

Crystallization of REE phases within La-Na-(Ca)-Cl-(F)-C-H-O systems

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ABSTRACT

Carbonatite-hosted rare earth element (REE) deposits provide the world's primary source of REEs. Understanding the relative stability of REE minerals within carbonatite systems is vital for deciphering the genesis of carbonatite-related REE deposits. Yet, experimental data of REE minerals at high pressure and high temperature conditions remain scarce. This study reports a series of crystallization experiments involving REE phases in the La-Na-(Ca)-Cl-(F)-C-H-O systems, conducted between 490 and 750 °C and at pressures of 0.3–0.5 GPa. In the F-free systems, Na-REE carbonate (carbocernaite) coexists with hydroxylbastnäsite and remains stable across the temperature range tested. The addition of Ca leads to their coexistence with calcite and induces a partial substitution $2\text{Ca} \leftrightarrow \text{Na} + \text{La}$ in carbocernaite. Increasing REE concentration promotes the formation of a completely new compound, a Cl-bearing REE carbonate ($\text{La}_3(\text{CO}_3)_4\text{Cl}$). In contrast, in the F-bearing systems, bastnäsite is the dominant REE phase, with elevated temperatures favoring the crystallization of REE fluoride (fluocerite, LaF_3). The addition of Ca results in bastnäsite coexisting with calcite and fluorite. Notably, Na-REE carbonates do not form in F-bearing runs, even at low F concentrations (~0.9 wt%). These findings suggest two main implications: first, the formation of LaF_3 at higher temperatures relative to bastnäsite supports field evidence that fluocerite crystallizes at higher temperatures and serves as a precursor to bastnäsite. Second, the absence of Na-REE carbonates in F-bearing experiments may explain why some deposits have no evidence of former existence of Na-REE carbonates.

1. Introduction

The rare earth elements (REEs) encompass lanthanides, scandium, and yttrium, typically categorized into light (LREEs) and heavy (HREEs) groupings. LREEs span La–Eu, while HREEs comprise Gd–Lu, Sc, and Y. Despite the abundance of crustal REEs in comparison to more common industrial metals like Cr, Ni, Cu and W, as well as precious metals such as Pt and Au, exploitable REE ore deposits, especially for HREEs, remain exceptionally rare (Chen, 2011; Haxel, 2002). The escalating demand for REEs, pivotal in advanced high-technology applications, necessitates the urgent discovery of new exploitable REE deposits. This

pursuit hinges on a comprehensive grasp of REE deposit formation. Carbonatites constitute the primary source of global REE reserves, fueling a surge in research investigating the genesis of carbonatite-associated REE deposits (e.g., Anenburg et al., 2021; Xie et al., 2020).

A critical aspect of understanding the formation of REE deposits lies in deciphering the origins of predominant ore minerals. While REE fluorocarbonates such as bastnäsite, and parisite and phosphates like monazite and xenotime are key contributors to the global REE resource pool (Chakhmouradian and Wall, 2012), other REE phases, including REE fluorides like fluocerite (Strzelecki et al., 2022; Terribili et al., 2024; Zhang et al., 2023), hydrous REE carbonates such as ancylite (Kozlov

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et al., 2020), and Na-REE carbonates like burbankite and carbocearnite (Anenburg et al., 2021), are also thought to play important roles in REE deposit formation processes. Hence, understanding the factors that govern the formation of REE minerals is crucial for enhancing insights into the genesis of carbonatite-related REE deposits.

Recent studies have focused on elucidating the formation processes of carbonatite-related REE deposits, shedding light on the evolution of carbonatites and the diverse forms of REE mineralization through a blend of experimental and field studies (e.g., Anenburg et al., 2021; Anenburg et al., 2020; Hou et al., 2015; Hou et al., 2023; Liu and Anenburg, 2025; Nikolenko et al., 2022; Strzelecki et al., 2022; Wei et al., 2022; Xie et al., 2020; Yuan et al., 2024; Yuan et al., 2023; Zhang et al., 2023). Anenburg et al. (2021) outlined a model for the formation of REE ores associated with carbonatites in reconciling preexisting field and experimental observations. In summary, during the evolution of carbonatite system, following the extensive crystallization of carbonates such as calcite and dolomite, carbonatite melt evolves into a brine-melt stage characterized by a composition rich in Na, K, H₂O, chlorides, and fluorides. The brine-melt stage is a pivotal phase for REE deposition.

Current research suggests that Na-REE carbonates, REE fluorocarbonates, and even REE fluorides can primarily crystallize during the brine-melt stage of mineral formation (e.g., Giebel et al., 2017; Liu and Anenburg, 2025; Zhang et al., 2023). While a limited number of experiments (e.g., Anenburg et al., 2020; Nikolenko et al., 2022; Strzelecki et al., 2022; Terribili et al., 2024; Yuan et al., 2024) have sought to elucidate the mutual stability relationships of these REE phases under controlled laboratory conditions—such as investigating the effects of alkali metals (Na or K) on the crystallization processes—the overall body of experimental work in this field remains relatively sparse. This scarcity underscores the need for further studies into how thermodynamic parameters—specifically temperature and chemical composition—influence the stability and formation of REE minerals.

In this study, we undertake a series of experiments aimed at exploring the stability relationships among various REE minerals—specifically Na-REE carbonates, REE fluorocarbonates, and REE fluorides—in the context of La-Na-(Ca)-Cl-(F)-C-H-O systems. These experiments are conducted over a temperature range of 490 to 750 °C and at pressures of 0.3 to 0.5 GPa. Our primary objective is to investigate how variations in temperature and chemical composition affect the crystallization behavior of these REE phases, thereby providing insights into their formation conditions and stability fields within natural systems.

2. Experiments

2.1. High pressure-temperature experiments

Two sets of high pressure-temperature experiments were conducted using a large volume press apparatus at the Institute of Geochemistry, Chinese Academy of Sciences in Guiyang, China. One series was performed under F-bearing conditions (runs from #1-F to #7-F), and the other under F-free conditions (runs from #1-#8). The experimental procedure closely followed the methodology established in previous studies (Xu et al., 2018; Zhou et al., 2001).

For the F-free experiments, mixtures of LaCl₃·6H₂O and NaHCO₃ were prepared in molar ratios of 1:3 and 3:8. In the F-bearing experiments, LaCl₃·6H₂O, NaHCO₃, and NaF were mixed in a molar ratio of 1:2:1. An additional mixture with a reduced NaF content at a molar ratio of 1:2:0.25 was used to investigate the influence of F concentration on the crystallization behavior of REE phases. In the Ca-bearing experiments, calcite (CaCO₃) was introduced to form mixtures of LaCl₃·6H₂O, NaHCO₃, and CaCO₃ in molar ratio of 1:3:2 for the F-free series, and 1:2:2:1 for the F-bearing series, which also included NaF.

The starting materials were enclosed within copper capsules. Temperature elevation was achieved using a cylindrical stainless-steel assembly and monitored via a type-K thermocouple. Samples were

initially compressed to the target pressure (0.3/0.5 GPa) at a rate of 0.01 GPa/min, followed by heating to the desired temperature range of 490–750 °C at a rate of 15 °C/min. After holding at these conditions for 38 to 86 h, the samples were rapidly quenched to room pressure and temperature within 2 min. Subsequently, the experimental products were extracted from the sample chamber. A summary of the experimental conditions and characteristics of the resulting products is provided in Table 1.

2.2. Sample characterization

Upon completion of each experiment, the products underwent a thorough cleaning process involving five cycles of ultrasonic washing with water and ethanol to remove water-soluble impurities like NaCl, and other soluble substances that may exist. For runs #6, #7, #6-F and #7-F, unwashed products were also used for subsequent sample characterizations.

Selected crystals of varying shapes from each experiment were analyzed using Raman spectroscopy to determine their structures (Figs. S1-S5). Raman spectra were acquired using a Renishaw inVia Reflex spectrometer system equipped with a standard confocal microscope and a Renishaw diode-pumped solid-state laser emitting 532 nm excitation light at 1 mW power. The spectral resolution was set at 1.2 cm⁻¹ with an 1800 grooves/mm grating, and silicon standard was used for wavenumber calibration. A small portion (less than 5 mg) of each sample was subjected to morphological and chemical analysis (Figs. 1–2, S6-S8 and Table S1) using a scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM-EDS) at the Institute of Geochemistry, Chinese Academy of Sciences and East China University of Technology. The operational parameters included a 15–20 kV accelerating voltage, 3.2–6.8 nA beam current, and a 7–9 mm working distance.

Additionally, Powder X-ray diffraction (PXRD) was employed to identify the phases present in the samples (Fig. 3). Approximately 10 mg of each sample was powdered, pressed into a disk measuring ~150 μm in thickness and 300 μm in diameter, and then subjected to PXRD analysis using a Rigaku NanoPix-We powder diffractometer equipped with monochromatized MoKα radiation. LaB₆ powder served as the diffraction standard, with a beam size of 500 μm and an exposure time of 20

Table 1

The experimental run conditions and products.

Run no.	Mixture	P (GPa), T (°C)	Time (hour)	Products
F-free				
#1	A + 3B	0.5, 560	34	cbc + hbsn
#2	A + 3B	0.5, 635	38	cbc + hbsn
#3	A + 3B	0.5, 750	38	cbc + hbsn
#4	A + 3B	0.3, 500	37	cbc + hbsn
#5	A + 3B	0.3, 645	38	cbc + hbsn
				cbc + hbsn +
#6	3 A + 8B	0.3, 500	38	La ₃ (CO ₃) ₄ Cl
#7	A + 3B + 2C	0.3, 590	37	cbc + hbsn + cal
#8	A + 3B + 2C	0.3, 590	86	cbc + hbsn + cal
F-bearing				
#1-F	A + 2B + D	0.5, 565	38	bsn
#2-F	A + 2B + D	0.5, 635	38	bsn
#3-F	A + 2B + D	0.5, 700	48	bsn + fcrt
#4-F	A + 2B + D	0.3, 490	38	bsn
#5-F	A + 2B + D	0.3, 540	37	bsn
	A + 2B +			
#6-F	0.25D	0.3, 500	37	hbsn + La ₃ (CO ₃) ₄ Cl
	A + 2B + 2C +			
#7-F	D	0.3, 590	86	cal + bsn + flr

Note: The mixtures are expressed in molar ratio. Phase abbreviations: A-LaCl₃·6H₂O; B-NaHCO₃; C-CaCO₃; D-NaF; bsn-bastnäsite; fcrt-fluocerite; cbc-carbocearnite; hbsn-hydroxylbastnäsite; cal-calcite; flr-fluorite.

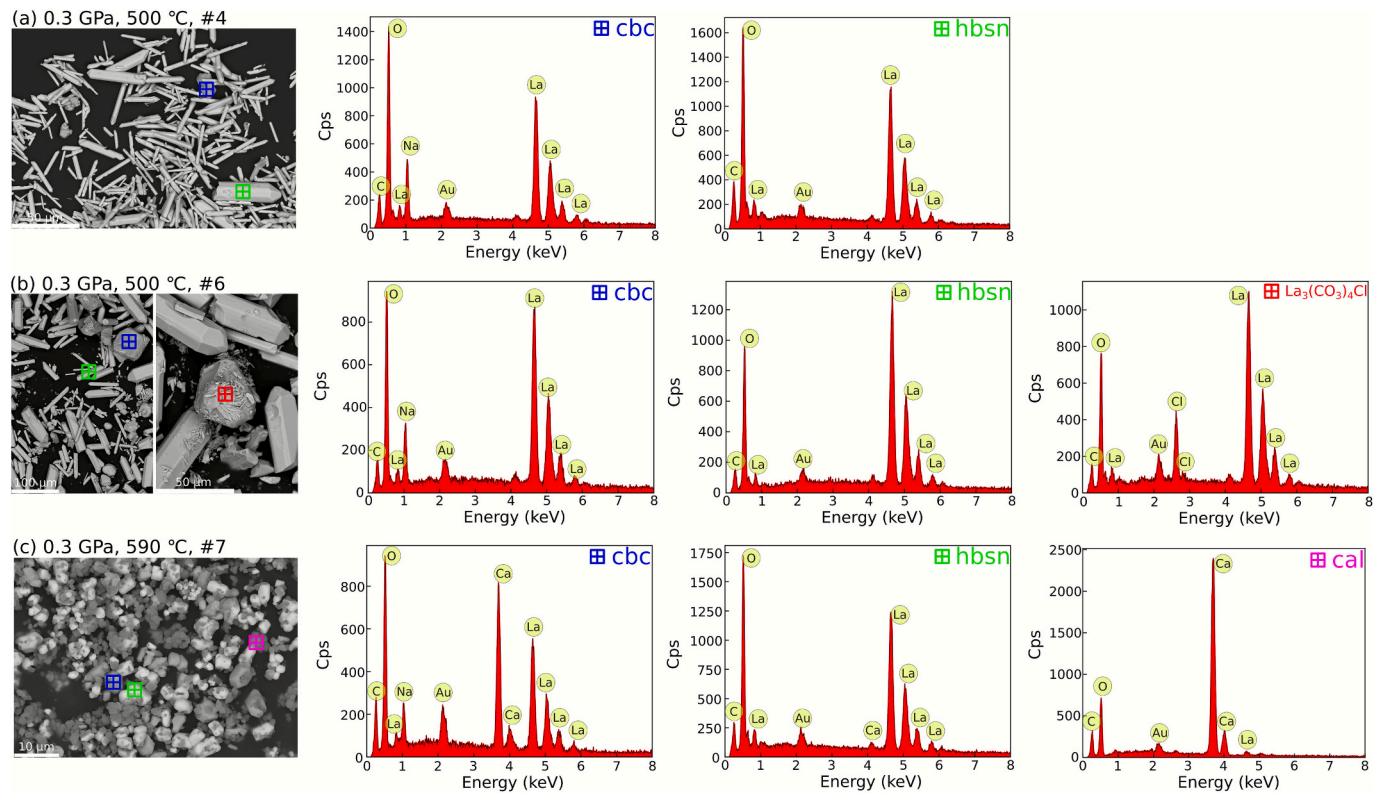


Fig. 1. Back scattering electron (BSE) images of the products from selected F-free runs (for BSE images from other runs, please refer to the supplementary materials). The EDS spectra of the identified crystal grains are presented alongside each BSE image. Phase abbreviations: bsn-bastnäsite; fcrt-fluocerite; flr-fluorite; cbc-carbocernaite; hbsn-hydroxylbastnäsite; cal-calcite.

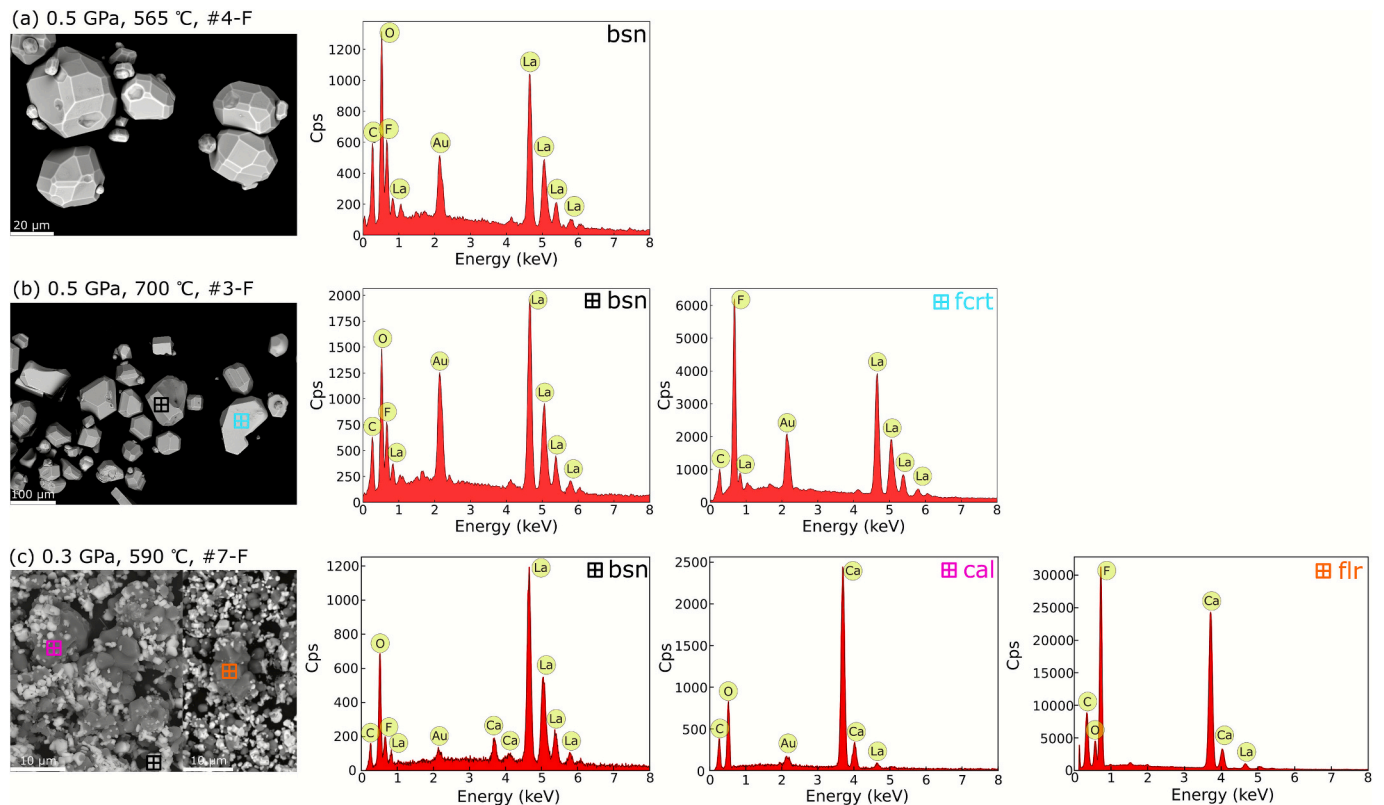


Fig. 2. Back scattering electron (BSE) images of the products from selected F-bearing runs. Phase abbreviations are the same as those in Fig. 1.

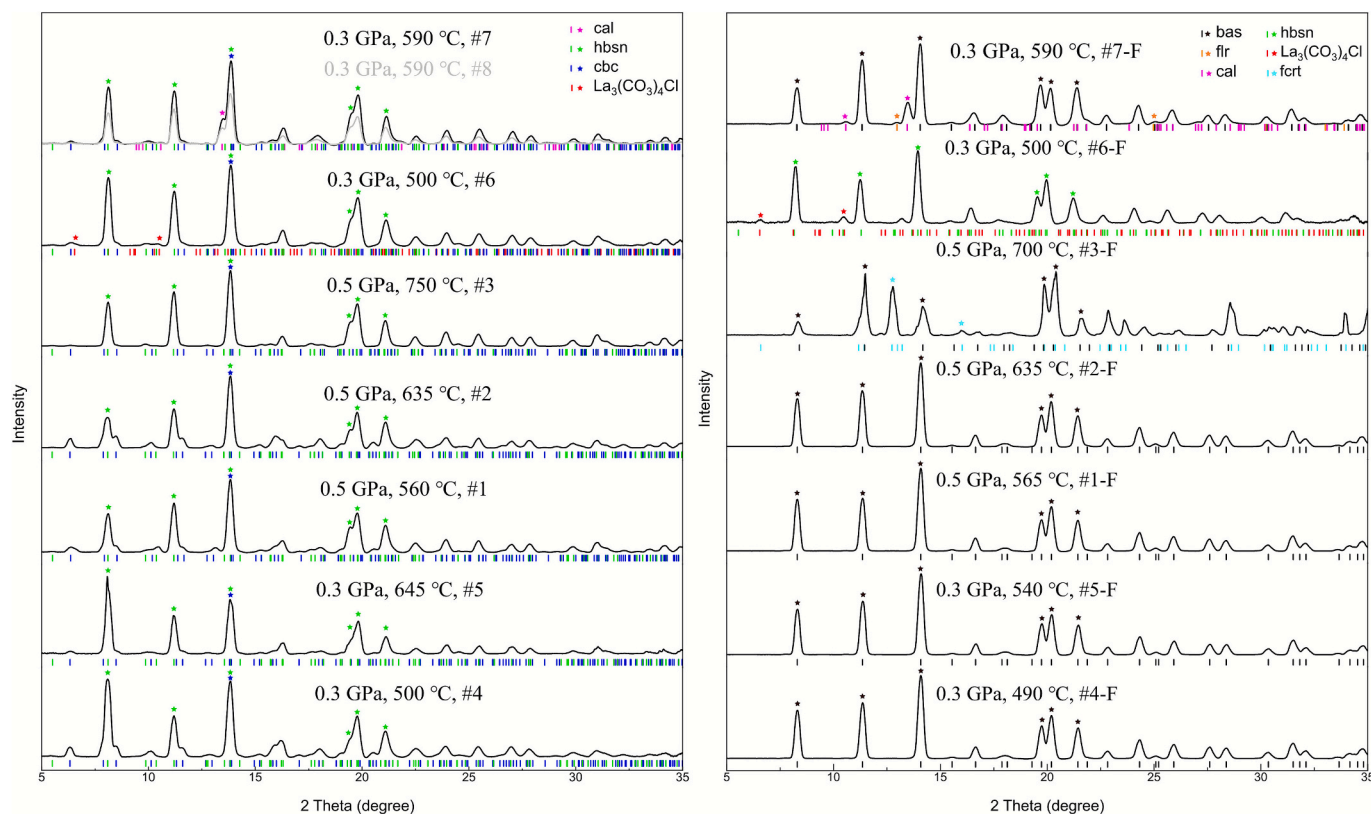


Fig. 3. Powder X-ray diffraction patterns of the products for the F-free (left) and F-bearing (right) runs. The pressure, temperature, and run number of each run are shown nearby. The vertical bars show the diffraction peak positions of the contributing phases. Selected characteristic peaks of these phases are marked with asterisks. Phase abbreviations: bsn-bastnäsite; fct-fluocerite; cbc-carbocernaite; hbsn-hydroxylbastnäsite; cal-calcite; flr-fluorite.

min. The PXRD data were processed using the Dioptas software (Prescher and Prakapenka, 2015). In cases where phase identification from Raman and PXRD data was inconclusive, single-crystal X-ray diffraction (SCXRD) was utilized to elucidate the crystal structures of certain crystals within the samples (Figs. 4–5, S10 and Table 2). SCXRD experiments were conducted using a Bruker D8 Advance diffractometer with graphite-monochromatized MoK α radiation, and data collection involved frame widths of 0.5° and a counting time of 10 s per frame. LaB₆ powder was used as the diffraction standard, and data reduction was performed using the Bruker APEX3 software suite. The crystal structures were solved and refined using the Shelx software (Sheldrick, 2008) with assistance from the Olex2 interface (Dolomanov et al.,

2009), and the visualization of structures was achieved using the VESTA software (Momma and Izumi, 2011).

3. Results

3.1. General description of the products

Table 1 summarizes the details of the high-pressure, high-temperature experiments. Upon extraction from the sample chamber, the products were found to be wet, indicating that the reactions occurred under water-saturated conditions. This observation aligns with the initial water content in the sample mixtures, which was approximately 20 wt%, contributed by the waters of LaCl₃·6H₂O and NaHCO₃.

In the runs conducted without F and Ca, three distinct REE phases were identified in the products (Figs. 1 and S6). Runs #1 to #5, performed at pressures ranging from 0.3 to 0.5 GPa and temperatures from 500 to 645 °C, revealed the coexistence of two phases: carbocernaite (NaLa(CO₃)₂) and hydroxylbastnäsite (LaCO₃OH). Carbocernaite occurred as prismatic crystals, whereas hydroxylbastnäsite exhibited needle-like morphologies (Figs. 1 and S6). At 0.5 GPa and 750 °C, Raman spectroscopy of individual grains detected only hydroxylbastnäsite, which appeared as prisms, subrounded grains, and plates (Fig. S6). However, SEM-EDS and PXRD analyses confirmed the presence of carbocernaite as well (Figs. 3 and S6).

In run #6, which utilized a mixture of 3LaCl₃·6H₂O and 8NaHCO₃, an additional Cl-REE carbonate phase detected. To our knowledge, this represents a newly discovered Cl-REE carbonate, with SEM-EDS (Fig. 1) and SCXRD (Fig. 4 and Table 2) analyses suggesting the chemical formula La₃(CO₃)₄Cl. In run #7, which included Ca, the identified phases comprised calcite, hydroxylbastnäsite and Ca-bearing carbocernaite. These crystals exhibited somewhat similar, subrounded grain morphologies (Fig. 1). Run #8 was a replicate of run #7 but with a

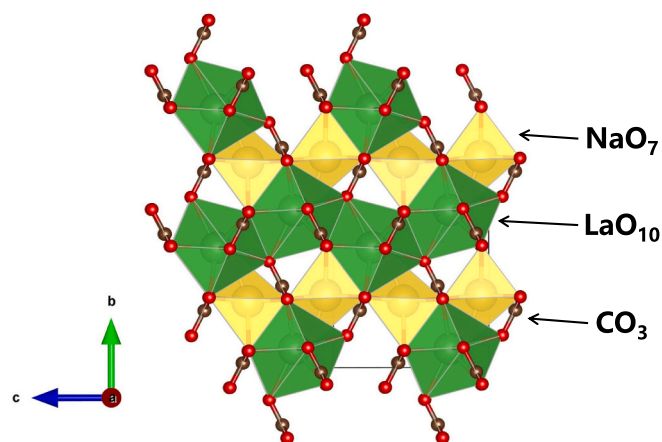


Fig. 4. Crystal structure of NaLa-carbocernaite obtained from the F-free runs. The NaO₇, LaO₁₀ and CO₃ building units are also indicated.

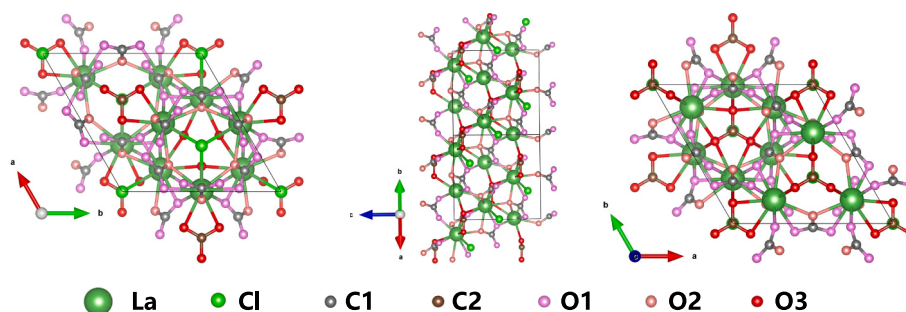


Fig. 5. Crystal structure of the $\text{La}_3(\text{CO}_3)_4\text{Cl}$ phase obtained from the F-free run at 0.3 GPa and 540 °C. The structure is shown in different orientations to detail the bonding of Cl (left), the $\text{C1O}_{1.5}\text{O}_2$ (middle) and C2O_3 (right) unit.

Table 2

Crystallographic information for $\text{La}_3(\text{CO}_3)_4\text{Cl}$ and NaLa-carbocernaite.

	$\text{La}_3(\text{CO}_3)_4\text{Cl}$	NaLa $(\text{CO}_3)_2$
<i>a</i> (Å)	9.9691(4)	5.1433(6)
<i>b</i> (Å)	9.9691(4)	6.4115(7)
<i>c</i> (Å)	8.8639(6)	7.1823(7)
<i>V</i> (Å ³)	762.90(7)	236.85(4)
Space group	<i>R</i> 3 <i>m</i>	<i>Pmc</i> 2 ₁
<i>Z</i>	3	2
Radiation	MoK α	MoK α
No. of reflections	675	779
No. with (<i>F</i> _o > 4 σ (<i>F</i>))	669	768
<i>R</i> ₁ , %	1.93	1.68
<i>wR</i> ₂ , %	4.53	3.62

significantly longer duration, and its phase identification results closely matched those of run #7 (Figs. 1, 3 and S6 and Tables 1 and S1).

Bastnäsite ($\text{LaCO}_3[\text{F}, \text{OH}]$) was recovered from F-bearing runs #1-F to #5-F and #7-F (Table 1). The crystals displayed a variety of morphologies, including hexagonal plates, subrounded grains, prisms, and irregular plates (Figs. 2 and S7). For Ca-free runs in the temperature range of 490–635 °C, bastnäsite was the sole REE phase identified, as confirmed by PXRD patterns (Fig. 3). However, in run #3-F, conducted at 0.5 GPa and 700 °C, additional phases were observed: fluocerite (LaF_3) was identified in PXRD and Raman spectra (Figs. 3 and S5). Fluocerite crystals appeared as irregular tabular forms, as illustrated in Fig. 2.

For the run with lower F content (run #6-F), SEM-EDS and Raman analyses identified predominantly hydroxylbastnäsite, which mostly crystallized as columnar grains (Fig. S7). Nevertheless, PXRD data indicated the presence of an additional phase, whose diffraction pattern matched well with that of the Cl-REE carbonate $\text{La}_3(\text{CO}_3)_4\text{Cl}$ (Fig. 3). In the Ca-bearing run (#7-F), calcite and fluorite crystals were identified alongside bastnäsite.

SEM-EDS analysis of the unwashed products from run #7-F revealed NaCl and a minor unknown phase rich in Na, Ca, Cl, F, La, and Cu, whose structure could not be resolved due to its small crystal size (Fig. S8). Despite this, PXRD data indicate its presence in run #7-F and, in contrast to the SEM-EDS results, also indicate its existence in runs #6, #7, and #6-F, where only NaCl was detected by SEM-EDS (Fig. S9).

3.2. Structural and chemical characterization of the REE phases

The Raman spectra of the identified phases are presented in Figs. S1–S5. The Raman spectra of carbocernaite obtained from F-free runs #1 to #6 (Fig. S1) diverge somewhat from those reported for natural carbocernaite (Chakhmouradian et al., 2017), though both share two prominent peaks in the 1050–1100 cm^{-1} range. SEM-EDS analyses confirm that Na and La are the primary metal constituents of this phase (Fig. 1). SCXRD results (Fig. S10 and Table 2) reveal that this synthetic phase possesses a structure closely resembling natural carbocernaite (Fig. 4).

Unlike natural carbocernaite, which crystallizes in a monoclinic system with space group *P11m*, the synthetic phase adopts an orthorhombic structure with space group *Pmc*2₁ (Table 2). The structural discrepancy between the NaLa end-member carbocernaite and its natural counterpart, as supported by distinctions in Raman spectra (Fig. S1) and SCXRD data (Table 2), is primarily attributable to the extensive Ca–Na and Sr–REE substitutions present in natural specimens (Chakhmouradian et al., 2017).

For carbocernaite recovered in run #7, the Raman peaks exhibit distinct broadening compared to runs #1 to #6, especially within the frequency ranges of 100–300 cm^{-1} , 1050–1150 cm^{-1} and 1400–1500 cm^{-1} (Fig. S1). Nevertheless, PXRD data confirm the identification of this phase as carbocernaite (Fig. 3), likely reflecting a substitutional scheme $2\text{Ca} \leftrightarrow \text{Na} + \text{La}$.

Regarding hydroxylbastnäsite identified in the F-free runs, its Raman spectra (Fig. S2) are highly consistent with those of synthetic end-member hydroxylbastnäsite documented by Michiba et al. (2011), exhibiting five distinct peaks between 3400 and 3800 cm^{-1} that correspond to five crystallographically unique OH groups. However, in the hydroxylbastnäsite from the F-bearing run (#6-F), additional Raman peaks were observed near 3570 cm^{-1} (Fig. S2), likely resulting from partial substitution of OH by F (Fig. S7).

The newly discovered $\text{La}_3(\text{CO}_3)_4\text{Cl}$ phase in F-free run #6 exhibits a trigonal crystal system, with its crystal structure resolved and refined in the *R*3*m* space group (Fig. 5 and Table 2). Within the structure, there is a single crystallographically distinct La and Cl, where every three La atoms share one Cl atom. In contrast, two distinct C atoms (C1 and C2) are present. Each C1 is bonded to one O1 atom and two O2 atoms. In the C1O_3 unit, C1 shares O2 with three La atoms and O1 with two La atoms. Each C2 is bonded to three O3 atoms, sharing each O3 with three La atoms. The Raman spectrum of this phase is displayed in Fig. S3, revealing two prominent peaks around 1100 cm^{-1} attributed to two symmetric stretching modes of $[\text{CO}_3]$. This aligns with the crystal structure's presence of two crystallographically distinct C atoms (C1 and C2). Moreover, the average C1–O bond length in the C1O_3 unit (1.298 (6) Å) is larger than the average C2–O bond length (1.281(3) Å) in the C2O_3 unit. Hence, the lower and higher frequency peaks correspond to the C1O_3 and C2O_3 units, respectively. Notably, there is no significant Raman signal in the high-frequency region, consistent with the structural analysis indicating this phase is nominally anhydrous.

The Raman spectra of bastnäsite (Fig. S2) observed in this study closely resemble that of natural bastnäsite (e.g., RRUFF ID: R060550.2) within the frequency range of 100–1500 cm^{-1} . In the high-frequency region (3400–3800 cm^{-1}), two distinct Raman peaks were consistently observed for bastnäsite across all experiments: one near 3510 cm^{-1} and a more intense peak around 3580 cm^{-1} . This differs from previous reports, which described a broad band spanning 3450 to 3800 cm^{-1} (Yang et al., 2008). The two peaks detected in our study correspond to two O–H stretching modes, reflecting the presence of two crystallographically distinct F sites in the bastnäsite structure (Donnay and Donnay, 1953). The Raman spectra of fluocerite align well with those previously

reported for LaF_3 by Oreshonkov et al. (2018) (Fig. S5).

4. Discussion

In the F-free runs, results from #1 through #5 indicate that variations in temperature (500–750 °C) do not alter the observed REE phases. Carbocernaite and hydroxylbastnäsite consistently coexist and remain stable throughout the investigated pressure-temperature range (Table 1). With the addition of Ca, these phases remain stable in the presence of calcite; however, the composition of carbocernaite undergoes substantial modification, with significant amount Ca substituting for Na and La. The occurrence of $\text{La}_3(\text{CO}_3)_4\text{Cl}$ alongside carbocernaite and hydroxylbastnäsite in the Ca-free run #6 suggests that an increased REE concentration favors the formation of REE carbonates with higher REE content. Notably, $\text{La}_3(\text{CO}_3)_4\text{Cl}$ contains approximately 60 wt% La—significantly greater than the 49 wt% in carbocernaite. It is important to note that the identification of this phase in our experiments does not unequivocally prove its broad thermodynamic stability; its formation could be favored by the specific kinetic conditions or local supersaturation in our experiments.

The discovery of $\text{La}_3(\text{CO}_3)_4\text{Cl}$ in our experiments raises important questions regarding its potential occurrence and preservation in natural systems. Geologically, the most plausible environment for its formation would be during the brine-melt stage of carbonatite evolution, where high-temperature (400–600 °C), saline, Cl-dominated fluids coexist with a carbonate melt enriched in REEs. This scenario aligns well with our experimental conditions (~500 °C, Cl-rich).

However, the extreme rarity of such Cl-dominated REE carbonate minerals in nature, decrespignyite (Rius et al., 2020) serving as a rare example, suggests two potential limiting factors. First, stability field. $\text{La}_3(\text{CO}_3)_4\text{Cl}$ may have a narrow stability field, sensitive to decreases in temperature, Cl or REE concentration. Second, fluid composition. In most natural carbonatitic systems, F is also present and often competes strongly with Cl for REEs. As our F-bearing runs show, a certain amount of F drive crystallization towards bastnäsite, potentially suppressing Cl-REE carbonate phases.

Therefore, while $\text{La}_3(\text{CO}_3)_4\text{Cl}$ represents a credible candidate mineral in the high-temperature REE-Cl-carbonate system, its preservation in the rock record is probably ephemeral. Future mineralogical investigations of REE deposits should pay particular attention to inclusions in early formed minerals (e.g., fluorite, calcite) or to unusual compositions within alteration assemblages, as these may be the key localities to discover this or related rare chloride-carbonate phases.

For the F-bearing runs, experiments #1-F, #2-F, #4-F, and #5-F show that bastnäsite is the sole stable REE phase within 0.3–0.5 GPa and 490–635 °C. The addition of Ca in run #7-F does not affect the stability of bastnäsite, though it coexists with two additional phases—calcite and fluorite (Table 1). However, run #3-F reveals that elevated temperatures above 700 °C favor the crystallization of fluocerite, a phase suppressed at lower temperatures in this experimental study. These results could in part support field observations (Zhang et al., 2023) suggesting that fluocerite crystallizes at higher temperatures and serves as an early phase precursor to bastnäsite, which subsequently replaced fluocerite at lower temperatures during magmatic-hydrothermal evolution.

Moreover, run #6-F demonstrates that a reduced F concentration in the system results in facilitating the crystallization of hydroxylbastnäsite and promoting the formation of Cl-REE carbonate (Figs. 3 and S2).

In the F-bearing runs of this study, neither Na-REE carbonates such as carbocernaite, nor Na-REE fluorcarbonates like lukechangite were crystallized (Table 1). This contrasts with recent experimental findings (Nikolenko et al., 2022; Yuan et al., 2024) concerning REE phase crystallization. For example, Nikolenko et al. (2022) synthesized two Na-REE carbonates—burbankite and lukechangite—using a mixture of LaCO_3F , CaCO_3 , and Na_2CO_3 at 0.1 GPa and 625 °C. Similarly, Yuan et al. (2024) identified carbocernaite as the crystallized REE phase from a mixture of natural bastnäsite, Na_2CO_3 , and H_2O at 0.95 GPa and

690 °C.

Given that the pressures (0.3–0.5 GPa) and temperatures (490–700 °C) employed in this study are comparable to those in these previous investigations, the absence of Na-REE phases here is most reasonably attributed to differences in system composition. The principal distinction lies in the Cl-bearing nature of the experiments reported herein. Although Na-REE carbonates (carbocernaite) were observed consistently in all F-free runs, no such phases appeared in the F-bearing experiments. Within these F- and Cl-bearing systems, the absence of Na-REE carbonates may stem from their higher Gibbs free energy of crystallization relative to that of NaCl and Na-free REE fluorcarbonates under the given experimental conditions. Notably, even run #6-F, characterized by relatively low F content (~0.9 wt% F), yielded no Na-REE carbonates, suggesting that even modest F concentrations are sufficient to inhibit their formation.

In naturally occurring carbonatite-hosted REE deposits, the predominant ore minerals are REE fluorcarbonates such as bastnäsite rather than Na-REE carbonates like burbankite and carbocernaite. Nonetheless, several deposits—including Kangankunde (Broom-Fendley et al., 2017) and Vuoriyarvi (Kozlov et al., 2020)—present compelling evidence that their REE fluorcarbonates originated through hydrothermal replacement of earlier-formed Na-REE carbonates. By contrast, notable deposits such as Maoniuping (Liu and Anenburg, 2025) and Mountain Pass (Castor, 2008) have thus far yielded no indication of Na-REE carbonate minerals. Specifically, detailed recent mineralogical studies of Mountain Pass (Watts and Andersen, 2025) have confirmed the absence of these phases. This observation aligns well with our experimental findings that in F-bearing runs, Na-REE carbonates fail to crystallize.

At Maoniuping, intense interaction with the surrounding country rock has led to sodium depletion. This process likely explains why REEs crystallized directly as fluorcarbonates rather than as Na-REE carbonates (Liu and Anenburg, 2025). However, in larger, kilometer-scale carbonatite intrusions such as Kangankunde, Vuoriyarvi, and Mountain Pass, the influence of country rocks should be comparatively negligible. Intriguingly, despite similar intrusion scales, Kangankunde and Vuoriyarvi exhibit clear evidence of pre-existing Na-REE carbonates, whereas Mountain Pass does not. This suggests that beyond country-rock interaction, intrinsic factors—perhaps differences in the intrusive rock compositions—acted to preclude the formation of Na-REE carbonates at Mountain Pass.

Previous experimental investigations (Nikolenko et al., 2022; Yuan et al., 2024) have demonstrated that both Na-REE carbonates and REE fluorcarbonates can crystallize in simulated systems containing F but no Cl. In contrast, our results indicate that in Cl-bearing yet F-free systems, Na-REE carbonates coexist with hydroxylbastnäsite and calcite, whereas the introduction of F suppresses the crystallization of Na-REE carbonates. These findings imply that the concentrations of both F and Cl could influence whether Na-REE carbonates form. However, this remains qualitative speculation, founded on limited crystallization experiments. Only with the acquisition of comprehensive thermodynamic data on these REE phases—which still requires substantial research investment—will it become possible to quantitatively assess their crystallization behavior under such complex chemical conditions.

While our experiments isolate and demonstrate the significant role of F in suppressing Na-REE carbonates within Cl-bearing systems, it is crucial to emphasize that natural carbonatitic REE mineralization is governed by a more complex interplay of variables. Factors including but not limited to the concentrations of S, P, Si, other alkali metals, and the temporal evolution of the fluid-melt assemblage all exert major influences on the final REE mineral paragenesis. Our findings therefore highlight only one piece of this multifaceted puzzle.

The experimental durations (38–86 h) and reproducible results, including from the longer-duration runs (#8 and #7-F), are consistent with an approach to equilibrium for the major phases. However, in complex fluid-rich systems like those investigated, the possibility of kinetic influences or the crystallization of metastable phases cannot be

entirely ruled out, particularly for phases that appear only under specific conditions (Duan et al., 2021). Thus, while we interpret the phase assemblages in terms of relative stability, the absence of a phase in our experiments does not necessarily imply its thermodynamic instability under the conditions explored, and the presence of a phase, while strongly indicative, may also reflect favorable nucleation kinetics (e.g., $\text{La}_3(\text{CO}_3)_4\text{Cl}$).

5. Conclusions

Based on a series of high-pressure and high-temperature crystallization experiments in the La-Na-(Ca)-Cl-(F)-C-H-O system, this study reveals some thermodynamic factors influencing the crystallization of REE phases in carbonatitic systems. The relative stability of bastnäsite and fluocerite is sensitive to temperature, with fluocerite stabilizing at higher temperatures than bastnäsite. This provides experimental support for field-based models proposing fluocerite as a high-temperature precursor to bastnäsite. In the F-free systems, elevated REE concentrations promote the formation of a novel Cl-REE carbonate $\text{La}_3(\text{CO}_3)_4\text{Cl}$, whereas the introduction of Ca leads to solid solution in carbocernaite (via the substitution $2\text{Ca} \leftrightarrow \text{Na} + \text{La}$). F concentration is identified as an important control on the crystallization of Na-REE carbonates, which are absent in our F-bearing experiments even at low F contents. The inhibition of Na-REE carbonate crystallization observed in these experiments thus provide a plausible explanation for the bastnäsite-dominated mineralogy in deposits such as Mountain Pass. It should be noted, however, that in natural systems the absence of Na-REE carbonate precursors could also be influenced by factors beyond F concentration, including the overall alkali and Ca concentration, the presence of S, P or Si, and the specific pressure-temperature-fluid evolution path of the carbonatitic melt.

CRedit authorship contribution statement

Jingui Xu: Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Qifa Zhong:** Writing – review & editing, Data curation. **Wei Zhao:** Writing – review & editing, Data curation. **Dongzhou Zhang:** Writing – review & editing, Data curation. **Li Zhou:** Writing – review & editing, Funding acquisition, Data curation. **Yi Zhou:** Writing – review & editing, Data curation. **Wei Zhang:** Writing – review & editing. **Wenge Zhou:** Writing – review & editing, Data curation, Conceptualization. **Dawei Fan:** Writing – review & editing, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2026.123255>.

Data availability

Data will be made available on request.

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