₂O-Cl-F-SiO₂-Na₂O conditions expected to prevail in carbonatite systems.
368 REE incorporation in apatite certainly obeys to various substitution mechanisms,
369 involving Si and Na, but more systematic work is needed to clarify this issue. Overall,
370 we use at this stage the average partition coefficient values from this study for each
371 REE in a carbonatite system in the following sections (Table 3).

372

373 *4.2. Magmatic apatite as a geochemical proxy for carbonatite melt compositions*

374 *4.2.1. A geochemical criterion for identifying magmatic apatites*

375 Sartori et al. (2023) suggested that calcite – apatite partitioning of light and heavy REE
376 could be used to distinguish magmatic from hydrothermal phases. Low La/Lu
377 partitioning ratios were shown to reflect hydrothermal signatures. This approach is
378 certainly valid but it requires the analysis of both coexisting phases, an information
379 which is not always available in studies on carbonatites. Here, we propose to use apatite
380 as magmatic proxy and discuss the way to identify such magmatic apatites.

381 The 745 natural apatites that we selected (red dots in figure 6) have been classified
382 according to the source papers as magmatic apatites formed from carbonatite melts
383 (Table S2). This is mostly based on mineralogical criteria. We further verified their
384 origin by comparing them with calculated compositions of apatite in equilibrium with
385 alkaline and carbonatite melts. Such putative carbonatite melts, resulting from silicate-
386 carbonate immiscibility, are described in Nabyl et al. (2020). They were calculated from

387 a GEOROC compilation of major and trace element compositions of alkaline melts
388 from the East African rift. These calculated magmatic apatites have Sr concentrations
389 >1000 ppm and a $(\text{La}/\text{Yb})_N$ ratios in the range of 20-300 (Fig. 6, see inset on the right
390 for the data distributions and the rectangle marked by the thick dashed red contours).
391 Most red dots in figure 5 match this Sr vs. La/Yb criterion, testifying to their magmatic
392 origin. A majority of blue points (hydrothermal apatite according to the source papers)
393 plots below the La/Yb threshold of 20. Lower La/Yb ratios are expected for secondary
394 apatite crystallized from fluids since La is more fluid mobile than Yb. We however
395 recognize that a significant number of blue dots, categorized by the authors as
396 hydrothermal, plots above La/Yb=20, where equilibrium magmatic apatite should form
397 in such systems. Those cases were probably only moderately affected by metasomatic
398 events and/or preserved a geochemical signature intermediate between magmatic and
399 hydrothermal, possibly involving hydrosaline brine (e.g. Yuan et al., 2023; Walter et
400 al., 2021). Finally, we underline that the Sr-La/Yb data for natural apatite found in
401 carbonatites (red dots) and those found in alkaline melt (red area with dashed grey
402 contours in fig.6) are indistinguishable, suggesting an overwhelming genetic link
403 between these magmas, that is to say, an equilibration by silicate-carbonate
404 immiscibility.

405 *4.2.2. Range of REE-contents in carbonatite melts from apatites*

406 Using the D_{REE} averages (and standard deviations) in Table 3 and the magmatic apatite
407 compositions (red dots in figure 6), we calculated the REE contents of the coexisting
408 carbonatite melts. The REE contents of the selected apatites are shown in Fig. 7a, and
409 the calculated REE contents of the equilibrated carbonatite melts are shown in Fig. 7b.
410 The calculated REE abundances of the carbonatite melts show marked variation,
411 covering more nearly three orders of magnitude, i.e., ranging from ~100 ppm to
412 >10,000 ppm for La normalized to chondrites. This defines the REE content of
413 carbonatite melts in equilibrium with apatite. These are probably not primary
414 carbonatite liquids, but they define the REE contents of the melt when apatite saturation
415 was reached.

416 As a sensitivity test, we modelled the effect of crystallization on the REE contents of
417 the carbonatite melts. We considered the crystallization of both calcite and apatite,
418 because of their abundance in carbonatite rocks (Chakhmouradian et al., 2017;

419 Anenburg et al., 2020; Mollé et al., 2021; Sartori et al., 2023; Yaxley et al. 2022;
420 Weindendorfer et al., 2017). Figure 7b shows the effect of 50% calcite crystallization
421 and 30% apatite crystallization modelled by the partition coefficients in Mollé et al.
422 (2021) and this study. The red and the green arrows indicate the changes in REE
423 contents in response to fractionation of apatite and calcite, respectively. One can see
424 that both crystallization processes have a moderate effect on the melt REE contents
425 (Fig. 7b). In detail, we note that apatite crystallization tends to deplete the carbonatite
426 melts in REE, but we do not expect more than 30 wt% apatite crystallization from such
427 melts. Therefore, the more than two orders of magnitude variation recorded by apatite
428 compositions and the inferred co-existing melts cannot be attributed to crystal
429 fractionation. The large variation in REE contents we see in Fig. 7b must be an original
430 feature of the carbonatite melts that can only be moderately affected by fractionation.
431 Hereafter, we show how the genesis of carbonatite melts can be interpreted using the
432 REE contents found in apatite.

433 *4.3. Capturing the origin of carbonatite melts by means of their REE contents*

434 Petrological constraints indicate that mantle carbonatite melts are unlikely to reach the
435 surface (Yaxley et al., 2021), making the assessment of their REE contents difficult.
436 Coltorti et al. (1999), who reconstructed mantle carbonatite REE contents using
437 metasomatized peridotites, suggested that carbonatite melts have low to intermediate
438 REE contents with e.g., La in the range of ~500 to 1000 normalized to chondrite. We
439 note that the inferred REE pattern for the mantle carbonatite melt is flatter than that of
440 the calculated melt compositions involving apatite (light brown field in Fig. 7b). More
441 recently, O'Reilly and Griffin (2000) defined the REE contents of mantle apatites,
442 which could directly be used here. However, it is unclear whether normalized or
443 unnormalized REE data are reported in their tables, regrettably rendering the use of
444 these data impracticable. Although we acknowledge that the REE-content range of
445 mantle carbonatites is poorly constrained, we suggest that the range of REE contents
446 shown in figure 7b is unlikely to be solely inherited from mantle partial melting.
447 Instead, we consider that other geological processes, i.e. liquid immiscibility, may
448 cause the diverse REE pattern of carbonatite melts in figure 7b.

449 Figure 7c shows the calculated REE contents for carbonatite melts produced by
450 immiscibility with strongly peralkaline silicate melts from the East African Rift (Nabyl

451 et al., 2020). The lowest REE contents correspond to carbonatite melts produced from
452 melilitic/nephelinitic melts, whereas the highest REE contents correspond to
453 carbonatite melts produced from phonolitic melts (Nabyl et al., 2020). The range of
454 REE contents determined for these melts almost perfectly matches the melt
455 compositions calculated using the apatite proxy (Fig. 7b, c). For both melt
456 compositions, i.e. calculated from apatite or from immiscibility, the lowermost values
457 for La, Sm and Lu normalized to chondrite are ca. 100, 40 and 5, respectively. The high
458 range for La, Sm and Lu recorded by our apatite proxy (Fig. 7b) is somewhat lower
459 than that of the carbonatite melts produced by immiscibility from phonolitic melts (Fig.
460 7c). This may be due to the fact that very REE-rich carbonatite melts are not
461 systematically apatite saturated (see Mollé et al., 2021). We thus suggest that the REE
462 contents of carbonatite melts as reconstructed using the apatite proxy are mostly
463 consistent with their genesis by liquid immiscibility from peralkaline melts. This is also
464 consistent with the fact that the Sr contents and the $(La/Yb)_N$ ratios of magmatic apatites
465 in equilibrium with silica-undersaturated peralkaline and carbonatite melts are
466 indistinguishable (Fig. 6). The variation in REE contents of carbonatite melts thus
467 largely reflects the level of differentiation of the parental peralkaline melts as suggested
468 by Nabyl et al. (2020).

469

470 *4.4. Comparison with carbonatite rocks and ore deposits*

471 The REE contents of more than 3500 natural carbonate rocks from the GEOROC
472 database are plotted in Fig. 1. The range of REE contents of the carbonate rocks from
473 various geological settings (rift volcanoes, intraplate volcanoes, ocean islands,
474 continental flood basalts and Archean cratons) show a similar variability to the
475 carbonatite melt compositions predicted by the apatite proxy (Fig. 7b) and by
476 immiscibility from strongly peralkaline melts (Fig. 7c). The lowest REE contents in
477 carbonatite rocks (Fig. 1) are indistinguishable from the lowest REE contents in inferred
478 carbonatite melts (Fig. 7b, c). The upper range of REE contents in the natural
479 carbonatite rocks (Fig. 1) is somewhat higher than the most REE-rich melts produced
480 by immiscibility from phonolitic melts, which could reflect fluid-related processes
481 (Anenburg et al., 2020; Louvel et al., 2022) or the fact that the most REE-rich
482 carbonated melts are not saturated in apatite (Mollé et al., 2021).

5. Conclusion

483
484

485 Our experimental calibration of the apatite-carbonatite partitioning shows that apatite
486 found in carbonatite rocks can be used as a proxy to constraint the composition of the
487 poorly defined carbonatite melts. This apatite proxy allows us to see through magmatic
488 crystallization and subsolidus metasomatic interactions. Our study reveals that
489 carbonatite melts display a large range of REE contents that can be linked to the
490 significant variations found in the REE contents of carbonatite rocks, including some
491 REE deposits. Our analysis indicates that carbonatite melts crystallizing apatites are
492 REE-rich (>10,000 ppm) to REE-poor (~100 ppm), which seemingly reflects
493 immiscibility at various differentiation stages. While subsolidus fluid-rock interactions
494 unquestionably affect and redistribute REE between minerals of carbonatites, we suggest
495 that the bulk rock REE contents are primarily controlled by magmatic processes.

496

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498

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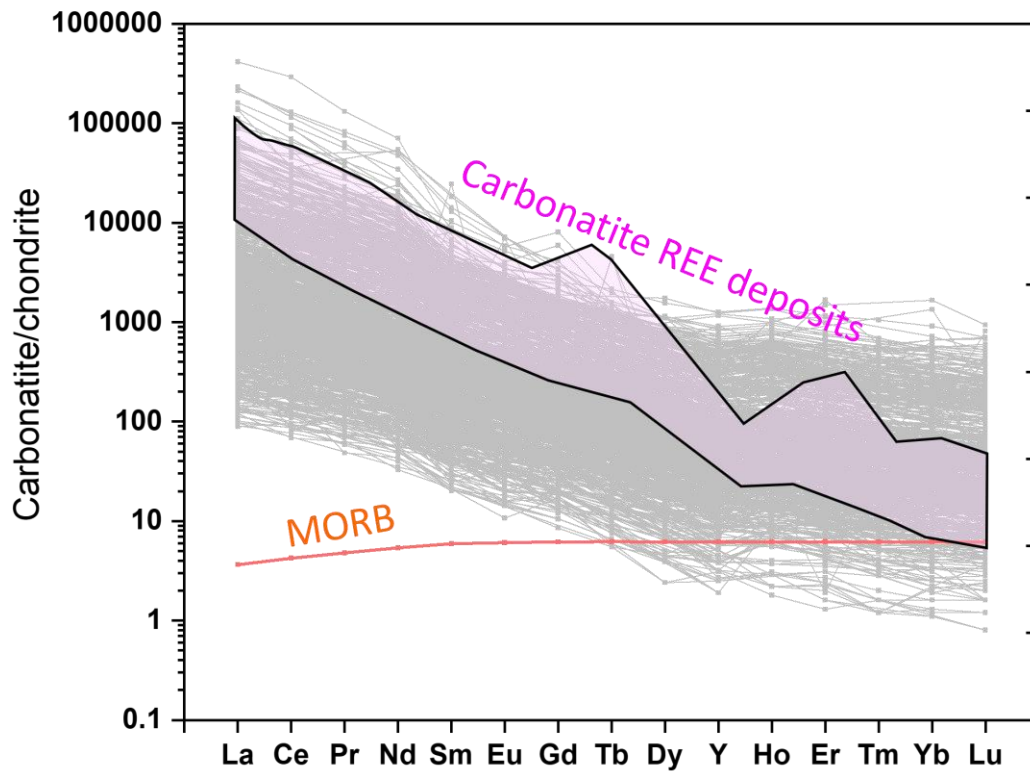
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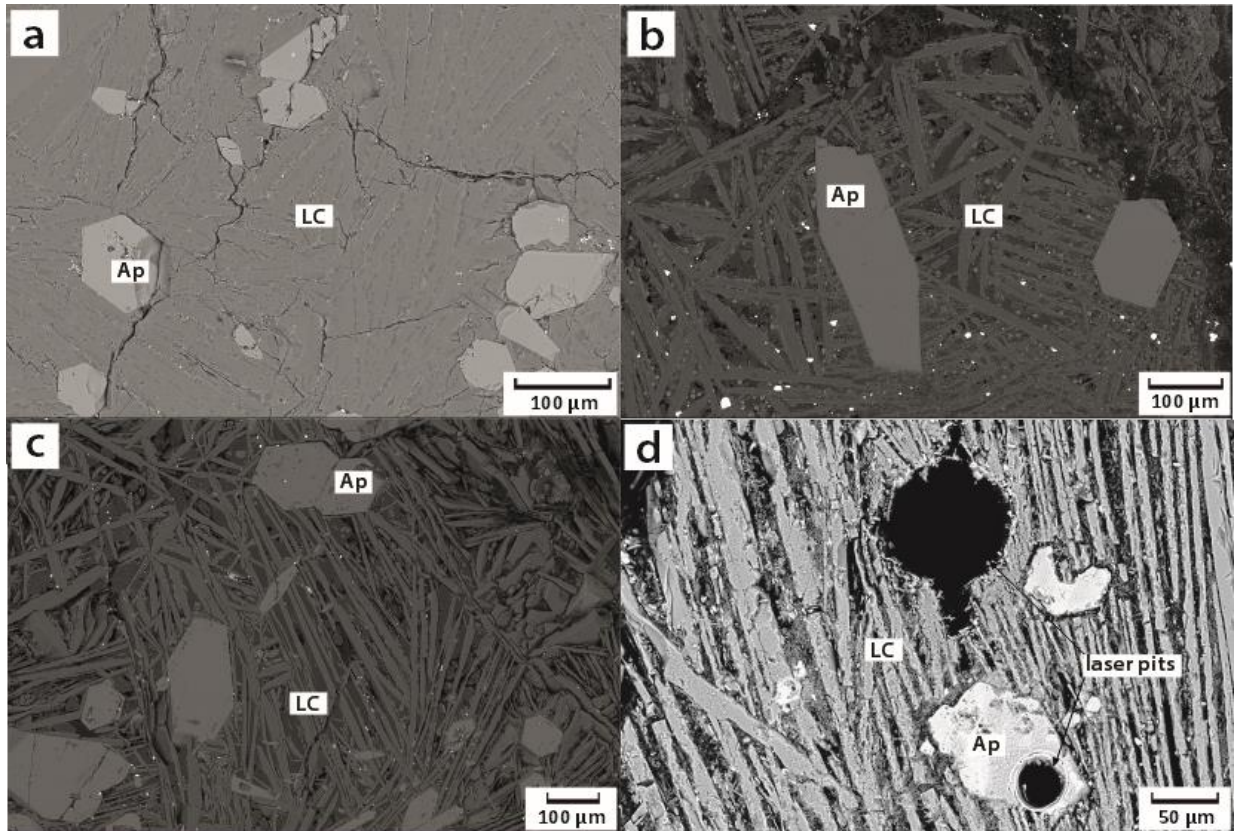
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633

634 Fig. 1. REE contents of carbonatite rocks (more than 3500 natural magmatic carbonatite
635 rocks from the GEOROC database; <http://georoc.mpch-mainz.gwdg.de/georoc/>)
636 normalised to the chondrite composition of McDonough and Sun (1995). The pink
637 pattern represents the compositional range of carbonatite REE deposits including Bayan
638 Obo, Mianing deposits and Mountain Pass (Verplanck et al., 2016).

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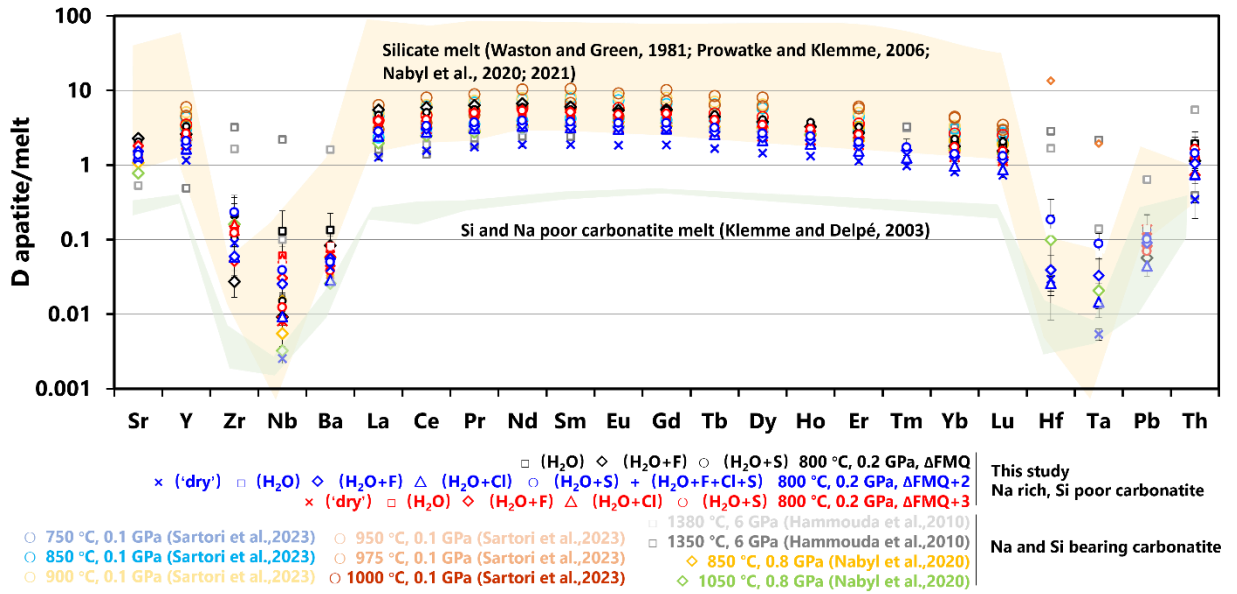
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641 Fig. 2. Back-scattered electron images of experimental run products. The carbonatitic
642 melt quenched as aggregates of sub-micrometer-size elongated crystals, with larger
643 apatite crystals in hydrous samples. (a) HGAP11 (carbonate + apatite); (b) HGAP08
644 (carbonate + apatite + H₂O + NaF); (c) HGAP12 (carbonate + apatite + H₂O); (d)
645 HGAP17 (carbonate + apatite + H₂O) with laser pits in the apatite and quenched melt.
646 Ap-apatite; LC-carbonatite melt. For details on the experiments, please see Table 1.

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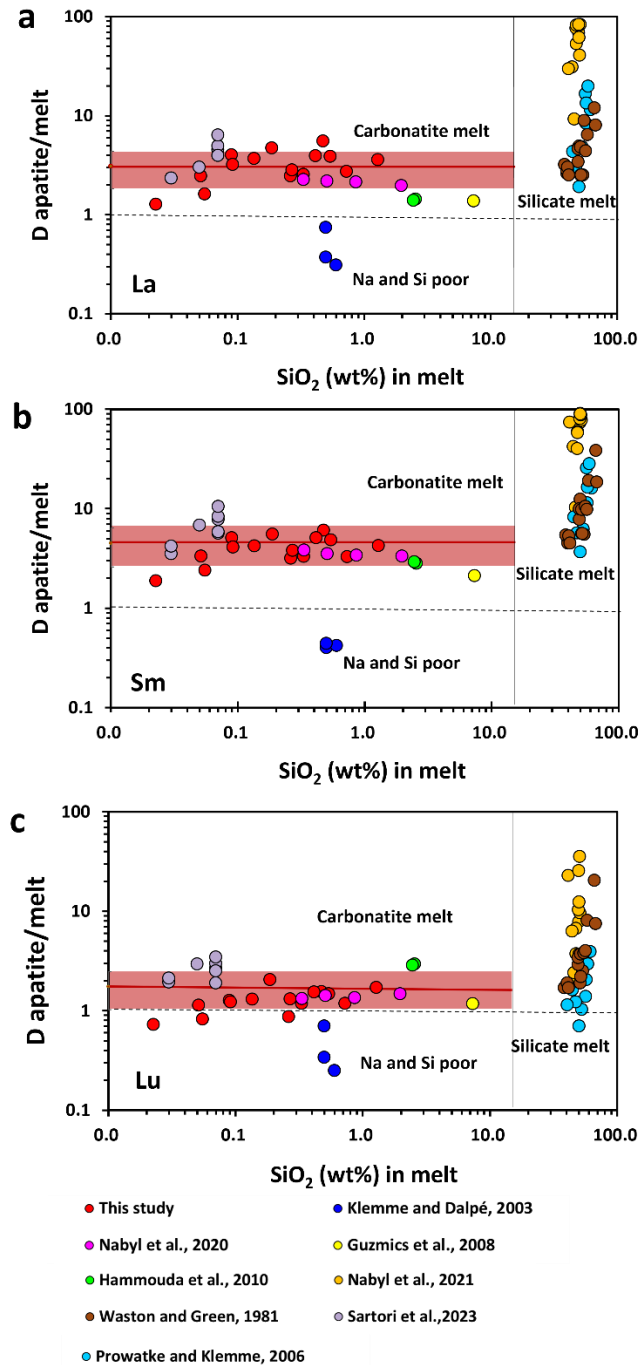


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652 Fig. 3. Experimentally determined partition coefficients for apatite and melt from this
 653 study and previous studies (Waston and Green, 1981; Klemme and Daple, 2003;
 654 Prowatke and Klemme, 2006; Hammouda et al., 2010; Nabyl et al., 2020; 2021).
 655 Apatite-melt partition coefficients for Na- and Si-bearing carbonatite melts (individual
 656 data points, see legend for details) fall between those of Si- and Na-poor carbonatite
 657 melts (indicated by the green compositional field) and silicate melt (indicated by the
 658 yellow compositional field).

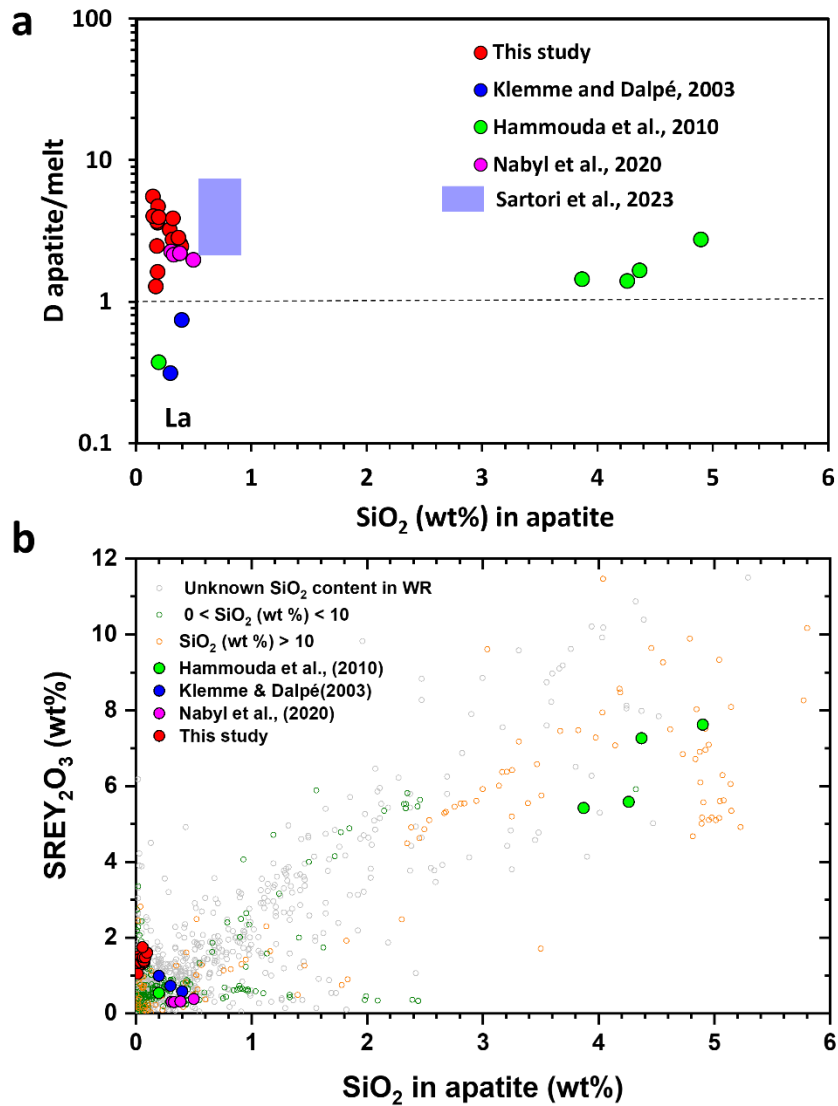
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661 Fig. 4. Partition coefficients for La, Sm and Lu between apatite and melt as a function
 662 of SiO_2 concentration in the melt. The horizontal red lines represent the average
 663 partition coefficients between apatite and carbonatite melt, and the red fields represent
 664 1 sigma standard deviations of the average partition coefficients. Note that the data from
 665 Klemme and Dalpé (2003) below the dashed black unit lines are not included in the
 666 average calculations, because the Na and Si poor experimental carbonatite
 667 compositions are not geologically realistic compositions.

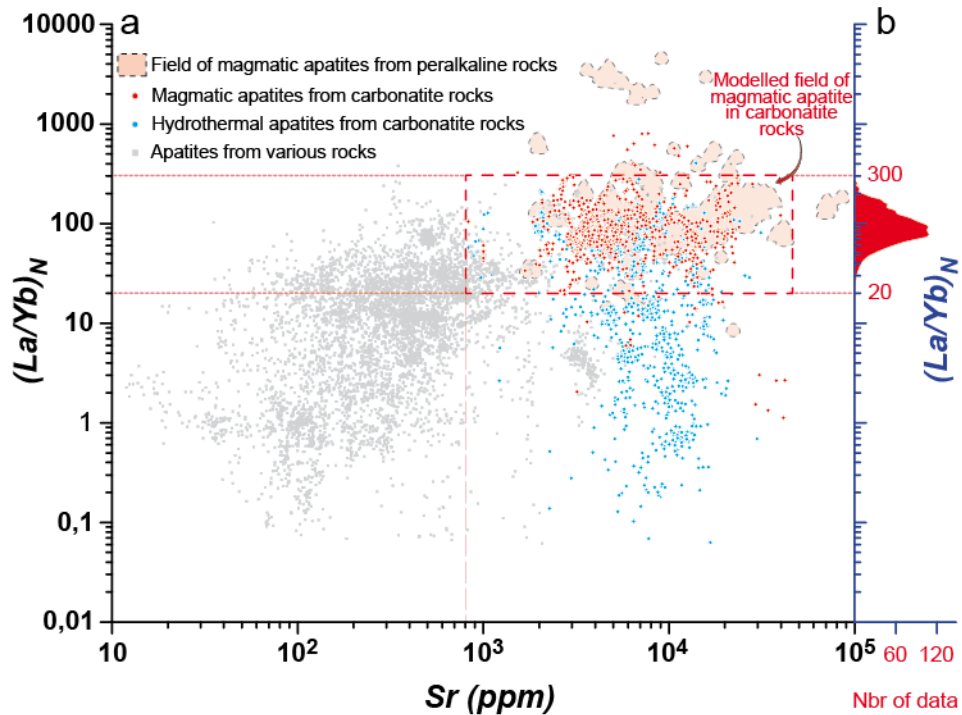
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670 Fig. 5. (a) Partition coefficients for La between apatite and melt as a function of SiO_2
 671 concentration in apatite. (b) SREY_2O_3 (total of REE and Y) content (wt%) vs. SiO_2
 672 content (wt%) in natural apatite. The color circles represent the experimental data. The
 673 natural apatite data are for whole-rock compositions (WR) with unknown SiO_2 content,
 674 SiO_2 in WR < 10 wt%, and SiO_2 in WR $> 10\%$ wt%.

675

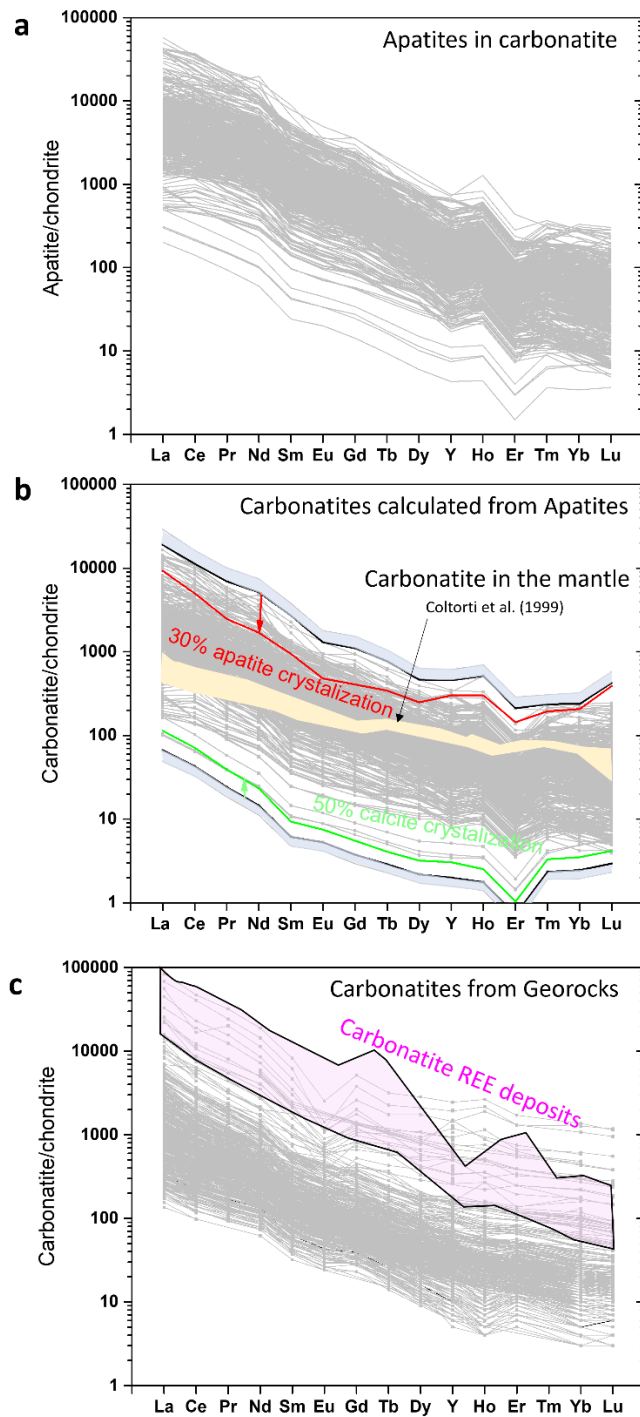


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678 Fig. 6. (a) Sr concentrations vs. $(La/Yb)_N$ ratios in apatite from various geological
 679 environments. The $(La/Yb)_N$ ratios are values normalised to the chondrite composition
 680 of McDonough and Sun (1995). All data are from the GEOROCK database and
 681 additional literature in supplementary materials. Magmatic apatite in carbonatites has
 682 relatively high $(La/Yb)_N$ values and Sr concentrations. (b) Calculated $(La/Yb)_N$ ratios
 683 for apatite crystals in equilibrium with silica-undersaturated peralkaline and carbonatite
 684 immiscible melts (see Nabyt et al 2020 for the source data); number of data for
 685 magmatic apatite in carbonatite rocks.

686



687

688 Fig. 7. REE contents of apatites and carbonatite melts normalised to the chondrite
 689 composition of McDonough and Sun (1995). (a) REE contents of 745 magmatic
 690 apatites identified as magmatic in origin. (b) REE contents of carbonatite melts were
 691 calculated from the magmatic apatite compositions; blue areas show the compositions
 692 with consideration of Ds (partition coefficients between apatite and carbonatite melts)

693 with 1 sigma standard deviation; green and red broken lines, respectively, show the
694 effects of calcite and apatite crystallization on the REE abundance of carbonatite melts
695 calculated assuming equilibrium fractionation. The yellow field is the composition of
696 carbonatite in the mantle obtained from Coltorti et al. (1999). (c) REE contents of
697 carbonatites calculated as immiscible melts in equilibrium with mafic to felsic alkaline
698 melt compositions (data after Nabyl et al., 2020). The pink field represents the
699 compositions of carbonatite REE deposits including Bayan Obo, Mianing deposits and
700 Mountain Pass (Verplanck et al., 2016).

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