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Reaction pathways towards the formation of bastnäsite: replacement of calcite by rare earth carbonates.

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Abstract

The interaction of rare earth bearing (La, Nd, Dy) aqueous solutions with calcite crystals at ambient and hydrothermal conditions (25-220 °C) results in the solvent-mediated surface precipitation and subsequent pseudomorphic mineral replacement of calcite by rare earth carbonates. The newly formed rare earth carbonates follow the crystallisation sequence lanthanite [REE₂(CO₃)₃·8H₂O] → kozoite [orthorhombic REECO₃(OH)] → hydroxylbastnäsite [hexagonal REECO₃(OH)]. The specific rare earth involved in these processes and the temperature have strong control of the polymorph selection, crystallisation pathways and kinetics of mineral replacement. Kozoite-(La, Nd), grows oriented onto the calcite surface, forming an epitaxy. This phase forms elongated crystals on [100], with the {011} and {0-11} as major forms. The epitaxial relationship is (104) [010]_{cc} || (001) [100]_{koz} and is strongly dependent on the ionic radius of the rare earth in the structure of kozoite. These results have strong implications for the understanding of the mineralisation reactions occurring in rare earth bearing deposits, like carbonatite deposits, the most important resources of rare earths in the world.

1. Introduction

Rare-earth elements (REEs) comprise the fifteen elements corresponding to the lanthanides, which are fundamental strategic raw materials to maintain our daily life by providing high-technology devices, such as mobile phones, computers, batteries¹. REEs are widely used in civilian and military defence industries; magnets, catalysts, ceramics, glass and electronics require REEs for their production¹. Most of the renewable energy technologies contain REEs – electric vehicles, solar cells, generators of wind turbines have at least one of the rare-earth elements¹⁻³.

Due to their essential role in our modern life, the demand for REEs is continuously growing, pressuring the mining industry to fulfil these needs. Despite their name, REEs can be found in a considerable amount in the Earth's crust, except promethium which is radioactive with a half-life of 17.7 years and therefore much more scarce compared to other REEs. Lanthanum and cerium are just as abundant as copper⁴. In fact, REEs are more abundant than many of the platinum group metals⁵. However, minable deposits are hard to locate with concentrations high enough for economical extraction⁶. The biggest REEs provider is China, followed by Australia, Russia, India, Brazil, Vietnam and the United States. China supplies more than 80% of the REEs, thus, to avoid their monopoly there is a constant interest in finding alternative REEs ores, especially since 2010, when China gained almost absolute control above the REE market prices, by providing 95% of REE production globally^{1,4}.

Most of the research nowadays aim to find new REEs sources, while others target to develop cost-efficient recycling methods from waste. In particular, recycling of e-waste (electronic and/or industrial waste) has been gaining broad interest in EU, China and India⁷⁻¹². Less than 20% of the e-waste is predicted to be recycled and documented, while the rest (80%) is deposited without further treatment¹³. For example, in the United States, approximately 50 million metric tons of e-waste is deposited annually, and only 12.5% of this is recycled¹⁴. On the other hand, basically, every possible source is considered for potential REEs extraction.

For example, Menéndez et al.¹⁵, recently suggested the possibility of REEs extraction from palaeosoils in Gran Canaria, Spain. In India, beach placer deposits are targeted as an alternative source¹⁶. Besides, coal fly ash – which up until now was considered as a waste material– has also been studied for potential REE extraction¹⁷. Also, sedimentary phosphate deposits¹⁸ have been found to be enriched in REEs, and specifically, REE-bearing francolite (C-rich fluorapatite) has also been investigated as a source¹⁹⁻²¹. Other interesting potential sources are deep ocean sediments containing polymetallic nodules^{22,23}, ferromanganese crusts²⁴ and deep-sea mud²⁵. Moreover, the Moon and Mars²⁶ have been considered as possible long-term REE source in order to meet the future demand of humanity for rare-earth elements. Just the simple consideration of the off-Earth mining shows how critical it is to find a way to extract the needed amount of REEs.

Current methods of REE extraction and refinement are very expensive, both financially and environmentally²⁷. Typically, REEs are mined from open pits, underground mines, or leached in situ, and the extraction consumes more water and energy than any other metal²⁸. Carbonatites, igneous rocks containing >50% carbonate, are the primary deposits of REEs²⁹. The main sources of rare-earth elements are the REE-bearing minerals bastnäsite $(\text{REE})\text{CO}_3(\text{F},\text{OH})$ and apatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$ (where part of the Ca can be replaced by REE, Na, Sr, and Mn)³⁰. Following this, monazite (REEPO_4), xenotime (REEPO_4), loparite $[(\text{Na},\text{REE})\text{Ti}_2\text{O}_6]$, and lateritic ion-adsorption clays are the most important REE sources^{31,32}. These ores have magmatic, hydrothermal and/or metamorphic origin, while other ores are formed by erosion and weathering (mostly laterites and bauxites) and serve as secondary deposits¹. Carbonatites contain a complex set of carbonate minerals (e.g. calcite, dolomite, strontianite, siderite) and other accessory minerals such as iron-oxides or phosphates and the REE-bearing minerals (e.g., monazite, apatite, bastnäsite) as well^{33,34}. These deposits are dominated by the four light REE (LREE, La, Ce, Pr, Nd) and contain minor concentrations of heavy REE (HREE); however, REEs behave incompatibly throughout igneous differentiation of carbonatites. In alkali-free carbonatites, the REEs are concentrated in potentially economic

domains within the carbonatites and are hosted by relatively insoluble REE carbonate and phosphate minerals. Conversely, alkali-bearing carbonatites exsolve REE-rich fluids which migrate long distances, keeping high REE solubilities. As a consequence, Na and K produce higher HREE/LREE ratios in the transported fluids, but K-rich fluids tend to transport HREE relative to Na-rich fluids ³⁵. Also, recent thermodynamic calculations suggest that the main ligands responsible for the transport of REE at hydrothermal conditions are Cl^- and SO_4^{2-} , while F^- is a depositional ligand that reduces the range of conditions for which REE can be stabilised in hydrothermal solutions ³⁶⁻³⁹.

Rare earth elements have a known affinity for carbonates not just in natural but in experimental settings. Experimental work has demonstrated that rare earths adsorb on the surface of carbonate minerals ^{40,41} and that they are strongly partitioned into these minerals, substituting for Ca^{2+} ^{40, 42-50}. However, little is known about the fundamental physicochemical conditions governing the mobility and transport of REE at hydrothermal conditions in the presence of carbonate minerals.

As REEs are essential raw materials for emerging renewable energy resources, we are urged to obtain and use them in a sustainable manner to maintain current standards of living and ensure the quality of life for future generations. This will require continued research on REE-bearing mineral formation to better understand the geological processes by which these elements are concentrated. One of the major problems related to exploration and exploitation of rare-earth elements in carbonatites is the lack of understanding of the crystallisation mechanisms and pathways of REE carbonates and in particular their early stages of formation. In fact, carbonatite deposits are complex systems which are affected by several parameters (e.g., temperature, pressure, chemistry of solids and fluids). Due to this complexity of the participating factors, understanding the origin and all the mechanisms of formation of REE deposits involved in a complete system requires a deep understanding of the mineral-fluid reactions that drive the crystallisation and dissolution of carbonates in REE-bearing hydrothermal solutions. This includes, but does not limit to, direct nucleation from hydrothermal

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3 105 fluids, surface crystallisation, coprecipitation, or mineral replacement reactions. Many of these
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5 106 reactions in carbonate systems can be rapid, complex and multi-step, involving short-lived
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7 107 intermediate phases ⁵¹, requiring step-by-step analysis under well-defined laboratory
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9 108 conditions. Therefore, our work has focused on the interaction of calcite (CaCO₃) and three
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11 109 REE (La, Nd, and Dy) in solution at low hydrothermal conditions (21-220 °C). These three REE
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13 110 have been selected because of the balance between their chemical similarities and
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15 111 dissimilarities. La and Nd both belong to the group of LREE, while Dy is classified as HREE.
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17 112 There are slight contrasts in their chemical properties, like their ionic radii: La³⁺, Nd³⁺ and Dy³⁺
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19 113 average ionic radii are 1.15, 1.08 and 0.99 Å, respectively, values close to the radii of Ca²⁺
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21 114 (0.99 Å) and Sr²⁺ (1.13 Å) ^{52,53}. In addition, the U.S. Department of Energy identified Nd as
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23 115 critical element for both short and long term. Among all the REEs, Dy is labelled as the most
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25 116 critically needed rare-earth element ^{54,55}.
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29 117 In this study, the effects of the interaction of REE-rich aqueous hydrothermal solutions with
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31 118 calcite crystals were investigated with the purpose of mimicking potential recrystallisation or
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33 119 replacement reactions involving calcite in REE deposits during hydrothermal and metasomatic
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35 120 processes. In particular, our objectives were to determine (1) the fate of REE during these
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37 121 interaction processes, (2) the nature of potential newly formed phases as a function of aqueous
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39 122 chemistry and temperature, (3) the mechanisms and kinetics of crystal formation.
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124 2. Methods

125 The general experimental procedure consisted of adding 0.05 g (0.5 millimoles) of calcite
126 crystals (Iceland spar variety) with sizes of 0.5-1.0 mm to 50 mL of 10 mM rare earth bearing
127 aqueous (MilliQ) solutions (pH ≈ 5.4; Ca/REE molar ratio of ~ 1). Also, some additional
128 experiments with an excess of calcite (e.g., 0.30 g) were carried out to exhaust the REE during
129 the reaction process. Solutions containing one single rare earth element were prepared using
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3 130 $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ reagents (Sigma Aldrich; 99.99% trace
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5 131 metals basis). Experiments were carried out in 50 mL teflon-lined stainless-steel autoclaves at
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7 132 different temperatures (21, 50, 95, 160 and 220 °C) and saturated water vapor pressures. Solid
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9 133 samples were carefully extracted at increasing time intervals and then placed in an oven at 50
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11 134 °C during 30 min for drying.

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15 135 Samples were preliminarily examined using a binocular lens (ZEISS SteREO Discovery.V8
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17 136 with 8:1 Manual Zoom Range; 6.3-50.4 X) to determine any large visible changes in the
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19 137 morphology and colour of calcite crystals. Then, the samples were characterised with powder
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21 138 X-ray diffraction (XRD) for the identification and quantification of any newly formed crystalline
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23 139 compounds. Conventional powder XRD patterns were collected using a Bruker D5000 powder
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25 140 X-ray diffractometer (Cu K α radiation, 0.01° step⁻¹ from 5 to 60° 2 θ at 1° min⁻¹). Identification
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27 141 of crystalline phases was carried out with the Diffract Suite EVA software from Bruker in
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29 142 combination with the Powder Data File (PDF-4, The International Centre for Diffraction Data).
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31 143 Pattern-matching refinement and quantification of crystalline phases were carried out with the
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33 144 Rietveld refinement software TOPAS⁵⁶.

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37 145 Scanning electron microscopy (SEM) was used to characterise the changes in the morphology
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39 146 of calcite, potential newly formed phases, and to obtain elemental analysis of areas of interest.
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41 147 All samples were carbon-coated and placed into a Tescan MIRA XMU FE-SEM operating
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43 148 under high vacuum conditions and equipped with an Oxford Instruments NanoAnalysis X- Max
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45 149 80 mm² Energy Dispersive Spectroscopy (EDS) detector running Oxford Instruments
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47 150 NanoAnalysis AZtecTimed analysis software. Analyses were performed using an accelerating
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49 151 voltage of 20 kV and a beam current of 300 pA.

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53 152 Lastly, the saturation indexes of solid phases during the equilibration of the REE-bearing
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55 153 aqueous solutions with respect to calcite were calculated with the hydrogeochemical code
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57 154 PHREEQC⁵⁷ using the LLNL database and the solubility products of REE-bearing carbonates
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59 155 determined by Essington and Mattigod⁵⁸ and Voigt et al⁵⁹.

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157 3. Results

158 The analysis of solid samples obtained from our experiments revealed that the interaction of
159 calcite with rare earth bearing solutions was translated into the formation of a series of surface
160 precipitates that partially or totally replaced the host crystals. The combination of powder XRD
161 and SEM-EDS allowed the identification and quantification of newly formed phases, as well as
162 the interpretation of the mechanisms of surface precipitation.

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164 3.1 Observations in visible light (binocular lenses)

165 The preliminary observation with binocular lens of solid samples extracted from the La-, Nd-
166 and Dy-rich solutions at different times and temperatures allowed to gain information on the
167 level of influence of temperature on the crystallisation process. These observations already
168 revealed a series of surface precipitates on the surface of calcite. The presence and the extent
169 of the precipitates varied depending on the temperature and reaction time. At 21 °C, the
170 formation of surface precipitates on calcite took the most prolonged period of time: a precipitate
171 on the surface of calcite was observed after 14 days in the La experiments but took 145 days
172 to form in the Nd and Dy experiments. In the case of 50 °C experiments, the formation of a
173 surface crust on calcite in the La-, Nd- and Dy-bearing experiments occurred after 5, 2 and 9
174 days of reaction, respectively. Samples obtained from all experiments at 95 °C revealed
175 surface precipitates after the first 24 hours of reaction. Finally, at the highest temperatures
176 (160 and 220 °C) thick crusts were observed in all experiments after 24 hours of reaction. In
177 addition to this, changes in the colour and opacity of the calcite grains were observed in all
178 experiments. Calcite (Iceland spar) crystals placed in the aqueous solution were initially
179 transparent and colourless, but they became more translucent with time and were completely
180 opaque at the end of all experiments (e.g., Figure SI-1). After the interaction with La- Nd- and

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3 181 Dy-bearing solutions, all calcite crystals became light-pink, dark-pink and yellowish,
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12 184 **Powder X-ray Diffraction**
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15 185 Powder XRD allowed us to identify newly formed secondary minerals. A series of different
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17 186 rare-earth bearing carbonate minerals were detected: La- and Nd-lanthanite
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19 187 $[(\text{REE})_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}]$, La-, Nd- and Dy-kozoite, $[(\text{REE})\text{CO}_3(\text{OH})]$ and La- and Nd-
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21 188 hydroxylbastnäsite $[(\text{REE})\text{CO}_3(\text{OH})]$. Powder XRD patterns of these newly formed phases
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23 189 obtained at the end of the experiments are presented in Figures 1-3, and all experimental
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25 190 results are summarised in Table 1. Phase quantification using Rietveld refinement revealed
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27 191 that the kinetics of crystallisation of the secondary REE-bearing minerals and the polymorph
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29 192 selection were controlled by temperature and also by the ionic radius of the rare earth.
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31 193 Regardless of the composition of the newly formed crystals, all calcite grains were fully
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33 194 replaced by crystalline rare earth carbonates at temperatures $\geq 50^\circ\text{C}$ (e.g., Figure 4). The
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35 195 kinetics of these replacement reactions were temperature-dependent: in the ambient
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37 196 temperature experiments, the replacement reactions did not complete, with calcite being
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39 197 replaced a maximum of 15 weight% by the newly-formed phases after 145 days. However, at
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41 198 50, 95 and above 160°C , calcite was replaced after 20, 11 and 1 days, respectively. Also, the
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43 199 kinetics of replacement of calcite by secondary phases in the La-bearing experiments was
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45 200 always faster compared to the other two rare earths. Conversely, the onset of crystallisation
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47 201 and the kinetics of replacement for the Dy-bearing experiments were the slowest (Table 1).
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52 202 The interaction of La-bearing solutions with calcite crystals at ambient temperature resulted in
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54 203 the formation of La-lanthanite (PDF 00-014-0190) (Figure 1, bottom) after 14 days of reaction,
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56 204 remaining stable during the full duration of the experiments (145 days). At 50°C La-lanthanite
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58 205 was not detected at any time and after 5 days La-kozoite (PDF 00-049-0981) crystallised
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(Figure 1, middle), remaining stable until the end of all experiments. The evolution of the experiments carried out at 95 °C was similar, but the onset of the crystallisation of La-kozoite was much faster (<1 day) and only at the very end of the experiment (154 days) minor amounts (~ 2 weight%) of La-hydroxylbastnäsite (PDF 00-026-0815) were found along with La-kozoite. At 160 °C, La-kozoite took >21 days to fully transform to La-hydroxylbastnäsite, while at the maximum temperature studied, 220 °C, only La-hydroxylbastnäsite formed in less than 24 hours and no other crystalline phases were observed (Figure 1, top). The experiments performed with Nd-bearing solutions produced similar results to the La counterpart: At ambient temperature Nd-lanthanite (PDF 00-030-0678) was found in the ambient solution experiments after 145 days (Figure 2, bottom). Nd-kozoite (PDF 00-027-1296) was found at 50 and 95 °C (Figure 2, middle) after 2 and < 1 days, respectively. At 50 °C Nd-kozoite remained stable during the full duration of the experiment, while at 95 °C minor amounts (< 1 weight%) of Nd-hydroxylbastnäsite (PDF 00-038-0400) were detected after 154 days (Table 1). At 160 °C only Nd-kozoite formed but no transformation to Nd-hydroxylbastnäsite was observed in 28 days. Finally, at 220 °C Nd-kozoite transforming to Nd-hydroxylbastnäsite was identified (Figure 2, top), a transformation which was completed after 7 days. Finally, the interaction of calcite with Dy-bearing solutions resulted in the temperature-dependent crystallisation of Dy-kozoite (PDF 04-014-4506) (Figure 3) after 145 days (21 °C), 9 days (50 °C) and < 1 day (≥ 95 °C). This was the only crystalline phase detected in the Dy-bearing experiments at all temperatures, remaining stable during the full duration of the experiments.

Scanning Electron Microscopy

The SEM images obtained after different periods of the interaction of the calcite grains with the rare earth bearing solutions revealed the formation of precipitates on the surface of calcite. A representative example is presented in Figure 5, which shows the surface of a typical calcite grain after 0.75, 1.75 and 13 days of reaction with a La-bearing parent solution at 95 °C. The

surface of calcite showed clear dissolution signs and started to be covered by small ($\sim 40 \mu\text{m}$) individual crystals with slightly elongated morphologies (Figure 5a). Afterwards, this precipitate began to grow and extend (Figure 5b) to quickly cover the full surface of calcite forming a crust. The final result was a pseudomorphic replacement in which the original morphology and dimensions of the calcite grains remained constant (Figure 5c), but the host mineral was fully replaced by the newly formed rare earth carbonates as also revealed by XRD (e.g., Figure 4). SEM images also confirmed that the initiation of the surface precipitation process, the kinetics of the full replacement reaction and the morphology of the secondary minerals (Table 1) were controlled by the temperature and the rare-earth element in the aqueous solution. Results from energy dispersive spectroscopy (EDS) microanalysis of selected crystals supported the chemistry of the newly formed phases already identified with powder XRD, consisting of oxygen and the rare-earth (La, Nd or Dy). The content of Ca in all the newly formed phases was very low (atomic % ≤ 1) or below the detection limit of the instrument (Table SI-1).

Regarding the crystal morphology, the rare-earth bearing carbonates showed very different morphologies. La- and Nd-Lanthanite developed very thin, platy morphologies (Figure 6). La-Lanthanite formed aggregates fully covering all calcite grains after 14 days of reaction (Figure 6a,b), with sizes ranging between 10 and 100 μm , while Nd-lanthanite consisted of 20-50 μm single crystals disseminated on the surface of calcite (Figure 6c,d) that did not even cover the full surface of the host grains after 145 days of reaction. La- and Nd-kozoite had similar sizes (10-20 μm) but while the former consisted of small prisms (Figure 7a and b), the latter had bladed or spindle-shaped morphologies (Figure 7c and d). These two phases, especially Nd-kozoite, grew oriented onto the calcite surface in most experiments (Figure 7b, c and d) but sometimes also showed random orientation, especially when the replacement reaction was completed. On the other hand, the Dy-kozoite typically precipitated as bow-tie aggregates showing some branching (Figure 7e). These aggregates were on average 50 μm long, formed by spindle-shaped individual crystals usually smaller than 25 μm . The size and morphology of Dy-kozoite crystals at 160 and 220 $^{\circ}\text{C}$ was different compared to lower temperature

experiments in this system and consisted of tabular and prismatic crystals with sizes smaller than 50 μm (Figure 7f). Finally, the highest temperature phases, La-hydroxylbastnäsite and Nd-hydroxylbastnäsite showed similar morphologies (Figure 8): The former crystallised as triangular prisms with sizes usually smaller than 20 μm (Figure 8a) and the later consisted of slightly larger ($\sim 40 \mu\text{m}$) rectangular prisms (Figure 8b).

SEM observations revealed that the crystallisation of La- and Nd-kozoite on the surface of calcite took place via the formation of individual crystals following a clear non-random orientation (Figure 9a). La- and Nd-kozoite crystals with lengths of $\sim 10 \mu\text{m}$ developed to form an oriented overgrowth on the (104) surface of calcite (Figure 9 b). With time, the calcite surface got completely covered by oriented kozoite crystals and also by crystals with random orientations, most of them formed on the top of the epitaxial overgrowth (Figure 9 c). Although the initial neoformed crystals of La- and Nd-kozoite exhibited spindle-shaped morphologies, with time these crystals became more elongated and slightly more prismatic, reaching lengths no longer than $\sim 50 \mu\text{m}$. In this epitaxial overgrowth of calcite and kozoite (Figure 10) the [010] direction of calcite and the [100] direction of kozoite are parallel on the epitaxial faces calcite (104) and kozoite (001). La- and Nd-kozoite form elongated crystals on [100], with {011} and {0-11} as major forms. An explanation of the epitaxial overgrowth requires further consideration on the atomic arrangement of the structures of calcite and kozoite, which will be discussed in the next section.

4. Discussion

The sorption of dissolved REE at all studied temperatures, mediated by the surface of calcite, occurred via surface precipitation, leading to the subsequent crystal growth of different REE carbonates. The interaction of the REE-bearing solutions and calcite grains led to the release of Ca^{2+} and CO_3^{2-} from the surface of calcite to the aqueous solution. As the concentration of

284 Ca^{2+} and CO_3^{2-} increased with time, especially close to the calcite surface, the carbonate ions
285 reacted with the REE^{3+} ions in the solution favouring the precipitation different REE carbonate
286 polymorphs. The combination of XRD and SEM data showed that the interaction of calcite with
287 the REE-bearing fluid was always translated into a solution-mediated pseudomorphic
288 replacement of calcite by lanthanite, kozoite or hydroxylbastnäsite. In all cases, a centripetal
289 replacement was observed, in which the calcite grains were replaced from their periphery
290 inwards. This type of replacement takes place because the newly formed phases are less
291 soluble than the host mineral at the P-T range studied. Reports of solubility product of La- and
292 Nd-lanthanite ⁵⁸, La- and Nd-kozoite and La- and Nd- hydroxylbastnäsite ⁵⁹, show that
293 lanthanites are 5-6 orders of magnitude more insoluble than calcite ⁶⁰ and the difference
294 between calcite and kozoite or hydroxylbastnäsite solubility products is even higher, of 14 and
295 16 orders of magnitude, respectively.

296 The evolution of our experiments taken as a whole (Figure 11) revealed the crystallisation
297 sequence started with lanthanite, followed by kozoite and ending with hydroxylbastnäsite,
298 except for these experiments carried out using Dy, in which the Dy-kozoite was the only stable
299 phase. The polymorph selection of REE carbonates during the experiments was temperature-
300 dependent: lanthanite (highly hydrated compound) formed at ambient temperature, while
301 kozoite and hydroxylbastnäsite (both anhydrous) at temperatures between 50 and 220 °C.
302 However, the polymorph selection was very strongly dependent on the ionic radii of the rare-
303 earths, also resulting in variations in the dimension of the unit cells of the newly formed crystals
304 (Table 2) and also in some differences in the crystallisation sequences in our three studied
305 REE systems. Our data shows that for each of the isomorphs, lanthanite, kozoite and
306 hydroxylbastnäsite, the largest unit cell parameters correspond to the lighter REE isomorphs,
307 a consequence of the decrease in ionic radii with atomic weight of the REE (lanthanide
308 contraction). This is in agreement with the usual crystal chemistry of these minerals in nature
309 and synthesis experiments. Lanthanite-type isomorphs contain light rare-earth, with larger
310 ionic radius, like La, Ce and Nd ⁶¹⁻⁶⁴ forming a structure with two types of RE-O polyhedra in

10-fold and 8-fold coordination. The REE-O coordination in kozoite isomorphs is 10, and these can be synthesized using light and intermediate rare-earths (La, Nd, Dy; ⁶⁴⁻⁶⁷). However, heavier REE than Dy do not form kozoite but result into different structures with orthorhombic and tetragonal crystal systems and smaller (8- and 9-fold) RE-O coordination numbers ⁶⁶. In hydroxylbastnäsite, the REE-O coordination is 9-fold, forming a hexagonal mineral structure that involves light REE (La, Ce, Nd; ^{64,68}), while the crystallisation of pure hydroxylbastnäsite isomorphs containing heavier REE requires high-pressure conditions ⁶⁹⁻⁷¹.

This general crystallisation evolution is consistent with a progressive dehydration sequence and also agrees with the sequences observed by Vallina et al. ^{64, 67} in their homogeneous nucleation experiments performed by mixing carbonate and rare-earth bearing solutions. Vallina et al. ^{64, 67} crystallisation sequences also included metastable poorly-ordered precursors at the very beginning of the reactions. It is well known that in aqueous systems the driving force required to produce these poorly-ordered precursors prior to crystallisation is a rapid increase in supersaturation levels in the solution ^{51,72}. In our experiments, no evidence of poorly-ordered precursors were observed at any stage of the experiments. This is interpreted as a consequence of the gradual dissolution of calcite and therefore, lower increase in supersaturation levels in the aqueous solution compared to homogeneous nucleation experiments. On the other hand, and also in agreement with the previous studies, the crystallisation sequence observed proceeded through two transient (metastable) phases, lanthanite and kozoite, prior to the formation of the most insoluble and thermodynamically stable polymorph (hydroxylbastnäsite), a known phenomenon referred to as "Ostwald's Rule of Stages" ⁷³, observed in many mineral systems (e.g., Bots et al. ⁷⁴; Van Driessche et al. ⁷⁵). The total absence of hydroxylbastnäsite in all the Dy-bearing experiments is a consequence of the smaller size of the Dy³⁺ ion (0.99 Å) compared to La³⁺ (1.15 Å) and Nd³⁺ (1.08 Å), impeding the crystallisation of this phase under our experimental P-T conditions ⁶⁶.

In order to determine the saturation indices (SI) for the REE-bearing carbonates, the activities of the ions in the solution and the solubility products of the solid phases need to be known.

The solubility measurements of some of these REE-bearing carbonates have been carried out at ambient temperature (e.g., Nd-kozoite and La-hydroxylbastnäsite and Nd-hydroxylbastnäsite⁵⁹). However, there is a lack of measurements at higher temperatures due to insufficient data about the stabilities of the aqueous complexes that REE form with carbonates and OH⁻ ions. This is complicated by the great discrepancies in the experimentally calculated solubility products of some of the compounds; e.g., variations of experimentally calculated solubility products of La-Lanthanite differ in 6 orders of magnitude as a result of having used natural samples also containing other REEs (e.g., log K ranging from -29.91 to -35.45^{58,76,77}). Also, no solubility product has been yet determined for Dy-kozoite.

Our PHREEQC calculations show that when the REE-bearing solution is equilibrated with calcite at ambient temperature, it is already highly supersaturated for La-lanthanite (SI>9.0), La-hydroxylbastnäsite (SI>8.5), Nd-lanthanite (SI>10.9), Nd-kozoite (SI>5.9) and Nd-hydroxylbastnäsite (SI>7.4). The saturation indices of the REE-bearing phases are still positive even before equilibrium has been reached for calcite (e.g., SI_{calcite} = -5). Therefore, although the calculations correspond to ambient temperature conditions, they show that the formation of the observed REE carbonates is likely to occur during the very early stages of calcite dissolution. Besides, we suggest that the dissolution of a few monolayers of the calcite surface results in a fluid boundary layer that is highly supersaturated to the more stable REE-bearing phases, promoting the formation of surface precipitates. The precipitation of the newly-formed REE carbonates on the surface of calcite would enhance the dissolution rate of calcite, increasing as a consequence the growth rate of the overgrowth^{78,79}.

Epitaxial overgrowth

One of the most significant features of the interaction of calcite with the La-bearing and the Nd-bearing aqueous solutions is the oriented overgrowth of newly kozoite formed on the

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3 363 surface of calcite during the first stages of the replacement reaction (Figures 7b-d, 9 and 10).
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5 364 Despite the centripetal replacement resulted in the depletion of all calcite in the experiments,
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7 365 the very early stages of this reaction can be considered as an epitaxy. Figure 12 shows the
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9 366 projections of a (104) slice of calcite and the (001) slice of kozoite. Kozoite grows with its [100]
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11 367 elongation direction following the [010] direction of calcite substrate.
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15 368 A key parameter to understand and quantify the epitaxial relationship between the substrate
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17 369 and the overgrowth is the lattice misfit (*mf*), which is described using this expression ⁸⁰:
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$$mf(\%) = \frac{t_{[uvw]_{sub}} - t_{[uvw]_{over}}}{t_{[uvw]_{over}}} \cdot 100 \quad [1]$$

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31 373 where $t_{[uvw]_{sub}}$ and $t_{[uvw]_{over}}$ correspond to the repeating period along the matching directions
32
33 374 $[uvw]$ of the substrate (calcite) and the overgrowth (kozoite), respectively. For La-kozoite and
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35 375 calcite, the misfit between the $[010]_{cc} \parallel [100]_{koz}$ alignments is only -0.93%. This misfit is 0.72%
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37 376 in Nd-kozoite. Also, the misfit between the $[2-21]_{cc} \parallel [010]_{koz}$ is -5.71% in La-kozoite and -
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39 377 4.55% in Nd-kozoite (Figures 10 and 12). The misfit with a positive value indicates that the
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41 378 matching direction or the Nd-kozoite is very slightly contracted along that [100] direction
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43 379 compared to the unit cell of calcite. The misfits with negative values indicate an expansion of
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45 380 the unit cell of La-kozoite in the [010] and [2-21] directions compared to the unit cell of the
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47 381 calcite substrate. In the case of Nd-kozoite this expansion relative to the unit cell of calcite
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49 382 occurs in the [010] direction. All these values are clearly below the limits of the generally
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51 383 accepted values of misfit (15-20%) required for an epitaxial overgrowth to occur ⁸¹.
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55 384 One question of interest is to understand why no oriented overgrowth was observed for the
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57 385 Dy-kozoite. In the case of an epitaxial overgrowth of Dy-kozoite on calcite, the misfit values for
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59 386 the $[010]_{cc} \parallel [100]_{koz}$ and $[2-21]_{cc} \parallel [010]_{koz}$ alignments would be 3.09% and -4.12%,
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respectively. These values are close to the other two kozoite isomorphs and are a direct consequence of the small variations in their unit cell parameters and interatomic distances as a consequence of the different ionic radii of the REE³⁺ (Table 2). Therefore, although the epitaxial overgrowth of the Dy-kozoite and calcite seems theoretically possible, there are some factors inhibiting this oriented overgrowth. Our hypothesis relies on the mechanism of growth of this phase. Experiments showed two main differences in the crystallisation of Dy-kozoite compared to the La- and Nd-kozoite isomorphs: first, the growth morphology of Dy-kozoite (bow-tie aggregates made of spindle-shaped crystals; Figure 7e,f) is very different compared to La- and Nd-kozoite (Figure 7a-d), showing more single crystals at the beginning of the crystallisation process. Second, the induction time of Dy-kozoite crystallisation was much longer than the La- and Nd-bearing isomorphs. These two differences can be explained taking into account the combined effect of the ionic potential of the REE³⁺ ions⁵². The ionic potential is expressed as the charge of the cation divided by its ionic radius. All ions are solvated in solution and, in order to become part of a crystalline structure, they need to remove their solvation shells. The ionic potential of the REE³⁺ cation is proportional to its strength to hold the water molecules of the solvation shell^{52,82}. Therefore, the higher the ionic potential, the higher the energy needed to remove the solvation layer of the ion and hence the highest the temperature or the longer the time that is required for the crystal nucleation process to begin⁸³. This is a well-known variable that affects the onset of nucleation during the homogeneous crystallisation of REE-carbonates^{62,64} and Ca-Mg carbonates^{84,85}. In the case of the REE, the ionic potential of La³⁺ is 2.60, Nd³⁺ is 2.77, while the largest value belongs to Dy³⁺, 3.03. Thereby Dy³⁺ requires the highest energy (or the longest time) to desolvate before it incorporates into the lattice of the growing crystals. This longer induction time compared to the La- and Nd-bearing experiments allows more time for the release of Ca²⁺ and CO₃²⁻ ions from the surface of calcite to the aqueous solution, resulting in higher supersaturation levels for Dy-kozoite. Supersaturation is the driving force for nucleation and growth, and it dictates the mechanism of crystallisation and crystal morphology. The observed morphologies for Dy-kozoite are consistent with the growth morphologies observed in other carbonate minerals

415 during spherulitic growth processes, which require high supersaturation conditions (e.g.
416 ^{51,64,84,86,87}). These spherulitic morphologies are a consequence of a rapid (i.e., few minutes)
417 nucleation and growth of new crystals on the surface of already existing crystals via non-
418 crystallographic branching, resulting in aggregates with orientational defects, as there is no
419 structural relationship between the newly nucleated crystals and the already existing ones ⁸⁸⁻
420 ⁹¹. Compared to the La-kozoite and Nd-kozoite isomorphs, the more rapid growth kinetics of
421 Dy-kozoite and the large number of orientational defects would prevent the formation of an
422 oriented overgrowth on the surface of calcite.

423 From a wider perspective, it is essential to highlight that all the kozoite-type isomorphs
424 obtained in our experiments are members of the ancylite mineral group ⁹², a group with a large
425 chemical variability. Our experiments had targeted chemistry, and therefore all products only
426 contained a single rare earth element. Also, their Ca²⁺ content was very low (atomic % < 1.4
427 or below detection limit; Table SI-1). However, some of the members of the ancylite group
428 contain not only rare earth elements, but also divalent cations (Ca²⁺, Sr²⁺, Pb²⁺ ⁹³ like ancylite-
429 (Ce) (CeSr(CO₃)₂(OH)·H₂O)⁹⁴, ancylite-(La) (LaSr(CO₃)₂(OH)·H₂O)⁹⁵, several Ca-rich
430 calcioancylites with Ce and Nd ^{96,97}, the Pb-rich gysinite-(Nd) (PbNd(CO₃)₂(OH)·H₂O ⁹⁸, and all
431 the kozoite isomorphs ⁹². The ancylite group is, in fact, a series of complex solid-solutions
432 formed as a consequence of coupled substitutions REE³⁺ + OH⁻ = Me²⁺ + H₂O (where Me²⁺=
433 Ca²⁺, Sr²⁺, Pb²⁺) and most of the existing structural information about them has been obtained
434 from natural samples (carbonatite deposits, pegmatites of alkaline rocks) ^{92,94}, and some
435 hydrothermal synthesis experiments ^{64,66,67}. This large chemical variability of ancylite is
436 translated into variations of unit cell parameters and interatomic distances in their structures,
437 which can promote or inhibit the oriented overgrowth of these phases on calcite. Furthermore,
438 the chemistry of the substrate need also to be considered: our SEM analysis did not detect
439 any Mg (or other elements) in calcite and powder XRD patterns showed that the main Bragg
440 peak of calcite (104) corresponded to a d-spacing of 3.035 Å, consistent with a pure (non-Mg-
441 bearing) calcite ⁹⁹. However, it is important to consider that the incorporation of some elements

in the structure of calcite (e.g., Mg^{2+})¹⁰⁰ also results in changes to the unit cell dimensions and interatomic distances in this mineral, potentially affecting the described oriented overgrowth.

5. Implications for natural systems

Mineral replacement reactions are common in hydrothermal systems, including carbonatites and other REE-bearing deposits, and they reflect changes in the environmental conditions or fluid composition during the evolution of the system. The crystallisation of REE-bearing carbonates is known to be an efficient process for the immobilisation of REE, and this can happen as a consequence of fluid mixing at hydrothermal conditions, fluid-rock interactions, or changes in PT conditions, among other factors¹⁰¹. Our results have sound implications for the understanding of mineralisation reactions occurring in carbonatite deposits.

Metasomatic alteration has been identified as a common process taking place in carbonatite deposits³⁰, where replacement reactions may have played an important role in the formation of REE-bearing carbonates. Some examples are the Bayan Obo deposit (Mongolia, China), the largest REE resource in the world, which is a metamorphosed and metasomatically altered carbonatite¹⁰². Also, REE deposits in Vietnam are described as crushed zones in Paleozoic limestone affected by metasomatism¹⁰³. In many of these deposits, REE-carbonates (e.g. ancylite, bastnäsite, monazite) are considered to be of secondary origin as a consequence of mineral replacement at hydrothermal conditions. Armbrustmacher¹⁰⁴ found carbonate minerals showing textures consistent with pseudomorphic replacements produced by the interaction of hydrothermal fluids with primary minerals in carbonatites from the Wet Mountains Area (Colorado, USA). Moore et al.¹⁰⁵ found similar results in carbonate deposits in the Bear Lodge carbonatite (Wyoming, USA). However, these deposits are very complex and the REE enrichment mechanism and the genesis of many of REE-carbonate minerals are still under debate due to their complicated mineralogy, element composition and geologic history.

The main REE-bearing minerals associated with carbonatites are fluorocarbonates, like bastnäsite, parisite ($\text{Ca}(\text{REE})_2(\text{CO}_3)_3\text{F}_2$), and synchysite ($\text{CaREE}(\text{CO}_3)_2\text{F}$), as well as hydrated carbonates like ancylite ($\text{REESr}(\text{CO}_3)_2(\text{OH})\cdot\text{H}_2\text{O}$), and phosphates like monazite (REEPO_4). These carbonatite deposits are enriched by the four LREE (La, Ce, Pr, Nd). Bastnäsite is the predominant ore mineral, and calcite and dolomite are also present as gangue. Bastnäsite and the other fluorocarbonates in carbonatites are considered to form by four main processes¹⁰⁶:

(i) Direct high-temperature crystallisation from a carbonatite magma, a mechanism that has been in-depth experimentally studied by Anenburg et al.³⁵. (ii) Replacement of initially alkali REE carbonates like burbankite ($(\text{Na,Ca})_3(\text{Sr,Ba,REE})_3(\text{CO}_3)_5$), or carbocernaite ($(\text{Ca,Na})(\text{Sr,REE,Ba})(\text{CO}_3)_2$) that results in the formation of characteristic textures consisting of fine-grained assemblages of REE fluorocarbonates, monazite, barite and strontianite pseudomorphs^{35, 107, 108}. (iii) Replacement of relatively insoluble REE-bearing minerals during weathering like apatite¹⁰⁹ or synchysite¹¹⁰. (iv) Hydrothermal alteration of calcite, with the REE derived from the calcite itself, to form¹¹¹.

Our experiments would be relevant for the understanding of the hydrothermal alteration processes taking place in REE-rich carbonatites (e.g., Okorusu deposit, Nabibia¹¹¹). Results demonstrate that REE can be rapidly immobilised even at low hydrothermal conditions as hydroxycarbonates, replacing calcite, and the fluid composition can have strong control of the kinetics, polymorph selection and crystallisation pathways towards bastnäsite during replacement reactions. Hydrogeochemical modelling from high-temperature experimental data has revealed that the main ligands responsible for the transport of the REE at hydrothermal conditions are Cl^- and SO_4^{2-} as well as bicarbonate/carbonate^{38, 112}. Other ligands like F^- and OH^- have been considered to be the main ligands enabling solubility and hydrothermal transport of REE^{112, 113}. Recently Migdisov et al.³⁸ have suggested that F^- is in fact, a depositional ligand. Our study suggests that at near-neutral and alkaline conditions, the contribution of the OH^- complexes to REE immobilisation could be also significant.

The reactions followed in this study revealed multi-step crystallisation pathways to bastnäsite. The two observed intermediate phases (lanthanite and kozoite) are not abundant in carbonatites. Kozoite has been found in association with an alkali olivine basalt⁹² and also in pegmatite deposits, while lanthanite has been observed in some carbonatites¹¹⁴. Although their detection can be complicated if they are present in very low quantities, our data and previous studies⁸⁵ suggest that they may form at hydrothermal conditions and rapidly transform to bastnäsite. Furthermore, the presence of F⁻ and Sr²⁺ ions would promote the formation of the more stable fluorcarbonates and the crystallisation of ancylite.

6. Conclusions

Pseudomorphic mineral replacement of calcite by REE carbonates (La, Nd, Dy) takes place at low hydrothermal conditions (50-220 °C) and is strongly controlled by structural constraints which in turn depend on the ionic radius of the involved REE. Calcite grains are replaced from their periphery inwards and the newly formed REE-bearing carbonates follow the crystallisation sequence lanthanite [REE₂(CO₃)₃·8H₂O] → kozoite [orthorhombic REECO₃(OH)] → hydroxylbastnäsite [hexagonal REECO₃(OH)]. In La- and Nd-rich fluids this solvent-mediated transformation is initiated with the crystallisation of La- and Nd-Kozoite forming an epitaxial overgrowth on the surface of calcite (104) face due to their structural similarities. Temperature and the fluid chemistry (i.e., REE element present in the aqueous solution) control the kinetics of the replacement reaction. These replacement processes are relevant for the understanding of mineralisation reactions occurring in REE-bearing carbonatite deposits and demonstrate that REE can be rapidly immobilised as REE hydroxycarbonates even at low hydrothermal conditions, replacing calcite. Besides, our method allows the synthesis of REE carbonates with tailored structures and chemistries for the production of new innovative materials.

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8. References

- (1) Balaram, V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geosci. Front.* **2019**, 10, 1285-1303.
- (2) Haxel, G. B.; Hedrick, J. B.; Orris, G. J. *Rare Earth Element Resources: A Basis for High Technology*; Fact Sheet 087-02, U. S. Department of Interior, U. S. Geological Survey, November, 2002.
- (3) Zhou, B.; Li, Z.; Chen, C. Global Potential of Rare Earth Resources and Rare Earth Demand from Clean Technologies *Minerals* **2017**, 7, 203.
- (4) van Gosen, B.S.; Verplanck, P.L.; Long, K.R.; Gambogi, J.; Seal II, R.R. *The rare-earth elements: Vital to modern technologies and lifestyles*; Fact Sheet 2014-3078, USGS Mineral Resources Program, U. S. Department of Interior, U. S. Geological Survey, Reston, VA, November 2014.
- (5) Kim, P.; Anderko, A.; Navrotsky, A.; Riman, R. Trends in Structure and Thermodynamic Properties of Normal Rare Earth Carbonates and Rare Earth Hydroxycarbonates. *Minerals* **2018**, 8, 106.
- (6) Chakhmouradian, A. R.; Wall, F. Rare Earth Elements: Minerals, Mines, Magnets (and More) Elements **2012**, 8, 333-340.
- (7) Sovacool, B.K.; Ali, S.H.; Bazilian, M.; Radley, B.; Nemery, B.; Okatz, J.; Mulvaney, D. Sustainable minerals and metals for a low-carbon future. *Science* **2020**, 367, 30-33.
- (8) Teubler, J.; Kiefer, S.; Liedtke, C. Metals for Fuels? The Raw Material Shift by Energy-Efficient Transport Systems in Europe. *Resources* **2018**, 7, 39.

- 554 (9) Goodenough, K.M.; Wall, F.; Merriman, D. The rare Earth elements: Demand, global
555 resources, and challenges for resourcing future generations. *Nat. Resour. Res.* **2018**, 27, 201–
556 216.
- 557 (10) Wall, F.; Rollat, A.; Pell, R.S. Responsible sourcing of critical metals. *Elements* **2017**, 13,
558 313–318.
- 559 (11) Nassar, N.T.; Du, X.; Graedel, T.E. Criticality of the rare earth elements. *J. Ind. Ecol.* **2015**,
560 19, 1044-1054.
- 561 (12) Goonan, T.G. *Rare Earth Elements – End Use and Recyclability*; U. S. Department of
562 Interior, U.S. Geological Survey, Scientific Investigations Report 2011-5094, Reston, Virginia,
563 2011.
- 564 (13) *New Circular Vision for Electronics - Time for a Global Reboot*. International
565 Telecommunication Union, Platform for Accelerating the Circular Economy; World Economic
566 Forum; January 2019.
- 567 (14) FACT SHEET: MANAGEMENT OF ELECTRONIC WASTE IN THE UNITED STATES
568 2008; National Service Center for Environmental Publications (NSCEP), U.S. Environmental
569 Protection Agency. [online] 2007, EPA530-F-08-014.
570 <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1000ZT5.txt> (accessed Nov 27, 2020).
- 571 (15) Menéndez, I.; Campeny, M.; Quevedo-González, L.; Mangas, J.; Llovet, X.; Tauler, E.;
572 Barrón, V.; Torrent, J.; Méndez-Ramos, J. Distribution of REE-bearing minerals in felsic
573 magmatic rocks and paleosols from Gran Canaria, Spain: Intraplate oceanic islands as a new
574 example of potential, non-conventional sources of rare-earth elements. *J. Geochem. Explor.*
575 **2019**, 204, 270-288.

- (16) Palaparthi, J.; Chakrabarti, R.; Banerjee, S.; Guin, R.; Ghosal, S.; Agrahari, S.; Sengupta, D. Economically viable rare earth element deposits along beach placers of Andhra Pradesh, eastern coast of India. *Arab. J. Geosci.* **2017**, 10, 201.
- (17) Scott, C.; Kolker, A. *Rare earth elements in coal and coal fly ash*; Fact Sheet 2019-3048, U. S. Department of Interior, U. S. Geological Survey, September 2019.
- (18) Emsbo, P.; McLaughlin, P. I.; Breit, G. N.; du Bray, E. A.; Koenig, A. E. Rare earth elements in sedimentary phosphate deposits: Solution to the global REE crisis? *Gondwana Res.* **2015**, 27, 776-785.
- (19) Broom-Fendley, S.; Brady, A. E.; Wall, F.; Gunn, G.; Dawes, W. REE minerals at the Songwe Hill Carbonatite, Malawi: HREE-enrichment in late-stage apatite. *Ore Geol. Rev.* **2017**, 81, 23-41.
- (20) Croll, R.; Swinden, S.; Hall, M.; Brown, C.; Beer, G.; Scheepers, J.; Redellinghuys, T.; Wild, G.; Trusler, G. *Mkango Resources Limited, Songwe REE Project, Malawi*; NI 43-101 Pre-feasibility Report by MSA Group (Pty) Ltd. for Mkango Resources Limited, November 2014.
- (21) Owens, C. L.; Nash, G. R.; Hadler, K.; Fitzpatrick, R. S.; Anderson, C. G.; Wall, F. Apatite enrichment by rare earth elements: A review of the effects of surface properties. *Colloid Interface Sci.* **2019**, 265, 14-28.
- (22) Hein, J.R.; Koschinsky, A.; Kuhn, T. Deep-ocean polymetallic nodules as a resource for critical materials. *Nat. Rev. Earth Environ.* **2020**, 1, 158–169.
- (23) Zhang, Z.; Du, Y.; Gao, L.; Zhang, Y.; Shi, G.; Liu, C.; Zhang, P.; Duan, X. Enrichment of REEs in polymetallic nodules and crusts and its potential for exploitation', *J. Rare Earths* **2012**, 30, 621-626.

- 598 (24) Baturin, G. N.; Yushina, I. G. Rare earth elements in phosphate-ferromanganese crusts
599 on Pacific Seamounts. *Lithol. Miner. Resou.* **2007**, 42, 101-117.
- 600 (25) Takaya, Y.; Yasukawa, K.; Kawasaki, T.; Fujinaga, K.; Ohta, J.; Usui, Y.; Nakamura, K.;
601 Kimura, J.-I.; Chang, Q.; Hamada, M.; Dodbiba, G.; Nozaki, T.; Iijima, K.; Morisawa, T.;
602 Kuwahara, T.; Ishida, Y.; Ichimura, T.; Kitazume, M.; Fujita, T.; Kato, Y. The tremendous
603 potential of deep-sea mud as a source of rare-earth elements. *Sci. Rep.* **2018**, 8, 5763.
- 604 (26) McLeod, C.L.; Krekeler, M.P.S. Sources of Extraterrestrial Rare Earth Elements: To the
605 Moon and Beyond. *Resources* **2017**, 6, 40.
- 606 (27) *Mineral and Commodity Summaries: Rare Earths*. U. S. Department of Interior, U.S.
607 Geological Survey, Reston, Virginia, 2018.
- 608 (28) Haque, M.; Hughes, A.; Lim, S.; Vernon, C. Rare earth elements: Overview of mining,
609 mineralogy, uses, sustainability and environmental impact. *Resources* **2014**, 3, 614-635.
- 610 (29) Leskelä, M.; Niinistö, L. Chapter 56 Inorganic complex compounds. *Handbook on the*
611 *Physics and Chemistry of Rare Earths*. Elsevier. **1986**; 8, 203 – 234.
- 612 (30) Wall, F. Rare earth elements. *Critical Metals Handbook*; Gunn G., Eds.; American
613 Geophysical Union. John Wiley & Sons, Ltd., 2014; pp. 454.
- 614 (31) Orris, G.; Grauch, R. *Rare Earth Element Mines, Deposits, and Occurrences*; U. S.
615 Department of Interior, U.S. Geological Survey, Open-File Report 02-189, 2002.
- 616 (32) *Mineral and Commodity Summaries: Rare Earths*; U. S. Department of Interior, U.S.
617 Geological Survey, Reston, Virginia, 2019.
- 618 (33) Amores-Casals, S.; Melgarejo, J.-C.; Bambi, A.; Gonçalves, A.O.; Morais, E.A.; Manuel,
619 J.; Neto, A.B.; Costanzo, A.; Martí Molist, J. Lamprophyre-Carbonatite Magma Mingling and

- 620 Subsolidus Processes as Key Controls on Critical Element Concentration in Carbonatites—
621 The Bonga Complex (Angola). *Minerals*, **2019**, 9, 601.
- 622 (34) Edahbi, M.; Plante, B.; Benzaazoua, M.; Kormos, L.; Pelletier, M. Rare Earth Elements
623 (La, Ce, Pr, Nd, and Sm) from a Carbonatite Deposit: Mineralogical Characterization and
624 Geochemical Behavior. *Minerals* **2018**, 8, 55.
- 625 (35) Anenburg, M.; Mavrogenes, J.A.; Frigo, C.; Wall, F. Rare earth element mobility in and
626 around carbonatites controlled by sodium, potassium, and silica. *Sci. Adv.* **2020**, 6, eabb6570.
- 627 (36) Williams-Jones, A.E.; Migdisov, A.A.; Samson, I.M. Hydrothermal mobilisation of the rare
628 earth elements – a tale of "Ceria" and "Yttria". *Elements* **2012**, 8, 355–360.
- 629 (37) Migdisov, A.A.; Williams-Jones, A.E. Hydrothermal transport and deposition of the rare
630 earth elements by fluorine-bearing aqueous liquids. *Miner. Depos.* **2014**, 49, 987–997.
- 631 (38) Migdisov, A.; Williams-Jones, A.E.; Brugger, J.; Caporuscio, F.A. Hydrothermal transport,
632 deposition, and fractionation of the REE: Experimental data and thermodynamic calculations.
633 *Chem. Geol.* **2016**, 439, 13–42.
- 634 (39) Migdisov, A.; Guo, X.; Nisbet, H.; Xu, H.; Williams-Jones, A.E. Fractionation of REE, U,
635 and Th in natural ore-forming hydrothermal systems: Thermodynamic modeling. *J. Chem.*
636 *Thermodyn.* **2019**, 128, 305–319.
- 637 (40) Lakshtanov, L.Z.; Stipp, S.L.S. Experimental study of europium (III) coprecipitation with
638 calcite. *Geochim. Cosmochim. Acta* **2004**, 68, 819–827.
- 639 (41) Gabitov, R.I.; Sadekov, A.; Migdisov, A. REE Incorporation into Calcite Individual Crystals
640 as One Time Spike Addition. *Minerals*, **2017**, 7, 204.
- 641 (42) Terakado, Y.; Masuda, A. The coprecipitation of rare-earth Elements with calcite and
642 aragonite. *Chem. Geol.* **1988**, 69, 103–110.

- (43) Zhong, S.; Mucci, A. Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25 °C and 1 atm, and high dissolved REE concentrations. *Geochim. Cosmochim. Acta* **1995**, 59, 443–453.
- (44) Curti, E.; Kulik, D.A.; Tits, J. Solid solutions of trace Eu (III) in calcite: thermodynamic evaluation of experimental data over a wide range of pH and pCO₂. *Geochim. Cosmochim. Acta* **2005**, 69, 1721–1737.
- (45) Tanaka, K.; Kawabe, I. REE abundances in ancient seawater inferred from marine limestone and experimental REE partition coefficients between calcite and aqueous solution. *Geochem. J.* **2006**, 40, 425–435.
- (46) Vodyanitskii, Y.N. Geochemical fractionation of lanthanides in soils and rocks: a review of publications. *Eurasian Soil Sci.* **2012**, 45, 56–67.
- (47) Toyama, K.; Terakado, Y. Experimental study of rare earth element partitioning between calcite and sodium chloride solution at room temperature and pressure. *Geochem. J.* **2014**, 48, 463–477.
- (48) Voigt, M.; Mavromatis, V.; Oelkers, E.H. The experimental determination of REE partition coefficients in the water-calcite system. *Chem. Geol.* **2017**, 462, 30–43.
- (49) Chebotarev, D.A.; Veksler, I.V.; Wohlgemuth-Ueberwasser, C.; Doroshkevich, A.G.; Koch-Müller, M. Experimental study of trace element distribution between calcite, fluorite and carbonatitic melt in the system CaCO₃ + CaF₂ + Na₂CO₃ ± Ca₃(PO₄)₂ at 100 MPa. *Contrib. Mineral. Petrol.* **2019**, 174, 4.
- (50) Möller, P.; De Lucia, M. Incorporation of Rare Earths and Yttrium in Calcite: A Critical Re-evaluation. *Aquat Geochem*, **2020**, 26, 89–117.

- 665 (51) Rodriguez-Blanco, J.D.; Sand, K.K.; Benning, L.G. Chapter 5 ACC and vaterite as
666 metastable intermediates in the solution based crystallization of CaCO_3 . *New Perspectives on*
667 *Mineral Nucleation and Growth*. van Driessche, A., Kellermeier, M., Benning, L.G., Gebauer,
668 D., Eds.; Springer International Publishing. Switzerland. 2017.
- 669 (52) Railsback, L.B. An earth scientist's periodic table of the elements and their ions'. *Geology*
670 **2003**, 31, 737–740.
- 671 (53) Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic
672 distances in halides and chalcogenides. *Acta Crystallogr. A*. **1976**, 32, 751–767.
- 673 (54) Weng, Z.; Jowitt, S.M.; Mudd, G.M.; Haque, N. A detailed assessment of global rare earth
674 element resources: opportunities and challenges. *Econ. Geol.* **2015**, 110, 1925–1952.
- 675 (55) Bauer, D.; Diamond, D.; Li, J.; Sandalow, D.; Telleen, P.; Wanner, B. Technical Report.
676 *U.S. Department of Energy Critical Materials Strategy*; United States, December 2010.
- 677 (56) Coelho, A. A. *TOPAS Academic: General Profile and Structure Analysis Software for*
678 *Powder Diffraction Data*. 5th ed.; Bruker AXS: Karlsruhe, Germany, 2012.
- 679 (57) Parkhurst, D. L.; Appelo, C.A.J. *Water-Resources Investigations Report Report:*
680 *PHREEQC (Version 2)-A Computer Program for Speciation, Batch-Reaction, One Dimensional*
681 *Transport, and Inverse Geochemical Calculations*; U. S. Department of Interior, U. S.
682 Geological Survey; Denver, Colorado, 1999.
- 683 (58) Essington, M.E.; Mattigod, S.V. Lanthanide Solid Phase Speciation. *Soil Sci. Soc. Am. J.*
684 **1985**, 49, 1387-1393.
- 685 (59) Voigt, M.; Rodriguez-Blanco, J.D.; Vallina, B.; Benning, L.G.; Oelkers, E.H. An
686 experimental study of hydroxylbastnasite solubility in aqueous solutions at 25 °C. *Chem. Geol.*
687 **2016**, 430, 70-77.

- 688 (60) Plummer, L. N.; Busenberg, E. The Solubilities of calcite, aragonite and vaterite in CO₂-
689 H₂O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system
690 CaCO₃-CO₂-H₂O. *Geochim. Cosmochim.* **1982**, 46, 1011-1040.
- 691 (61) Atencio, D.; Bevins, R.; Fleischer, M.; Terry Williams, C.; Williams, P. Revision of the
692 lanthanite group and new data for specimens from Bastnäs, Sweden, and Bethlehem, USA.
693 *Mineral. Mag.* **1989**, 53, 639-642.
- 694 (62) Rodriguez-Blanco, J. D.; Vallina, B.; Blanco, J. A.; Benning, L. G. The role of REE³⁺ in the
695 crystallization of lanthanites. *Mineral. Mag.* **2014**, 78, 1373-1380.
- 696 (63) Shinn, D. B.; Eick, H. A. Crystal structure of lanthanum carbonate octahydrate. *Inorg.*
697 *Chem.* **1968**, 7, 1340-1345.
- 698 (64) Vallina, B.; Rodriguez-Blanco, J. D.; Brown, A. P.; Blanco, J. A.; Benning, L. G. The role
699 of amorphous precursors in the crystallization of La and Nd carbonates. *Nanoscale*, **2015**, 7,
700 12166-12179.
- 701 (65) Doert, T.; Rademacher, O.; Getzschmann, J. Crystal structure of dysprosium hydroxide
702 carbonate DyOHCO₃. *Z. Kristallogr. NCS.* **1999**, 214, 11–12.
- 703 (66) Tahara, T.; Nakai, I.; Miyawaki, R.; Matsubara, S. Crystal chemistry of RE(CO₃)OH. *Z.*
704 *Kristallogr. Cryst. Mater.* **2007**, 222, 326-334.
- 705 (67) Vallina, B.; Rodriguez-Blanco, J. D.; Brown, A. P.; Blanco, J. A.; Benning, L. G.
706 Amorphous dysprosium carbonate: Characterization, stability, and crystallization pathways. *J.*
707 *Nanopart. Res.* **2013**, 15, 1438.
- 708 (68) Hsu, L.C. Synthesis and stability of bastnaesites in a part of the system (Ce,Ln)-F-H-C-
709 O. *Mineral. Petrol.* **1992**, 47, 87–101.

- (69) Michiba, K.; Tahara, T.; Nakai, I.; Miyawaki, R.; Matsubara, S. Crystal structure of hexagonal RE(CO₃)OH. *Z. Kristallogr. Cryst. Mater.* **2011**, 226, 518-530.
- (70) Michiba, K.; Miyawaki, R.; Minakawa, T.; Terada, Y.; Nakai, I.; Matsubara, S. Crystal structure of hydroxylbastnäsite-(Ce) from Kamihouri, Miyazaki Prefecture, Japan, *J. Mineral. Petrol. Sci.* **2013**, 108, 326-334.
- (71) Williams-Jones, A. E.; Wood, S. A. A preliminary petrogenetic grid for REE fluorocarbonates and associated minerals. *Geochim. Cosmochim. Acta* **1992**, 56, 725-738.
- (72) Meldrum, F.C.; Cölfen, H. Controlling Mineral Morphologies and Structures in Biological and Synthetic Systems. *Chem. Rev.* **2008**, 108, 4332.
- (73) Ostwald, W. Zeitschrift fuer Physikalische Chemie. *Z. Phys. Chem.* **1897**, 22, 289-330.
- (74) Bots, P.; Benning, L.G.; Rodriguez-Blanco, J.D.; Roncal-Herrero, T.; Shaw, S. Mechanistic insights into the crystallization of amorphous calcium carbonate to vaterite. *Cryst. Growth Des.* **2012**, 12, 3806-3814.
- (75) Van Driessche, A.E.S.; Benning, L.G.; Rodriguez-Blanco, J.D.; Ossorio, M.; Bots, P.; García-Ruiz, J.M. The Role and Implications of Bassanite as a Stable Precursor Phase to Gypsum Precipitation. *Science*, **2012**, 336, 69-72.
- (76) Firsching, F.H.; Mohammadzadei, J. Solubility products of the rare-earth carbonates. *J. Chem. Eng. Data* **1986**, 31, 40-42.
- (77) Ciavatta, L.; Ferri, D.; Grenthe, I.; Salvatore, F.; Spahiu, K. Studies on Metal Carbonate Equilibria. 3. The Lanthanum(III) Carbonate Complexes in Aqueous Perchlorate Media. *Acta Chem. Scand.* **1981**, 35a, 403-413.

- 731 (78) Anderson, J.G.; Doraiswamy, L.K.; Larson, M.A. Microphase-assisted 'autocatalysis' in a
732 solid-liquid reaction with a precipitating product — I. Theory. *Chem. Eng. Sci.* **1998**, 53, 2451-
733 2458.
- 734 (79) Anderson, J.G.; Larson, M.A.; Doraiswamy, L.K. Microphase-assisted "autocatalysis" in a
735 solid-liquid reaction with a precipitating product — II. Experimental. *Chem. Eng. Sci.* **1998**, 53,
736 2459-2468.
- 737 (80) Van Der Merwe, J.H. The role of lattice misfit in epitaxy. *Crit. Rev. Solid State Mater. Sci.*
738 **1978**, 7, 209-231.
- 739 (81) Walton, A. G. Nucleation in Liquids and Solutions. *Nucleation*; Zettlemoyer, A. C., Eds.;
740 Dekker: NewYork, 1969; pp. 225–307.
- 741 (82) Cartledge, G.H. Studies on the periodic system. I. The ionic potential as a periodic
742 function', *J. Am. Chem. Soc.* **1928**, 50, 2855–2863.
- 743 (83) Cartledge, G.H. Studies on the periodic system. li. The ionic potential and related
744 properties. *J. Am. Chem. Soc.* **1928**, 50, 2863–2872.
- 745 (84) Rodriguez-Blanco, J.D.; Shaw, S.; Bots P.; Roncal-Herrero, T.; Benning, L.G. The role of
746 Mg in the crystallisation of monohydrocalcite. *Geochim. Cosmochim. Acta* **2014**, 127, 204-220.
- 747 (85) Rodriguez-Blanco, J.D.; Shaw, S.; Benning, L.G. A route for the direct crystallization of
748 dolomite. *Am. Mineral.* **2015**, 100, 1172-1181.
- 749 (86) Vallina, B.; Rodriguez-Blanco, J. D.; Blanco, J. A.; Benning, L. G. The effect of heating on
750 the morphology of crystalline neodymium hydroxycarbonate, NdCO₃OH. *Mineral. Mag.* **2014**,
751 78, 1391-1397.

- (87) Sand, K.K.; Rodriguez-Blanco, J.D.; Makovicky, E.; Benning, L.G.; Stipp, S. Crystallization of CaCO_3 in water-ethanol mixtures: spherulitic growth, polymorph stabilization and morphology change. *Cryst. Growth Des.* **2012**, 12, 842-853.
- (88) Gránásy, L.; Pusztai, T.; Tegze, G.; Warren, J.A.; Douglas, J.F. Growth and form of spherulites. *Phys. Rev. E. Stat. Nonlin. Soft Matter. Phys.* **2005**, 72, 011605.
- (89) Beck, R.; Andreassen, J.P. Spherulitic Growth of Calcium Carbonate. *Cryst. Growth Des.* **2010**, 10, 2934–2947.
- (90) Andreassen, J.P.; Flaten, E.; Beck, R.; Lewis, A.E. Investigations of spherulitic growth in industrial crystallization. *Chem. Eng. Res. Des.* **2010**, 88, 1163-1168.
- (91) Shtukenberg, A.G.; Punin, Y.O.; Gunn E.; Kahr B. Spherulites. *Chem. Rev.* **2012**, 112, 1805-1838.
- (92) Miyawaki, R.; Matsubara, S.; Yokoyama, K.; Takeuchi, K.; Terada, Y.; Nakai, I. Kozoite-(Nd), $\text{Nd}(\text{CO}_3)(\text{OH})$, a new mineral in an alkali olivine basalt from Hizen-cho, Saga Prefecture, Japan. *Am. Mineral.* **2000**, 85, 1076-1081.
- (93) Belovitskaya, Y.V.; Pekov, I.V.; Gobechiya, E.R.; Yamnova, N.A.; Kabalov, Y.K.; Chukanov, N.V.; Schneider, J. Crystal structures of two ancylite modifications. *Crystallogr. Rep.* **2002**, 47, 223–228.
- (94) Dal Negro, A.; Rossi, G.; Tazzoli, V. The crystal structure of ancylite, $(\text{RE})_x(\text{Ca}, \text{Sr})_{2-x}(\text{CO}_3)_2(\text{OH})_x(2-x)\text{H}_2\text{O}$. *Am. Mineral.* **1975**, 60, 280-284.
- (95) Yakovenchuk, V.N.; Men'shikov, Y.P.; Pakhomovskii, Y.A.; Ivanyuk G.Y. Ancylite-(La), $\text{Sr}(\text{La}, \text{Ce})(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$ – a new carbonate from a hydrothermal vein at Kukisvumchorr Mountain (Khibiny massif) and its comparison with ancylite-(Ce). *Zap. Vses. Mineral. Obshch.* **1997**, 126, 96–108.

- 775 (96) Larsen, A.O.; Gault, RA. Calcio-ancylite-(Ce) from syenite pegmatite at Tvedalen, Oslo
776 Region, Norway', *Neues Jahrb. für Mineral. Monatshefte* **2002**, 9, 411-423.
- 777 (97) Orlandi, P.; Pasero, M.; Vezzalini, G. Calcio-ancylite-(Nd), a new REE-carbonate from
778 Baveno, Italy', *Eur. J. Mineral.* **1990**, 2, 413-418.
- 779 (98) Sarp, H.; Bertrand, J. Gysinite, $\text{Pb}(\text{Nd}, \text{La})(\text{CO}_3)_2(\text{OH}) \cdot \text{H}_2\text{O}$, a new lead, rare-earth
780 carbonate from Shinkolobwe, Shaba, Zaïre and its relationship to ancylite. *Am. Mineral.* **1985**,
781 70, 1314-1317.
- 782 (99) Arvidson, R.S.; Mackenzie, F.T. The dolomite problem: Control of precipitation kinetics by
783 temperature and saturation state. *Am. J. Sci.* **1999**, 299, 257-288.
- 784 (100) Paquette, J.; Reeder, R.J. Single-crystal X-ray structure refinements of two biogenic
785 magnesian calcite crystals. *Am. Mineral.*, **1990**, 75, 1151-1158.
- 786 (101) Jones, A.P.; Wall, F.; Williams, C.T. Formation of Rare Earth Minerals in Hydrothermal
787 Systems. In *Rare Earth Minerals: Chemistry, Origin and Ore Deposits*; The Mineralogical
788 Society Series: Springer Netherlands, 1996.
- 789 (102) Chao, E.C.T.; Back, J.M.; Minkin, J.A.; Yinchen, R. Host-rock controlled epigenetic,
790 hydrothermal metasomatic origin of the Bayan Obo REEFe-Nb ore deposit, Inner Mongolia,
791 P.R.C. *Appl. Geochemistry* **1992**, 7, 443-458.
- 792 (103) Premoli, C. Vietnamese metallic mineral resources. *Eng. Min. J.* **1989**, 190, 31-35.
- 793 (104) Armbrustmacher, T. J. Replacement and primary magmatic carbonatites from the Wet
794 Mountains area, Fremont and Custer counties, Colorado. *Econ. Geol.* **1979**, 74, 888-901.
- 795 (105) Moore, M.; Chakhmouradian, A. R.; Mariano, A. N.; Sidhu, R. Evolution of rare-earth
796 mineralization in the Bear Lodge carbonatite, Wyoming: Mineralogical and isotopic evidence.
797 *Ore Geol. Rev.* **2015**, 60, 499-521.

- 798 (106) Verplanck, P.L.; Mariano, A.N.; Mariano Jr., A. Rare earth element ore geology of
799 carbonatites. In *Rare Earth and Critical Elements in Ore Deposits*; Verplanck, P.L., Hitzman,
800 M.W., Eds.; Society of Economic Geologists, Littleton, Colorado, USA. 2016; Vol. 18, pp 5–
801 32.
- 802 (107) Andersen, A.K.; Clark, J.G.; Larson, P.B.; Donovan, J.J. REE fractionation, mineral
803 speciation, and supergene enrichment of the Bear Lodge carbonatites, Wyoming, USA. *Ore*
804 *Geol. Rev.* **2017**, 89, 780–807.
- 805 (108) Kozlov, E.; Fomina, E.; Sidorov, M.; Shilovskikh, V.; Bocharov, V.; Chernyavsky, A.;
806 Huber, M. The Petyayan-Vara carbonatite-hosted rare earth deposit (Vuoriyarvi, NW Russia):
807 mineralogy and geochemistry. *Minerals* **2020**, 10, 73.
- 808 (109) Anenburg, M.; Burnham, A.D.; Mavrogenes, J.A. REE redistribution textures in altered
809 fluorapatite: Symplectites, veins and phosphate-silicate-carbonate assemblages from the
810 Nolans Bore P-REE-Th deposit, NT, Australia. *Can. Mineral.* **2018**, 56, 331–354.
- 811 (110) Witt, W.K.; Hammond, D.P.; Hughes, M. Geology of the Ngualla carbonatite complex,
812 Tanzania, and origin of the Weathered Bastnaesite Zone REE ore. *Ore Geol. Rev.* **2019**, 105,
813 28–54.
- 814 (111) Cangelosi, D.; Broom-Fendley, S.; Banks, D.; Morgan, D.; Yardley, B. Light rare earth
815 element redistribution during hydrothermal alteration at the Okorusu carbonatite complex,
816 Namibia. *Mineral. Mag.* **2020**, 84, 49–64.
- 817 (112) Perry, E.P.; Gysi, A.P. Rare Earth Elements in Mineral Deposits: Speciation
818 in Hydrothermal Fluids and Partitioning in Calcite. *Geofluids* **2018**, 1–19.
- 819 (113) Banks, D.; Yardley, B.; Campbell, A.; Jarvis, K. REE composition of an aqueous
820 magmatic fluid: a fluid inclusion study from the Capitan Pluton, New Mexico, U.S.A. *Chem.*
821 *Geol.* **1994**, 113, 259–272.

1
2
3 822 (114) Zaitsev, A.N.; Wall, F.; Le Bas, M.J. REE-Sr-Ba minerals from the Khibina carbonatites,
4
5 823 Kola Peninsula, Russia: their mineralogy, paragenesis and evolution. *Mineral. Mag.* **1998**, 62,
6
7 824 225-250.

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17 827 **9. Figure Captions**

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23 829 **Figure 1:** Powder XRD patterns of La-lanthanite with calcite, La-kozoite and La-
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25 hydroxylbastnäsite obtained as final products of the experiments carried out at 21, 50 and 220
26 830 °C, respectively.
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31 832 **Figure 2:** Powder XRD patterns of Nd-lanthanite with calcite, Nd-kozoite and Nd-
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33 hydroxylbastnäsite, obtained as final products of the experiments carried out at 21, 50 and 220
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35 834 °C, respectively.

38 835 **Figure 3:** Powder XRD pattern of Dy-kozoite obtained as the final product of the experiment
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41 836 carried out at 95 °C.

44 837 **Figure 4:** Powder XRD patterns showing the full replacement of calcite by Nd-kozoite at 50
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46 838 °C. (a) 0 days, (b) 0.75 days h, (c) 1.75 days, and (d) 11 days.

49 839 **Figure 5.:** SEM micrographs of the surface of calcite grains exposed to La-bearing solutions
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51 840 at 95 °C. (a) After 0.75 days of reaction, some crystals of La-kozoite are scattered on the
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53 841 surface of calcite. (b) La-kozoite crystals quickly cover the available surface after 1.75 days.
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55 842 (c) The full calcite grain is replaced by La-kozoite after 13 days.

Figure 6.: SEM micrographs showing: (a) The surface of calcite completely covered by La-lanthanite after 42 days of reaction at 21 °C (b). Detail of La-lanthanite crystal aggregates. (c) Scattered crystals of Nd-lanthanite on the surface of calcite after 145 days of reaction at 21 °C. (d) Morphology of Nd-lanthanite single crystals.

Figure 7: SEM micrographs of (a) newly-formed La-kozoite with random orientation of the surface of calcite; (b) La-kozoite with some individual crystals oriented on calcite; (c) Nd-kozoite oriented on the (104) surface of calcite; (d) detail of single crystals of Nd-kozoite oriented on the (104) surface calcite; (e) Dy-kozoite overgrowth on calcite (f) Dy-kozoite with prismatic shapes crystallised on surface of calcite at 220 °C.

Figure 8: SEM images of (a) newly-formed La-hydroxylbastnäsite and (b) Nd-hydroxylbastnäsite replacing calcite formed at 220 °C.

Figure 9: SEM micrographs showing oriented Nd-kozoite grown onto the (104) surface of calcite. (a) Overall view of a calcite grain showing the early stages of development of Nd-kozoite; (b) detail of the calcite surface showing Nd-kozoite crystals attached to the calcite surface. (d) Calcite surface completely covered by Nd-kozoite crystals.

Figure 10: Schematic diagram showing the epitaxial relationship between kozoite and calcite crystals.

Figure 11: Reaction pathways towards bastnäsite observed during the replacement of calcite by rare earth carbonates. Continuous lines correspond to observed reactions, while dashed lines correspond to expected reactions that were not observed in our experiments. Each line shows the temperature at which the reaction takes place.

Figure 12: Projection of the crystal structures of a (104) slice of calcite and a (001) slice of kozoite showing the main directions of epitaxy and the repeating periods.

Table 1. Experimental conditions with identities and morphologies of the solid rare earth carbonate phases formed during the interaction of calcite with rare earth bearing aqueous solutions. Abbreviations Lan, Koz and HB, stand for lanthanite, kozoite and hydroxylbastnäsite, respectively.

La system Molar ratio Ca/La ~ 1					Nd system Molar ratio Ca/Nd ~ 1			Dy system Molar ratio Ca/Dy ~ 1		
T (°C)	Time (days)	% calcite consumed	Phase formed	Morphology	% calcite consumed	Phase formed	Morphology	% calcite consumed	Phase formed	Morphology
21	7	0	--	--	0	--	--	0	--	--
	14	6	Lan	Thin platy crystals						
	21	8								
	42	10								
	145	15	2	Lan	Thin platy crystals	<1	Koz	Fibrous aggregates with some branching		
50	1	0	--	--	0	--	--	0	--	--
	2	0			8					
	5	33	Koz	Small prisms	12	Koz	Spindle, some oriented, more elongated			
	7	55		52						
	9	89		88						
	14	99		96						
	20	100		100						
	28									
60	Koz	Fibrous aggregates with some branching								
94										
100										
95	0.25	0	--	--	0	--	--	0	--	Fibrous aggregates with some branching
	0.75	3			2			1		
	1	9			9			2		
	1.5	11			12			7		
	1.75	14			16			12		
	11	100	100	> 99% Koz < 1% HB						
	13									
	154									
	> 98% Koz < 2% HB									
160	1	100	Koz	Elongated prisms	100	Koz	Spindle, some oriented, more elongated	100	Koz	Tabular and prismatic crystals
	2		Koz							
	5		16 % Koz 84 % HB	Elongated prisms (Koz) + triangular prisms (HB)						
	7		20% Koz 80% HB							
	14		20% Koz							

			80 % HB									
	21		< 1% Koz > 99% HB	Triangular prisms								
	28		100 % HB									
220	1	100	HB	Triangular prisms (HB)		100	Koz	Spindle, elongated (Koz) + rectangular prisms (HB)		100	Koz	Tabular and prismatic crystals
	5						55% Koz 45% HB					
	7						HB					

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Table 2. Unit cell parameters of original calcite and the La-, Nd- and Dy-bearing carbonate minerals crystallised in the experiments.

Mineral	Space group	La-system	Nd-system	Dy-system
Calcite	$R\bar{3}c$ $a = b = 4.989 \text{ \AA}$ $c = 17.062 \text{ \AA}$ $\text{Vol} = 367.78 \text{ \AA}^3$	–	–	–
Lanthanite	Pbnb	$a = 8.978(2) \text{ \AA}$ $b = 9.558(2) \text{ \AA}$ $c = 17.035(4) \text{ \AA}$ $\text{Vol} = 1461.8 \text{ \AA}^3$	$a = 8.893(2) \text{ \AA}$ $b = 9.440(3) \text{ \AA}$ $c = 16.924(5) \text{ \AA}$ $\text{Vol} = 1420.7 \text{ \AA}^3$	–
Kozoite	Pmcn	$a = 5.036(2) \text{ \AA}$ $b = 8.587(3) \text{ \AA}$ $c = 7.403(2) \text{ \AA}$ $\text{Vol} = 320.1 \text{ \AA}^3$	$a = 4.953(1) \text{ \AA}$ $b = 8.482(2) \text{ \AA}$ $c = 7.221(1) \text{ \AA}$ $\text{Vol} = 303.3 \text{ \AA}^3$	$a = 4.839(6) \text{ \AA}$ $b = 8.444(4) \text{ \AA}$ $c = 6.984(1) \text{ \AA}$ $\text{Vol} = 285.3 \text{ \AA}^3$
hydroxylbastnäsite	$P\bar{6}2c$	$a = 12.629(8) \text{ \AA}$ $c = 10.046(3) \text{ \AA}$ $\text{Vol} = 1386.4 \text{ \AA}^3$	$a = 12.336(2) \text{ \AA}$ $c = 9.918(1) \text{ \AA}$ $\text{Vol} = 1309.0 \text{ \AA}^3$	–

For Table of Contents Use Only

Reaction pathways towards the formation of bastnäsite: replacement of calcite by rare earth carbonates.

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Synopsis

The interaction of rare earth bearing (La, Nd, Dy) fluids with calcite at ambient and hydrothermal conditions (25–220 °C) results in the solvent-mediated surface precipitation and subsequent pseudomorphic mineral replacement of calcite by rare earth carbonates, following the crystallisation sequence lanthanite $[\text{REE}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}] \rightarrow$ kozoite [orthorhombic $\text{REECO}_3(\text{OH})$] $\rightarrow$ hydroxylbastnäsite [hexagonal $\text{REECO}_3(\text{OH})$]. Kozoite grows oriented onto the calcite surface, forming an epitaxy.

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917 **Description of Supporting Information**

918 Supporting information includes (1) optical images of calcite crystals after reaction with a Nd-
919 bearing solution, and (2) Ca content (atomic%) in REE-bearing carbonates determined with
920 energy dispersive spectroscopy (EDS) analysis using scanning electron microscopy (SEM) .
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Figure 1: Powder XRD patterns of La-lanthanite with calcite, La-kozoite and La- hydroxylbastnäsite obtained as final products of the experiments carried out at 21, 50 and 220 °C, respectively.

84x56mm (1200 x 1200 DPI)

Figure 2: Powder XRD patterns of Nd-lanthanite with calcite, Nd-kozoite and Nd-hydroxylbastnäsite, obtained as final products of the experiments carried out at 21, 50 and 220 °C, respectively.

84x52mm (1200 x 1200 DPI)

Figure 3: Powder XRD pattern of Dy-kozoite obtained as the final product of the experiment carried out at 95 °C.

84x56mm (1200 x 1200 DPI)

Figure 4: Powder XRD patterns showing the full replacement of calcite by Nd-kozoite at 50 °C. (a) 0 days, (b) 0.75 days h, (c) 1.75 days, and (d) 11 days.

84x141mm (1200 x 1200 DPI)

Figure 5.: SEM micrographs of the surface of calcite grains exposed to La-bearing solutions at 95 °C. (a) After 0.75 days of reaction, some crystals of kozoite-(La) are scattered on the surface of calcite. (b) Kozoite-(La) crystals quickly cover the available surface after 1.75 days. (c) The full calcite grain is replaced by Kozoite-(La) after 13 days.

84x191mm (600 x 600 DPI)

Figure 6.: SEM micrographs showing: (a) The surface of calcite completely covered by lanthanite-(La) after 42 days of reaction (b). Detail of lanthanite-(La) crystal aggregates. (c) Scattered crystals of lanthanite-(Nd) on the surface of calcite after 145 days of reaction. (d) Morphology of lanthanite-(Nd) single crystals.

84x63mm (600 x 600 DPI)

Figure 7: SEM micrographs of (a) newly-formed kozoite-(La) with random orientation of the surface of calcite; (b) kozoite-(La) with some individual crystals oriented on calcite; (c) kozoite-(Nd) oriented on the (104) surface of calcite; (d) detail of single crystals of kozoite-(Nd) oriented on the (104) surface calcite; (e) DyCO₃(OH) overgrowth on calcite (f) DyCO₃(OH) with prismatic shapes crystallised on surface of calcite at 220 °C.

177x89mm (600 x 600 DPI)

Figure 8: SEM images of (a) newly-formed bastnasite-(La) and (b) bastnasite-(Nd) replacing calcite formed at 220 °C.

84x127mm (600 x 600 DPI)

Figure 9: SEM micrographs showing oriented kozoite-(Nd) grown onto the (104) surface of calcite. (a) Overall view of a calcite grain showing the early stages of development of kozoite-(Nd); (b) detail of the calcite surface showing kozoite-(Nd) crystals attached to the calcite surface. (c) Calcite surface completely covered by kozoite-(Nd) crystals.

84x191mm (600 x 600 DPI)

Figure 10: Schematic diagram showing the epitaxial relationship between kozoite and calcite crystals.

84x75mm (1200 x 1200 DPI)

Figure 11: Reaction pathways towards bastnäsite observed during the replacement of calcite by rare earth carbonates. Continuous lines correspond to observed reactions, while dashed lines correspond to expected reactions that were not observed in our experiments. Each line shows the temperature at which the reaction takes place.

84x61mm (300 x 300 DPI)

Figure 12: Projection of the crystal structures of a (104) slice of calcite and a (001) slice of kozoite showing the main directions of epitaxy and the repeating periods.

84x150mm (1200 x 1200 DPI)