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► **To cite this version:**

Haihao Guo, Johann Tuduri, Zineb Nabyl, Saskia Erdmann, Xiaochun Li, et al.. Rare earth elements in apatite: A proxy for unravelling carbonatite melt compositions. *Earth and Planetary Science Letters*, 2024, 642, pp.118863. 10.1016/j.epsl.2024.118863 . insu-04649882

**HAL Id: insu-04649882**

**<https://insu.hal.science/insu-04649882v1>**

Submitted on 25 Sep 2024

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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% CO<sub>2</sub>, 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 (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, Cl, F)), fluorite (CaF<sub>2</sub>), barite (BaSO<sub>4</sub>), carbonate (various minerals  
60 with compositions (Ca,Mg,Fe)CO<sub>3</sub>) 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  $\sim \Delta FMQ + 0$  to  $\Delta FMQ + 3$ ; 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.

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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        ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{SrCO}_3$ , and  $\text{BaCO}_3$ ) and  
138        natural magnesite ( $\text{MgCO}_3$ ). 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 ( $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  
141         $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  
142         $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{PbO}$ ,  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{MoO}_3$  and  $\text{WO}_3$ ). 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         $\text{Na}_2\text{SO}_4$  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  $\text{P}_2\text{O}_5$  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  $\text{H}_2\text{O}$  (resistivity higher than  $180000 \Omega \cdot \text{m}$ ) was loaded into the capsules using  
158        a 1-10  $\mu\text{L}$  micropipette. In IHPV charges, 9-11 wt%  $\text{H}_2\text{O}$  was added to capsules,  
159        whereas 3-6 wt% was added to capsules used in hydrated PC runs (Table 2). After  
160        loading  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  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-H<sub>2</sub> mixtures (0.15–0.6 MPa H<sub>2</sub> total pressure) in order to vary  $fO_2$  conditions  
176 (cf. Scaillet et al., 1992). The more H<sub>2</sub> 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  $\pm 2$  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 (Pt<sub>90</sub>Rh<sub>10</sub>/Pt) were placed at the top  
187 and bottom of the samples to monitor the temperature with an accuracy of at least  $\pm 5$   
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 ( $\sim 100$  °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  $\mu\text{m}$ , 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,  $\text{Al}_2\text{O}_3$  for Al,  
217  $\text{Fe}_2\text{O}_3$  for Fe,  $\text{MnTiO}_3$  for Mn and Ti,  $\text{SrSO}_4$  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  $\text{J cm}^{-2}$  on the sample surface. Spot analyses were performed using laser beam  
224 diameters of 32–60  $\mu\text{m}$ , depending on the size of the apatite crystals and quench-  
225 crystallized melt pools. Measured isotopes were  $^7\text{Li}$ ,  $^{23}\text{Na}$ ,  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{39}\text{K}$ ,  $^{44}\text{Ca}$ ,

226 <sup>47</sup>Ti, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>45</sup>Sc, <sup>51</sup>V, <sup>52</sup>Cr, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>85</sup>Rb, <sup>88</sup>Sr, <sup>89</sup>Y, <sup>90</sup>Zr, <sup>93</sup>Nb, <sup>95</sup>Mo, <sup>133</sup>Cs,  
227 <sup>137</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>153</sup>Eu, <sup>157</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm,  
228 <sup>172</sup>Yb, <sup>175</sup>Lu, <sup>178</sup>Hf, <sup>181</sup>Ta, <sup>182</sup>W, <sup>208</sup>Pb, <sup>232</sup>Th, and <sup>238</sup>U, 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 ( $D_{\text{REE}}$ ) range from 1 to 7 (Fig. 3a). We found that the apatite-melt partition  
278 coefficients do not correlate with the volatile contents ( $\text{H}_2\text{O}$ , 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  $D_{\text{REE}}$  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 SiO<sub>2</sub>  
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 SiO<sub>2</sub> content exceeds 20 wt%. Most likely, a change must occur in a range of melt  
301 SiO<sub>2</sub> 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 REE-elements in carbonatite  
304 systems (Table 3), since the carbonatite melts usually have less than 10 wt% SiO<sub>2</sub>.

## 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 CaCO<sub>3</sub>-  
312 Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(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  $D_{\text{REE}}$  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  $D_{\text{REE}}$  values for  
331 carbonatite systems, vs. high and highly variable  $D_{\text{REE}}$  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  $D_{\text{REE}}$  versus Si in apatite for  
336 the available experimental data. It appears unclear whether silica incorporation in  
337 apatite affects  $D_{\text{REE}}$ . All available data plot in the  $D_{\text{La}}$  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.  $\text{SiO}_2$  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  $\text{SiO}_2$  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  $\text{SiO}_2$  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  $\text{SiO}_2$ . For most of these  
353 low Si-rocks, data are located in a cloud of points at  $<2$  wt%  $\text{SiO}_2$  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 SiO<sub>2</sub> contents, where no Si-REE  
357 substitution is visible. This is consistent with the D<sub>REE</sub> data discussed in figure 4 and  
358 5a. Some data by Hammouda et al. (2010), however, plot clearly in the high SiO<sub>2</sub> 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<sub>REE</sub> 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<sub>REE</sub>.

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-fO<sub>2</sub>-H<sub>2</sub>O-Cl-F-SiO<sub>2</sub>-Na<sub>2</sub>O 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  $D_{\text{REE}}$  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

## Acknowledgments

497  
498

499 We gratefully acknowledge the constructive comments of journal editor Dr Rosemary  
500 Hickey-Vargas and two anonymous reviewers. This study was financially supported by  
501 the ANR LabEx VOLTAIRE (LABX-100-01), the ANR GASTON (ANR-18-CE31-  
502 0021) and the EquipEx PLANEX (ANR-11-EQPX-0036). National Natural Science  
503 Foundation of China (42373038, 42225202, 42073004, 42073007),  
504 Fundamental Research Funds for the Central Universities, China University of  
505 Geosciences (Wuhan) G1323523034, CUG230610, provided supports to H.G. during  
506 revision of this manuscript.

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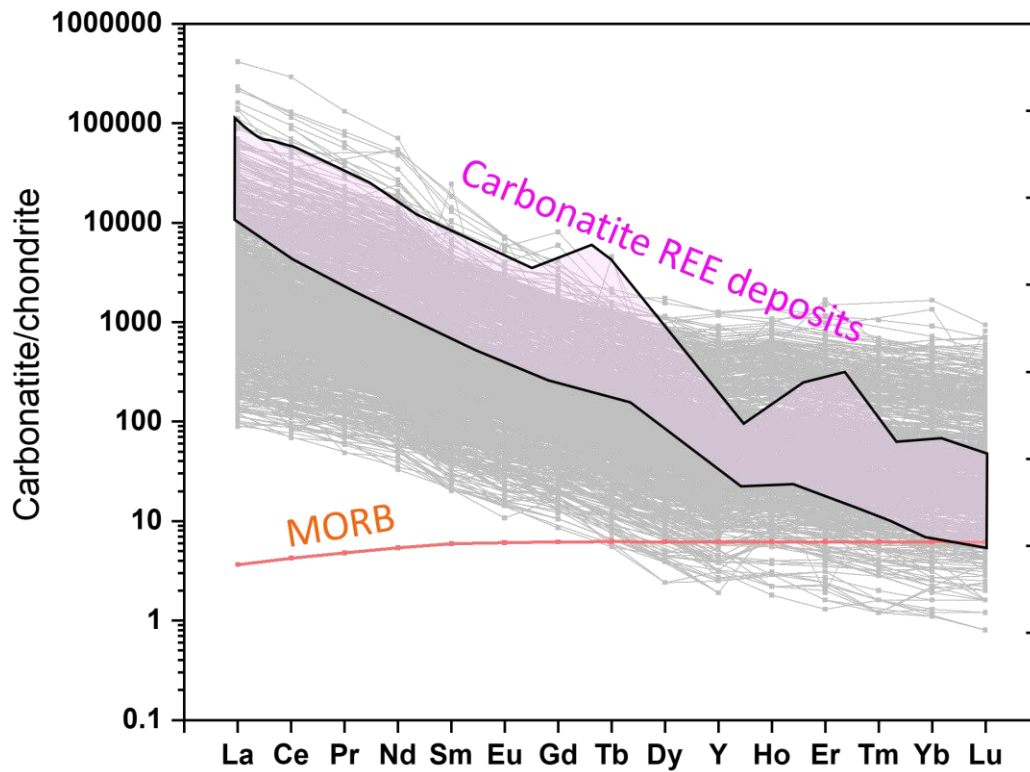
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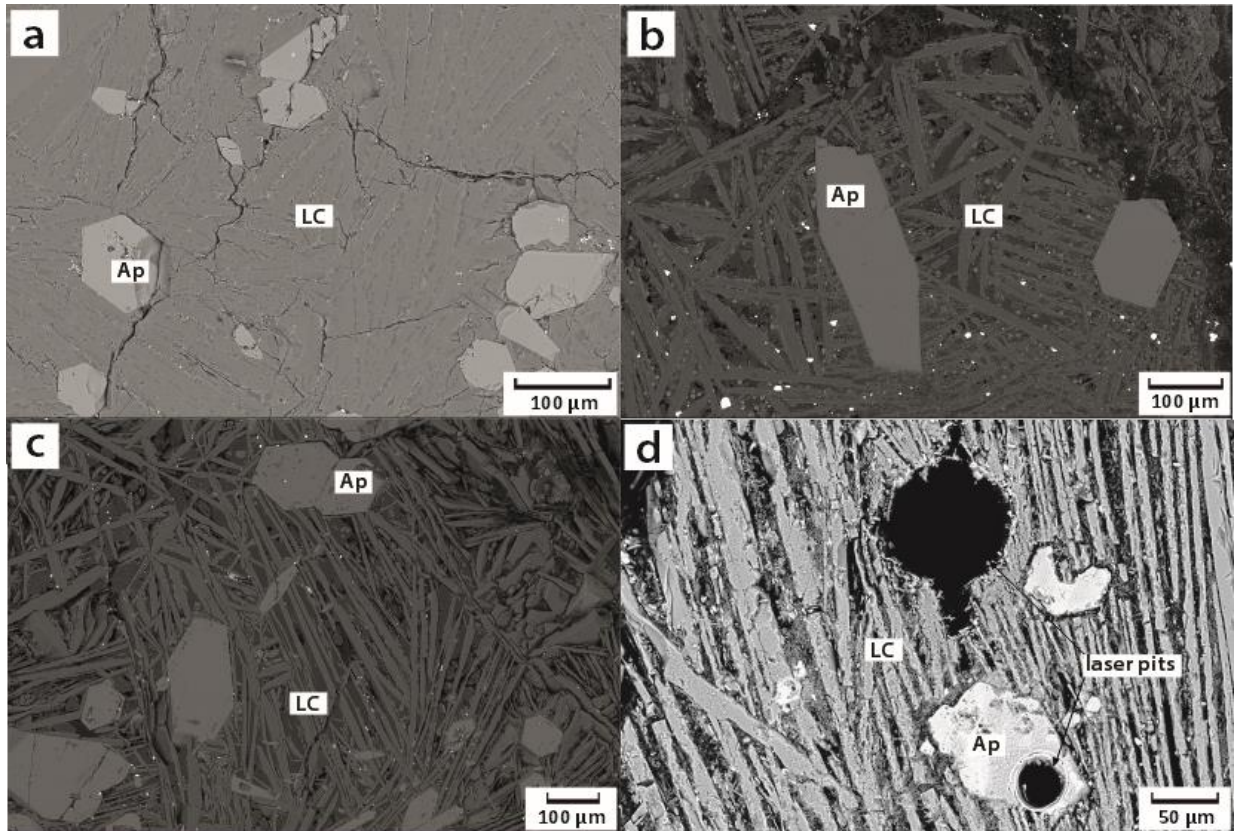
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633

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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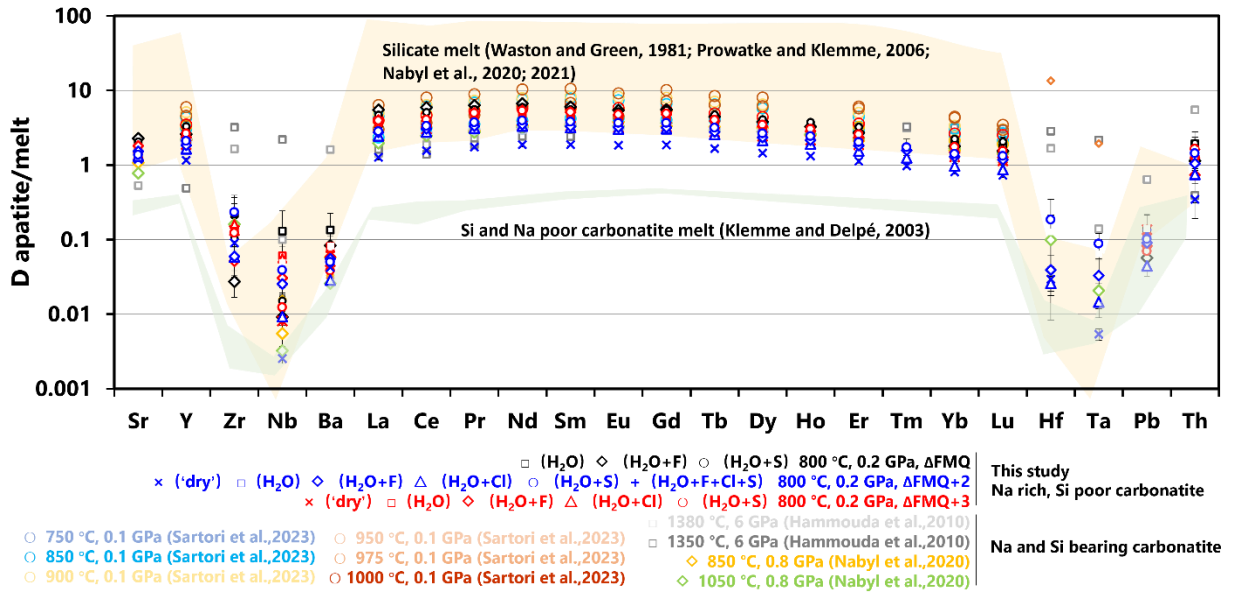
641 Fig. 2. Back-scattered electron images of experimental run products. The carbonatitic  
642 melt quenched as aggregates of sub-micrometer-size elongated crystals, with larger  
643 apatite crystals in hydrous samples. (a) HGAP11 (carbonate + apatite); (b) HGAP08  
644 (carbonate + apatite + H<sub>2</sub>O + NaF); (c) HGAP12 (carbonate + apatite + H<sub>2</sub>O); (d)  
645 HGAP17 (carbonate + apatite + H<sub>2</sub>O) 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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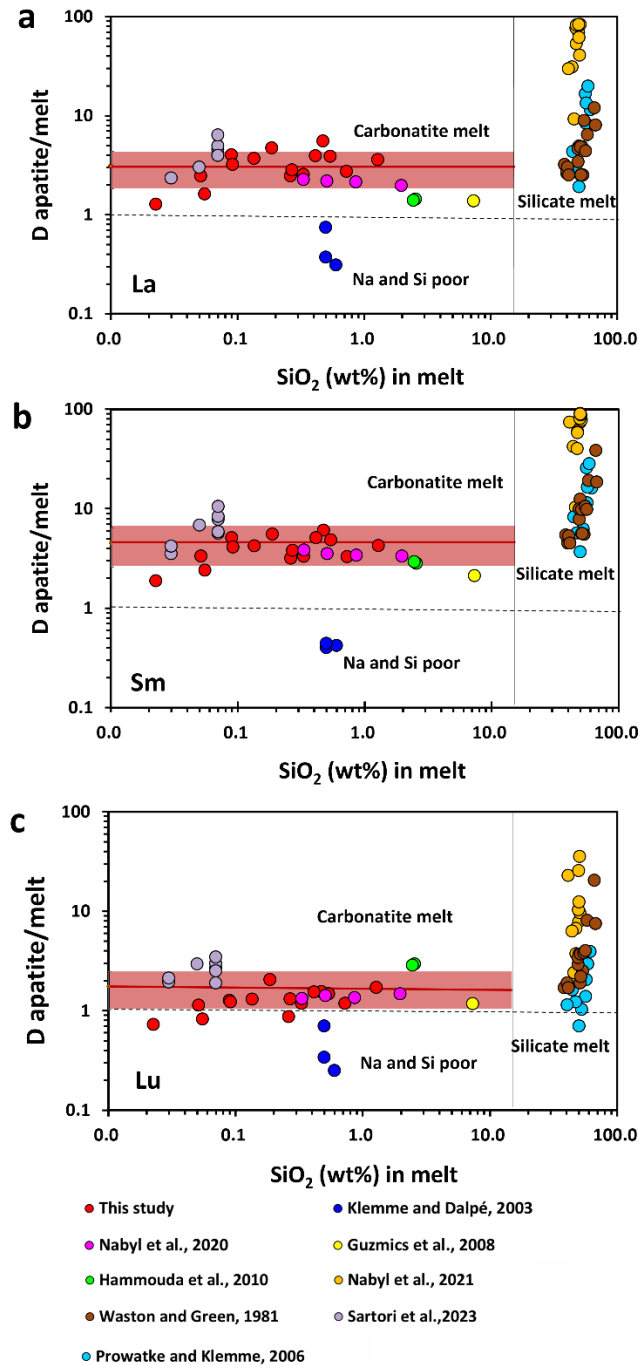


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652 Fig. 3. Experimentally determined partition coefficients for apatite and melt from this  
 653 study and previous studies (Waston and Green, 1981; Klemme and Daple, 2003;  
 654 Prowatke and Klemme, 2006; Hammouda et al., 2010; Nabyl et al., 2020; 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).

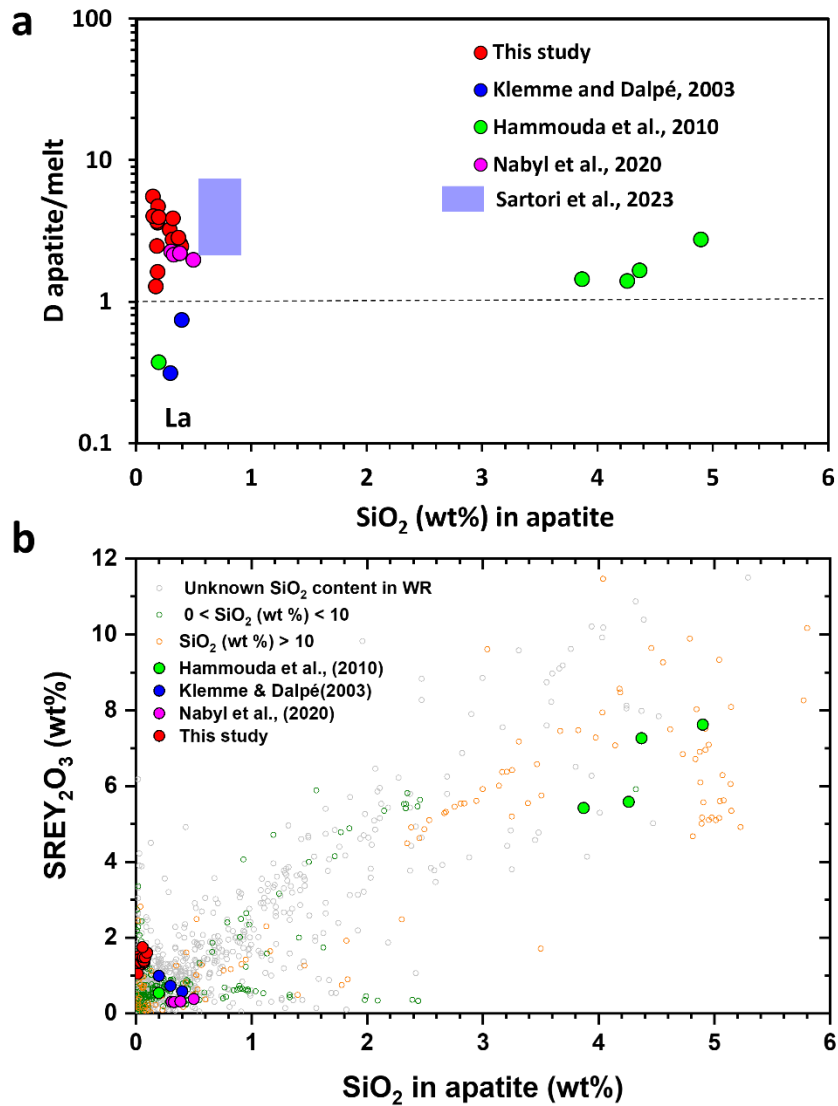
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661 Fig. 4. Partition coefficients for La, Sm and Lu between apatite and melt as a function  
 662 of  $\text{SiO}_2$  concentration in the melt. The horizontal red lines represent the average  
 663 partition coefficients between apatite and carbonatite 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.

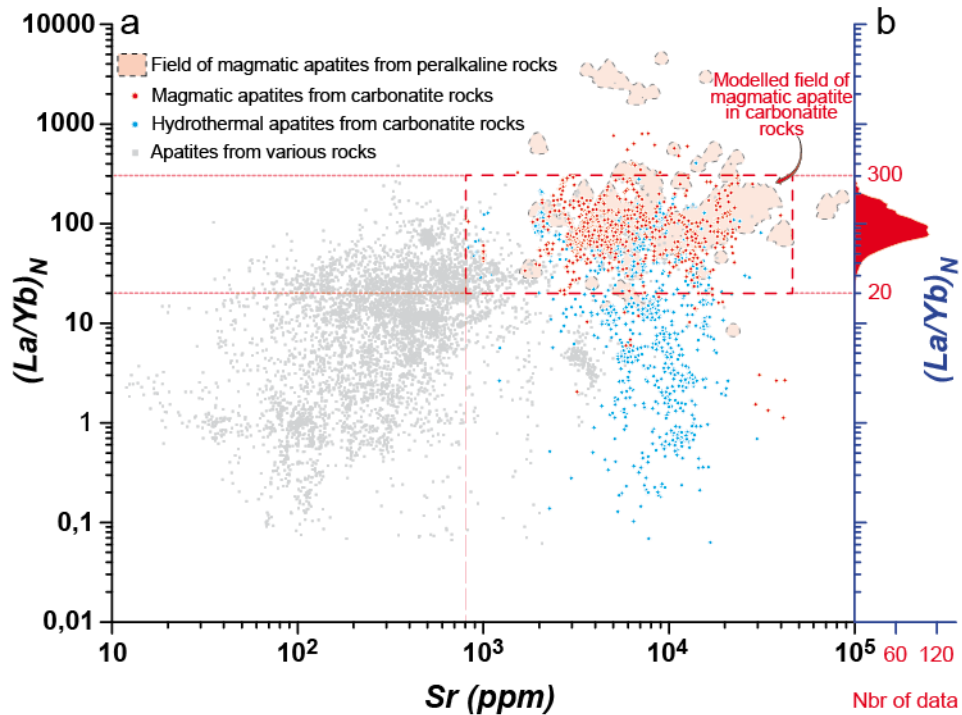
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670 Fig. 5. (a) Partition coefficients for La between apatite and melt as a function of  $\text{SiO}_2$   
 671 concentration in apatite. (b)  $\text{SREY}_2\text{O}_3$  (total of REE and Y) content (wt%) vs.  $\text{SiO}_2$   
 672 content (wt%) in natural apatite. The color circles represent the experimental data. The  
 673 natural apatite data are for whole-rock compositions (WR) with unknown  $\text{SiO}_2$  content,  
 674  $\text{SiO}_2$  in WR <10 wt%, and  $\text{SiO}_2$  in WR >10% wt%.

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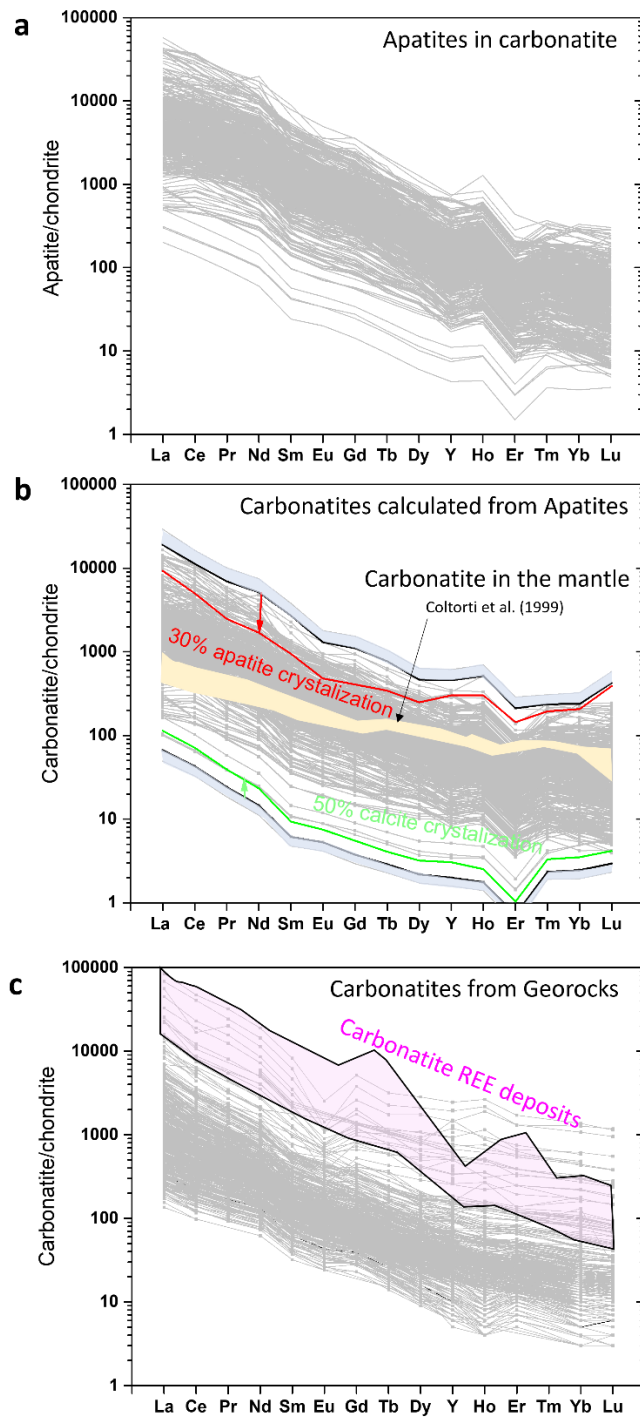


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678 Fig. 6. (a) Sr concentrations vs. (La/Yb)<sub>N</sub> ratios in apatite from various geological  
 679 environments. The (La/Yb)<sub>N</sub> ratios are values normalised to the chondrite composition  
 680 of McDonough and Sun (1995). All data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

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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  $D_s$  (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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