Carbonate complexation enhances hydrothermal transport of rare earth elements in alkaline fluids

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Rare earth elements (REE), essential metals for the transition to a zero-emission economy, are mostly extracted from REE-fluorcarbonate minerals in deposits associated with carbonatitic and/or peralkaline magmatism. While the role of high-temperature fluids (100 < T < 500 °C) in the development of economic concentrations of REE is well-established, the mechanisms of element transport, ore precipitation, and light (L)REE/heavy (H) REE fractionation remain a matter of debate. Here, we provide direct evidence from in-situ X-ray Absorption Spectroscopy (XAS) that the formation of hydroxyl-carbonate complexes in alkaline fluids enhances hydrothermal mobilization of LREE at T ≥ 400 °C and HREE at T ≤ 200 °C, even in the presence of fluorine. These results not only reveal that the modes of REE transport in alkaline fluids differ fundamentally from those in acidic fluids, but further underline that alkaline fluids may be key to the mineralization of hydrothermal REE-fluorcarbonates by promoting the simultaneous transport of (L)REE, fluoride and carbonate, especially in carbonatitic systems.
M. eting the increasing demand for rare earth elements (REE) requires a fundamental understanding of the geological processes that enable REE concentration in the Earth’s crust. Carbonatite and peralkaline intrusive complexes (nepheline syenites and granitic suites), as well as their alteration and weathering products (e.g., fenites, placers, and ion adsorption clays), are the primary sources of REE for economic extraction. In general, carbonatite-related systems are enriched in light-REE (HREE: Eu to Lu, general, carbonatite-related systems are enriched in light-REE and weathering products (e.g., fenites, placers, and ion adsorption (nepheline syenites and granitic suites), as well as their alteration enrichment1,2,14. In peralkaline syenites and granites, hydro-

followed by non-selective secondary hydrothermal remobilization concentration in magmatic calcite by fractional crystallization) primary source and magmatic enrichment processes (e.g., HREE the boundaries of said pseudomorphs or in hydrothermal veins (e.g., Thor Lake and Strange Lake and Canada)17–19 while LREE may be further mobilized and deposited in distal fractures. A key question however remains concerning the extent and conditions of hydrothermal remobilization and redistribution of REE in different localities, as the spatial distribution of hydrothermal ores, their mineralogy, grades, and LREE to HREE ratios vary widely1,10. Hydrothermal mineralization of REE in carbonatite systems generally results in preferential LREE mobilization over the HREE and the precipitation of strongly LREE-enriched phosphates and fluorocarbonates in veins and breccias. However, several carbonatite-related occurrences also present relative enrichments in the valuable HREE in late-hydrothermal xenotime or fluorapatite (e.g. Huanglongpu district, China; Lofdal and Okorusu, Namibia; Songwe Hill, Malawi; Amba Dongar, India)7,12,13,17. These unusual HREE enrichments have been suggested to result from (1) the preferential leaching of LREE out of the carbonatite magmas and/or magmatic ores; (2) sequential precipitation of HREE then LREE-bearing minerals upon cooling and mixing with meteoric water13, or (3) a combination of primary source and magmatic enrichment processes (e.g., HREE concentration in magmatic calcite by fractional crystallization) followed by non-selective secondary hydrothermal remobilization of the REE12,14. In peralkaline syenites and granites, hydro-
thermal processes have also been reported to promote either the dissemination of HREE through the formation of less concentrated pseudomorph assemblages within the magmatic intrusion (e.g., Ilimanussaq and Greenland)15,16 or their enrichment at the boundaries of said pseudomorphs or in hydrothermal veins (e.g., Thor Lake and Strange Lake and Canada)17–19 while LREE may be further mobilized and deposited in distal fractures. Based on the common Cl- and SO4-rich nature of fluid inclusions trapped in gange minerals14,20 and available experimental studies and thermodynamic models (see Migidisov et al.31 for review), REE hydrothermal mobilization and LREE/HREE redistribution in new phases are generally interpreted as the result of the selective solubility of REE minerals in evolving hydro-
thermal systems: REE complexation in acidic fluids promotes REE dissolution, while pH buffering or the addition of fluorine, phosphates, and carbonates from host rocks promotes precipitation21–27. Under acidic conditions, the increased stability of LREE-CI over HREE-CI aqueous complexes substantially experimentally at T > 200 °C is expected to favor the mobilization of LREE and hence promote LREE/HREE fractionation. In con-

trast, sulfate is deemed an unselective ligand22 and the formation of REE-SO4 aqueous complexes generally does not result in significant fractionation among the different REE14. This “acidic model” has been successfully applied to account for the hydro-
thermal redistribution of REE from LREE-enriched bastnäsite and HREE-enriched zirconosilicates (eudialyte or elpidite) within peralkaline granites and pegmatites (e.g., Strange Lake, Canada; Ambohimirahavavy, Madagascar)18,20,28,29. At Strange Lake, it has been suggested that the hydrothermal stage involves preferential LREE leaching as chloride complexes in high-
temperature acidic fluids, resulting in relative LREE enrichment of residual, leached minerals. Further fractionation of HREE in secondary phases was favored by the enhanced solubility of HREE-rich zircon and other zirconosilicates in low-temperature acidic F-rich fluids18,19. The acidic transport of REE as CI-, SO42-, and, to a lesser extent, F– complexes have also been suggested to account for a variety of late-stage REE enrichment in carbonatites, including the formation of calcite + bastnäsite + barite + fluorite + sulfides veins at the Weishan deposit, China30 or the replacement of magmatic monazite and bastnäsite by HREE-rich secondary phases at the Dushigou deposit, China12,14. However, the generalization of the acidic model to all types of REE enrichments, and notably those associated with carbonatite intrusions, is questionable as it does not account for all field observations. For example, the development of fenite aureoles in and around carbonatite intrusions attests to the circulation of high-temperature (T < 500–700 °C) alkali- and carbonate-rich fluids in these systems11,31. Furthermore, the abundance of calcite veins in these systems suggests that at least part of the hydrothermal activity may have been buffered to near-neutral to alkaline conditions. Together, these observations call for a better evaluation of the role of alkaline fluids in the REE concentration processes in carbonatitic systems. Both thermodynamic models and in-situ spectroscopic measurements demonstrated that under acidic conditions fluorine acts as a precipitating ligand, triggering near-quantitative precipitation of insoluble REE fluorides rather than contributing to their hydro-
thermal transport21,26,32. This leads to a particular conundrum in attributing a hydrothermal origin to the widespread REE-F-carbonate association found in carbonatitic systems via the acidic model since REE and fluorine cannot be transported effectively in the same fluid. A growing number of experimental studies also suggest the efficient mobilization of REE by high-temperature alkali- and carbonate-rich fluids. Tsay et al.33 originally demonstrated that high amounts of REE (100–1000 ppm) and especially HREE (Gd, Dy, Er, and Yb) could be dissolved in diluted Na2CO3 solutions (0.7 m Na2CO3) under the high P-T conditions of slab dehydration (800 °C, 2.6 GPa). However, experiments by Song et al.34 showed that REE strongly partitions into carbonatitic melts over aqueous fluids at 700–900 °C and 100–200 MPa, questioning the ability of carbonate-derived fluids to effectively mobilize REE under typical crustal conditions. More recent experiments by Anenburg et al.35 appear to support Tsay et al.’s observations, with alkali-, carbonate-, and F-rich fluids enabling REE and especially HREE (Dy) redistribution from crystallizing carbonate melts (>55 wt% CaCO3) into newly formed minerals (i.e., fluorapatite, barbukite, and bastnäsite) and quenched solid solutions between 1200 and 200 °C. Finally, a technical study of REE fractionation methods in fluids also reported 10’s to 100’s ppm of REE dissolved in Na2CO3/H2CO3 solutions to 100–200 °C and 4 MPa36, further confirming the potential of alkali- and carbonate-rich solutions to carry significant amounts of REE, and potentially scavenge and transport REE in and out of carbonate intrusions. While the relative HREE enrichments reported by Tsay et al.33, Anenburg et al.35, and Kokh et al.36 suggest that the REE complexes formed in alkali- and carbonate-bearing fluids could be HREE-selective, the actual speciation of REE in alkaline fluids remains unconstrained from such experiments. The only available constraints on REE speciation under neutral to alkaline conditions are from the early thermodynamic models of Haas et al.37 and Wood et al.38, which generated thermodynamics properties for REE(OH)2–
REE(OH)₂⁺, REE(OH)₆(aq), REE(OH)₄⁻ and REE(CO₃)²⁺ to ~1000 °C and 500 MPa via extrapolations from ambient conditions. As demonstrated recently for uranyl carbonate complexing, such semi-empirical extrapolations can be remarkably accurate, but may also fail spectacularly. Thus, current interpretations of hydrothermal mineralization associated with carbonatites remain limited as they can only rely on high-T thermodynamic properties for REE solids (REECl₃, REEF₃, REEPO₄, some fluorocarbonates [2119,24,25]) and aqueous complexes in acidic fluids (REE-Cl, REE-F, and REE-SO₄ at pH < 2).

Here, we overcome this limitation by investigating the solubility and speciation of REE in alkaline fluids via in situ X-ray absorption spectroscopy (XAS) measurements to 100–500 °C and 80 MPa. These experiments confirm that carbonate-rich fluids may transport significant amounts of REE under typical hydrothermal conditions and further reveal potential means of transporting REE, F, and other ligands together without the systematic precipitation of insoluble REE fluorides.

**Results**

High-temperature in situ XAS as an experimental window into the hydrothermal behavior of REE. The study of trace element behavior in hydrothermal fluids is challenging for a number of reasons, including low concentrations and potential backreactions upon quenching that lead to retrograde precipitation of new mineral phases, possibly obliterating the high-temperature information. Therefore, studies quantifying the solubility of REE minerals, their partitioning between different phases, or the mechanisms that enable their hydrothermal transport have been limited in terms of phases (e.g., the solubility of REECl₃(s), REEF₃(s), and, more recently, REEPO₄(s)) and pH.

To overcome quench-related issues, we have taken advantage of a dedicated autoclave equipped with X-ray transparent high-pressure windows that enable the in situ characterization of hydrothermal fluids to 600 °C and 150 MPa via XAS. This approach was used to assess separately the solubility of La³⁺, Sm³⁺, Gd³⁺, Er³⁺, Yb³⁺, and Y³⁺ in alkaline solutions containing varying amounts of OH⁻, F⁻, and CO₃²⁻ up to 500 °C and 40–80 MPa, and the geometry of Gd- and Yb-carbonate complexes at 200 °C and 80 MPa.

Concentration trends of REE in high-temperature alkaline fluids. REE concentrations in high T fluids are a complex function of REE aqueous speciation and the stability of different REE-bearing phases (REE₂O₃(s), REE(OH)₃(s), REEF₃(s), REEPO₄(s), or REE-fluorocarbonates) that may form under hydrothermal conditions. In situ XAS measurements were used to probe the evolution of REE concentrations in the high T fluids as a function of temperature, fluid composition, and pH. To separate the effect of fluid pH from that of different ligands present in solution (OH⁻, F⁻, and CO₃²⁻), the solubility of La, Nd, Sm, Gd, Yb, and Y oxides (REE₂O₃) was investigated to 500 °C and 40–80 MPa in (i) single salt solutions (NaF, LiCl) at neutral pH; (ii) NaOH ± NaF ± NaCl solutions at pH > 12; and (iii) Na₂CO₃ ± NaF solutions at pH ~10 (details in “Methods” section).

Due to a combination of experimental (i.e., low energy of the REE L₃-edges) and compositional (i.e., low solubility of REE phases) limitations, concentration values, which are calculated from the amplitude of the absorption edge from transmission XAS spectra, could only be obtained for Yb. For all other REE, we refer to an “apparent” solubility trend. The evolution of REE apparent concentrations with increasing T and different composition is evaluated by the so-called εH value (Figs. 1 and 2), which corresponds to the fluorescence absorption edge jump, i.e., the difference of fluorescence intensity before and after the REE L₃-edge that is proportional to the REE concentration in the sample at a given temperature, assuming a fixed photon path from sample to the detector. Additional information about calculated and apparent concentrations can be found in the “Methods” section.

To 500 °C, the apparent concentrations of Sm, Er, Yb, and Y in single salt and NaOH solutions remain at or below the detection limit of our in situ measurements (~10 ppm) (absorption edge is absent or barely visible on Fig. 1). The low concentrations of REE in neutral salt solutions tally with Pourtier et al.’s study that demonstrated solubility of monazite-Nd below ppm levels at 300 °C and 200 MPa. However, the addition of 1 m NaF to a 3.8 m NaOH solution appears to increase Sm solubility slightly, with aqueous concentrations up to an estimated ~30–50 ppm at 200 °C (Fig. 1B). Hence, contrary to acid systems where it acts as precipitating ligand and fluorine appears to promote REE mobility under basic conditions.

The amounts of dissolved REE (La, Gd, and Yb) further increase in carbonate (±F) solutions (Figs. 1 and 2). However, temperature affects LREE and HREE differently (Fig. 2): Gd and Yb display a retrograde solubility from 100 °C onwards, similar to what we previously reported for Eu, Yb, or Y in acidic Cl- and S-bearing solutions, on the contrary, La solubility increases suddenly from below detection limit (~10 ppm) at T < 300 °C.
(e.g., absorption edge is barely visible on Fig. 1A) to more than 10 times the detection limit at 400–500 °C (Figs. 1A and 2A). This is the first time we observe prograde solubility for an REE in our in situ experiments. In F-free experiments, the maximum apparent concentrations of Gd are estimated to reach 400–600 ppm at 100 °C (Fig. 2B). For Yb, the concentrations calculated from the transmission spectra are close to 900 ppm at 100 °C and decrease toward 400 ppm at 300 °C (Fig. 2C). The concentrations of La at T > 400 °C are difficult to assess due to the potential effect of decreasing fluid density on the fluorescence signal (see “Methods” section). Remarkably, the addition of fluorne did not suppress La, Gd, and Yb solubility; on the contrary, the maximum La and Yb concentrations are obtained for a mixed 0.7 m Na₂CO₃–0.3 m NaF solution. Furthermore, at T > 400 °C, the apparent La concentrations become lower in F-rich (0.6 m NaF) carbonate solutions (Fig. 2A), suggesting a “Goldilocks effect” for La hydrothermal remobilization in alkaline fluids, where the optimal conditions encompass moderate amounts of carbonate and fluorine. For Yb, the addition of F is associated with higher concentrations (1100 versus 650 ppm at 200 °C) and delays the solubility drop to 300–350 °C. At 400 °C, 400 ppm Yb are left in the alkaline fluid, about 3–4 times less than the amount of Yb that can dissolve in acidic Cl-rich fluids (0.35 m HCl), but still, a significant amount compared to REE-mineralizing fluids (0.35 m NaOH). The addition of F does not affect Gd apparent concentrations significantly: it is slightly lower at 200 °C, but pH values close to our detection limits suggest that only tens of ppm of Gd may be retained in both F-bearing and F-free carbonate fluids at T > 300 °C (Fig. 2B).

**Speciation of REE in (CO₃²⁻, F⁻)-bearing alkaline fluids.** The enhanced solubility of La, Gd, and Yb in (CO₃²⁻ + F⁻)-bearing fluids compared to pure salt and NaOH solutions suggests that carbonates and/or F⁻ are more effective ligands than hydroxide for REE transport under alkaline conditions. To test this hypothesis, the structural parameters describing Gd and Yb speciation in the 0.7 m Na₂CO₃ and 0.7 m Na₂CO₃ + 0.3 m NaF solutions were extracted from EXAFS spectra collected at 200 °C (Fig. 3 and Supplementary Material S1), where maximum concentrations (500–1500 ppm) were recorded for these elements. The same could not be done for La, due to the decreased signal-to-noise ratio at the lower energy of the La LIII-edge (5.483 keV, compared to 7.243 keV for Gd LIII and 8.944 keV for Yb LIII).

For Yb, there are obvious differences between EXAFS spectra reported from the CO₃²⁻ + F⁻ alkaline solutions and an acidic control solution containing 0.1 m HCl that was measured over similar P–T conditions: namely, the first EXAFS oscillation is shifted from ~3.2 to 3.0 Å⁻¹ and long-range oscillations (~4 Å⁻¹) display a different shape (Fig. 3). More strikingly, these alkaline data are unusual for aqueous fluids in that they exhibit a relatively large peak between 3 ≤ R ≤ 4 Å in the phase uncorrected Fourier transform (FT), which underlines the presence of a heavy atom in the second coordination shell. The same is observed for Gd (Supplementary Material S1).

Available spectroscopic studies and theoretical calculations suggest that, at ambient P–T conditions, REE form bidentate complexes with the carbonate/bicarbonate ions, with two of the oxygens from the carbonate ion facing the central REE atom, and the third one located at a larger distance in the second shell. The number of carbonate ligands is however disputed depending on
fluid composition and techniques employed: (i) REECO₃⁺ and [REE(CO₃)₂]⁻ have been reported in natural waters based on potentiometric measurements and partitioning experiments⁴⁶–⁴⁸; (ii) the tetra-carbonate [REE(CO₃)₄]⁻⁵, [REE(CO₃)₂H₂O]⁻⁵, or [REE(OH)(CO₃)₂]⁻⁶ complexes have also been suggested to form in highly concentrated solutions (0.5–5 m (Na,K)₂CO₃), based on UV–vis near-IR absorbance spectroscopy⁴⁹–⁵¹.

Here, our EXAFS analysis suggests that, in both solutions, the Yb atom is coordinated to eight O atoms located at around 2.29–2.30 Å in the first shell and that only two intermediate C atoms are present at a distance of 2.75 Å (Table 1). The distinctive second shell peak that occurs between 3 ≤ R ≤ 4 Å in the FT can be fitted with up to 12 O at an average distance of 4.09 Å (Table Supplementary Material S2). However, the best fits are obtained for a combination of 2–3 Yb and 4–8 O atoms located around 3.85 and 4.1–4.2 Å, respectively (Fig. 3). A similar structure, involving the second shell of 2 Gd and 8 O atoms at 3.87 and 4.28 Å is also fitted for Gd in 0.7 m Na₂CO₃ at 200 °C (Table 1). The formation of polynuclear carbonate species is well-documented for actinide ions⁵²–⁵⁴ and polynuclear hydroxide REE complexes have also been described during the hydrolysis of REE with help from organic multidentate ligands such as EDTA⁵⁵. In such contexts, polynuclear clusters are frequently observed in highly concentrated solutions (0.5–2 m Na₂CO₃) due to the high negative charge and multi-coordination: 

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[REE_3(CO_3)_{2}(OH)_4(H_2O)_{12}]^{3+}, \text{ Taking into account the basic pH of our high P–T fluids and the fact that the EXAFS best fits only account for two carbonate groups, our preferred structure is that of the [REE_3(CO_3)_{2}(OH)_4]^3+ hydroxyl-carbonate polynuclear cluster (Fig. 4a). The potential precipitation of lanthanite- ([REE_3(CO_3)_4(H_2O)](s)) or tengerite- ([REE_3(CO_3)_4(2–3H_2O)](s)) like carbonate hydrates in the beam-path can be discarded based on (1) the absence of absorption contrast in transverse transmission scans of the cell or glitches in the XAS spectra that are generally observed upon precipitation under the beam and (2) the presence of only two carbonate groups in the best fits, while lanthanite and tengerite-like structure involve coordination to 3–4 carbonate groups⁵⁹. While the lower REE concentrations found in the presence of F (Gd) or at T > 200 °C (Gd and Yb) hindered EXAFS analysis for these conditions, similarities in the XANES spectra suggest that similar REE hydroxyl-carbonate complexes may be stable to at least 300 °C in both F-free and F-bearing alkaline fluids (Supplementary Material S1).

**Discussion**

Experimental studies on the solubility of REE solids in high T (>250 °C) alkaline fluids have been extremely scarce, mostly limited to the fate of the phosphate mineral monazite–(Nd) in hydroxide solutions⁴₁. While the authors suggested that using the hydrolysis constant from Haas et al.³⁷ and Wood et al.³⁸ enables reproducing their observed solubility at 300 °C and 200 MPa, a set of recent experiments by Gisy et al.²⁵ instead points to a need to revise the thermodynamic properties of REE hydroxyl species for future solubility calculations. Our combined solubility and speciation work now suggest that carbonate may act as a more potent ligand than hydroxide alone and that hydroxyl-carbonate complexes may promote REE transport in alkaline fluids.

The retrograde solubilities of Gd and Yb suggest that HREE transport in alkaline fluids may be limited above 300 °C. As we could not recover any precipitates for analysis (only a fine powder coated the lower piston), it remains difficult to assess whether it is carbonates, fluorcarbonates, or hydroxides phases that control
Table 1 Structural parameters derived from the EXAFS analysis of Gd- and Yb-bearing alkaline solutions at 200 °C and 80 MPa.

| Solutions     | Gd            | Yb            |
|---------------|---------------|---------------|
| 0.7 m Na₂CO₃ | ΔSolutions    | O₁-shell      | C₁-shell      | REE₂-shell | O₂-shell      |
|               |               | R             | χ            | R           | R             |
|               |               | σ²            | R-factor     | σ²          | σ²            |
|               |               | E             | χ           | σ₀         | σ₀            |
|               | 7.9 (22)      | 4.28 (3)      | 0.002       | 41.3 (2)   | 4.12 (3)      |
|               | 2.39 (10)     | 2.31 (10)     | 0.002       | 2.47 (2)   | 2.48 (4)      |
|               | 0.009 (2)     | 0.002 (1)     | 0.006 (5)   | 0.008 (6)  | 0.008 (6)     |
|               | 1.02 (50)     | 0.002 (3)     | 0.003 (3)   | 0.007 (5)  | 0.0184 (3)    |
|               | 0.025         | 0.004 (4)     | 0.004 (4)   | 0.004 (4)  | 0.004 (4)     |
|               | 0.034         | 0.014         | 0.014       | 0.014      | 0.014         |
|               |               | 316           | 55          | 316        | 55            |

HREE solubility under these conditions. In contrast, LREE transport in alkaline fluids may be favored under high T conditions, as suggested by the prograde solubility of La from 300 to 500 °C in carbonate-bearing fluids (Fig. 2). While the low energy of La L₃-edge measurements precluded obtaining speciation information through EXAFS analysis, we suggest that hydroxyl-carbonate complexes similar to those reported for the HREE are behind this prograde solubility of La.

Contrary to what is observed under acidic conditions, fluoride ions do not act as a precipitating ligand in these fluids, at least to moderate concentrations (0.3 m), since F addition is found to increase both La and Yb aqueous concentrations (Fig. 2). Whether this solubility increase is favored by combined fluoride (as REEF³⁺, REEF₄⁺, or hydroxyl-fluorides REEF(OH)₃) and hydroxyl-carbonate complexation or the substitution of F⁻ for OH⁻ in the [REE(CO₃)₂(OH)(H₂O)](3−−x) polymeric complexes, however, remains to be constrained. Unfortunately, similarities between O and F ionic radii and interatomic distances render discrimination between hydroxyl and fluorine neighbors extremely difficult with XAS.

The lower La concentration reported in the 0.7 m Na₂CO₃–0.6 m NaF solution above 400 °C (Fig. 2) nevertheless suggests a “Goldilocks effect”, where intermediate fluorine contents (0.3 m NaF) promote LREE hydrothermal transport under high T conditions whereas higher concentrations (0.6 m) lead to precipitation of secondary REE phases. Though the high T precipitates were too few to be recovered and analyzed after the quench, it is likely they were fluorocarbonates that formed through gradual substitution of F⁻ for OH⁻ in fluids containing more than 0.3 m NaF. The [REE(CO₃)₂(OH)(H₂O)](3−−x) aqueous complex we propose from the results of the EXAFS analysis actually shares similarities with the structure of REE fluorocarbonates such as Na₂La₂(CO₃)₃F or horvathite-(Y), NaY(CO₃)F₂, where (REE + Y)O₃F₄ polyhedra are linked by carbonate groups, hence, aqueous polynuclear carbonate complexes could act as a precursor to mineral formation. More common hydrothermal fluorocarbonates such as bastnäsite (REECO₃F), synchysite (REECa(CO₃)₂F), or parasite (REE₂Ca(CO₃)₃F₂) could also directly precipitate following the same mechanism, where F replaces OH⁻ groups in hydroxyl-carbonate aqueous compounds.

Many field studies have invoked the high amounts of chloride and sulfate daughter minerals recorded in fluid inclusions in carbonatite-related REE deposits to underline the potential role of REE-Cl and REE-SO₄ complexation in the hydrothermal transport and concentration of the REE (Fig. 2). However, the thermodynamic model of Migdisov et al. stresses that such species may only be stable under acidic to near-neutral conditions in F-bearing systems (pH < 3–4 for REECl²⁺ and 3 < pH < 7 for REESO₄²⁻ at 400 °C, 100 MPa). Our results further call for a reevaluation of REE transport mechanisms in carbonatitic systems, as we observed high HREE (Gd, Yb) concentrations in low-temperature (C,CO₃²−)-rich alkaline fluids (<300°C); the apparent prograde solubility of LREE (La) to 500 °C in the same fluids; and characterized the structure of to date unreported hydroxyl-carbonate polynuclear REE complexes.

The nature of fluids circulating in and around carbonate intrusions is complex, and both orthomagmatic and mixed hydrothermal/meteoritic fluids have been invoked to account for REE mineralization at different sites. The magmatic-hydrothermal transition in carbonatites is characterized by alkali-, chloride-, sulfate-, and carbonate-rich fluids being expelled from the crystallizing carbonatite melts. This process ultimately results in pervasive or focused (veins) alkaline alteration of surrounding rocks (feminization) to different scales (see Elliott et al. for a review). Whether those fluids form gradually as the end products of

| Table 1 Structural parameters derived from the EXAFS analysis of Gd- and Yb-bearing alkaline solutions at 200 °C and 80 MPa. |
|---------------------------------------------------------------------------------------------------------------|
| **O₁-shell** | R | σ² | R-factor | σ₀ | σ₀ |
| Gd          | 7.9 (22) | 4.28 (3) | 0.002 | 41.3 (2) | 4.12 (3) |
| Yb          | 2.39 (10) | 2.31 (10) | 0.002 | 2.47 (2) | 2.48 (4) |
| 0.7 m Na₂CO₃| 0.009 (2) | 0.002 (1) | 0.006 (5) | 0.008 (6) | 0.008 (6) |
| 0.7 m NaF   | 1.02 (50) | 0.002 (3) | 0.003 (3) | 0.007 (5) | 0.0184 (3) |
| 0.025       | 0.004 (4) | 0.004 (4) | 0.004 (4) | 0.004 (4) | 0.004 (4) |
| 0.034       | 0.014 | 0.014 | 0.014 | 0.014 | 0.014 |
| 316         | 55 | 316 | 55 | 316 | 55 |

In conclusion, our studies provide new insights into the complex fluid-rock interaction processes occurring in carbonatitic systems and highlight the importance of considering the role of REE fluorocarbonates in these environments.
fractional crystallization of the carbonatite melt; are released as multiple pulses through immiscibility with the melt; lose their C through immiscibility between H2O–CO2 and Cl-rich fluids; or evolve differently as a function of their distance from the source and previous alteration has been a long-standing matter of debate.11,31,68,69 Experimental constraints on the conditions of fluid production from carbonatites are scarce, but homogenization temperature for fluid inclusions68–70 suggest that fertilization could occur from 700 to 800 °C down to the sub-solidus of (natro-)carbonatite, i.e., 500–600 °C.71 While aqueous, high salinity, multi-component fluid inclusions containing halite, nahcolite (NaHCO3), calcite, strontianite (SrCO3), fluorite, and sulfates have been reported at many carbonatite complexes (Kaiserstuhl, Palabora, Fen, Oka, Kalkfeld, Amba Donga, Jacupiranga, and Songwe Hill), their complex mineralogy makes it difficult to assess formation temperatures and original compositions.31,70 Recently, Walter et al.70 paved the way for a better evaluation of the high P-T compositions of these fluids by using a Margules-type solution model to recalculate the (Na,K)Cl, (Na,K)CO3, and (Na,K)SO4 bulk concentrations of multicomponent fluid inclusions from the Kaiserstuhl carbonatite (SW Germany). They suggest that the fluids derived from the carbonatites at the magmatic-hydrothermal transition contain up to 80 wt% [(Na,K)Cl + (Na,K)CO3 + (Na,K)SO4], and hence constitute brine-melts whose properties are intermediate between those of carbonate melts and dilute hydrothermal fluids such as those studied here. Raman measurements confirm that CO32− and HCO3− are the dominant carbon species in the more evolved fluids, demonstrating neutral to alkaline conditions similar to our experiments. Although the fluorine and REE contents of these brine-melts remain to be quantified, REE-bearing phases such as burbankite, bastnäsite or apatite have been reported as daughter minerals in such inclusions.65,72 Anenburg et al.53 further suggested that cooling of such fluids could both promote LREE concentration and preferentially remove HREE from the carbonatite body thanks to the formation of burbankite ((Sr, Ba,REE3)(Na, K, Ca)3(CO3)5) and carbocernaite ((Sr,REE, Ba) (Ca, Na, K)2(CO3)3), which concentrate the LREE but cannot incorporate large amounts of HREE. Such process could act as a precursor to the typical LREE-enriched carbonatite mineralization as monazite and fluorocarbonate pseudomorphs in carbonatite complexes. While our in situ experiments do not enable us to draw direct conclusions about the solubility of REE in such solute-rich fluids, studies of transition metals indicate little changes in coordination geometry of metals such as Au(I) and Cu(I/II) in the transition from brines to hydrated salt melts (brine-melts).73 Hence, we infer that alkali-REE-carbonate clusters could as well promote high REE concentrations in brine melts and the precipitation of burbankite or carbocernaite, in a comparable manner as reported for Zr–O–Si/Na alkali-zirconosilicate clusters and vlasovite in Si and Na-rich fluids.60

Our in situ constraints on REE in 0.7 m Na2CO3 ± NaF fluids apply directly to purely hydrothermal stages, where early “melt-brines” have been diluted to lower solute contents (<20 wt%) through cooling, fluid-rock interactions and/or mixing with meteoritic fluids. Such fluids may lead to the formation of veins and stockwork zones intruded in the alkaline-carbonatite sequences or host rocks (e.g., deposits of the Mianying Dechang belt, China).64,74,75 Late hydrothermal reworking of magmatic assemblages to hydrothermal fluorophosphates and fluorocarbonates such as reported at the Okorusu (Namibia), Amba Donga (India), or Kangankunde (Malawi) complexes63,66,67 is also more likely to involve fluids that will not completely leach the carbonate component away, i.e., near-neutral or alkaline fluids where REE may be mobilized as the newly characterized hydroxyl-carbonate complexes or as REE(SO4)2−.21,63,66 Our study suggests that depending on temperature conditions, hydroxyl-carbonate complexation should lead to preferential mobilization of the LREE (T > 300 °C) or of the HREE (T < 300 °C). In the Maonuping deposit (China), REE are mostly concentrated in late-stage bastnäsite in veins that crosscut previous calcite-fluorite-baryte precipitates. According to fluid inclusion studies, these bastnäsites formed at T ≥ 160–240 °C from sulfate and CO2/CO3−2-rich fluids.64 Based on our experiments, LREE-hydroxyl-carbonate complexation under “moderate” temperatures (~300–450 °C) and solubility drop at T < 300 °C (Fig. 2) could very well account for the formation of such mineralization. Our results also show that fluorine can be co-mobilized with REE in such fluids. The enhanced LREE mobility as hydroxyl-carbonate complexes at T > 300 °C may also explain the residual HREE enrichment of apatite at the Tundulu and Kangankunde carbonatites (Malawi).76 On the contrary, REE-SO4 complexation will scavenge REE without significant fractionation among LREE and HREE, and thus lead to the precipitation of secondary phases with LREE/HREE ratios similar to their magmatic source, as recently described by Cangelosi et al.53 for the Okorusu carbonatite.

Overall, our in situ study highlights new mechanisms that may contribute to the hydrothermal concentration of the rare earth elements and LREE/HREE fractionation in carbonatitic systems. They also reveal that co-transport of all the components present in REE-fluorocarbonate ores is possible under alkaline conditions, whereas fluorine acts as an efficient precipitating ligand under acidic conditions. The circulation of alkaline fluids is however not limited to carbonatite intrusions but its bearing on REE mineralization is not as obvious for nepheline syenite and peralkaline granites. At the Strange Lake deposit (Canada), recent fluid inclusion studies20,28 highlighted that the earliest hydrothermal stage involves high-temperature (400–500 °C) fluids with pH > 9. These early fluids contain C (trapped as CH4 bubbles in the fluid inclusions), Cl (23 wt% NaClaq), and F (0.2–0.6 wt%), and are enriched in LREE, with La/Yb ratios
Based on the absence of carbonate minerals in the early fluid inclusions, Vasyukova et al. speculate that early LREE mobilization in the high T Cl- and F-rich fluids are probably due to hydroxy-fluoride complexation similar to that suggested for Zr and Nb27,78 rather than carbonate complexation as described here. Alkaline alteration at the Illmauassaq nepheline syenite Complex in Greenland instead leads to preferential loss of the HREE and HFE from their primary source, as evidenced by their strong depletion in euclidean pseudomorphs15,16. The new hydroxy-carbonate species identified here may be the first of many unsuspected complexes and advocate for the reevaluation of the role of alkaline fluids in the genesis of REE deposits, via a more systematic characterization of fluid inclusions volatile and trace elements composition, as well as new high P–T solubility studies. Such a step may be critical for defining the key chemical and geochemical factors controlling enrichment in the most valuable rare earth (Nd, Pr, and Dy) and developing more effective exploration strategies to sustain REE production into the future.

Methods

Experimental set-up. All experiments were conducted in a dedicated autoclave that enables in situ X-ray absorption (XAS) on high-temperature, high-pressure fluids at the BM-30B beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France)47. The aqueous solutions are contained in a vitreous carbon tube that is placed within a small furnace enclosed in a high-pressure vessel. The vessel is equipped with three 0.8 mm Be windows that enable data collection in both transmission and fluorescence (90°) modes. The aqueous solutions are enclosed in the internal vitreous C tube by two vitreous C pistons that can move freely along the tube when pressurizing gas (He) is flushed in the high-pressure vessel or alternatively to accommodate volume expansion upon heating. In the current study, the samples were pressurized to 80 MPa (except for measurements at La LIII-edge, for which pressure was 40 MPa) and heated up to a maximum of 500–550 °C.

The ESRF is a 6.03 GeV ring and was operated in 7/8 multi-bunch mode, with a maximum current of 180 mA. The FAME beamline is a bending magnet beamline that has been described elsewhere47. Energy selection at the 117-th order of La, Sm, Gd, and Yb was achieved by 7,616, 4,243, 2,442, and 9,845 eV (Yb) Si microchannel plate detectors. Experiments involving Y were conducted at the Y K-edge (17.038 keV). The monochromator was focused down to 300 × 100 μm2 (H × V FWHM). Incident and transmitted beamline intensities I0 and I1 were measured with Si diodes, while the fluorescence radiation was collected with a Canberra 30 element solid-state detector set at 90° from the incoming beam.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fluorescence spectroscopy (EXAFS) spectra were collected at room temperature, and in steps of 50–100 °C at high pressure. The aqueous solutions were left to equilibrate for a few minutes after each heating step and the spectra were then collected for 1–3 h at each temperature depending on the aim of the measurements (solubility or speciation experiments – see below). The reader is referred to previous publications on Ce, Eu, Pr, Dy, Y, or Yb hydrothermal speciation for further details on the autoclave and beamline capacities at extreme P–T conditions30,31,42,43.

Estimation of REE aqueous concentrations from XAS spectra. The solubility of rare earth elements in neutral to alkaline solutions was investigated by loading a sintered piece of REE2O3 (Sigma Aldrich) together with salt, F, hydroxide, and/or carbonate-bearing solutions. Carbonate solutions were prepared by dissolving requisite amounts of Na2CO3 in deionized water. Hydroxide solutions were prepared by diluting requisite amounts of NaOH, 50–52% (Sigma-Alrich) in deionized water. When present, F and Cl were added as NaF and NaCl/LiCl (Sigma Aldrich/ACS, ≥ 99.0%). All investigated compositions are summarized in Table S1. The solubility of Yb was determined from the amplitude of the absorption edge Eb at each temperature condition. As our experimental set-up involves a fixed X-ray path, the amplitude of the absorption edge as measured in transmission spectra is directly proportional to the concentration of the excited atoms (Ci in mmol) according to Beer–Lambert’s law (1).

\[ C_i = \frac{\text{Eh}}{\text{Eh}_0} 
\]

where \( \Delta \phi \) is the change of the total absorption cross-section of the element i over its absorption edge (cm2 g–1), \( M_i \) the atomic weight (g mol–1), \( \sigma \) the optical path length through the sample (cm), and \( \rho_{\text{aq}} \) the density of the aqueous fluid (g cm–3).

For La, Sm, and Gd, the strong absorption of the signal by the experimental set-up (air between detectors and autoclave + Be windows) and sample (4 mm of aqueous solution) at the low LIII-edge energies (5.483–24.235 eV) however prevented collecting XAS spectra in transmission necessary to calculate their aqueous concentration. Instead, we based our calculations on Beer–Lambert’s law. Instead, we propose to use the absorption edge jump Eh from fluorescence spectra (calculated with Athena program38) as an indicator of apparent solubility trends. For a fixed photon path (i.e., autoclave and fluorescence detectors are kept at the same position throughout the experiments), the fluorescence signal is correlated to the concentration of the excited atoms, but also the density and the absorption of the different solutions at different P–T conditions.

To evaluate the effect of density and absorption on the amplitude of the fluorescence absorption edge jump, we reported in Figure S2 the Eh values for reference solutions of 0.1 wt% La in 5 m Cltot, 200 ppm Gd + 200 ppm Yb in 0.1 m HCl and 400 ppm Gd + 350 ppm Yb in 0.1 m HCl that were collected from 25 to 450 °C and pressure between 40 MPa (La) and 80 MPa (Gd, Yb) during the same beamtime as our experimental data. For all compositions, Eh values remain stable within error while fluid densities decrease from 1.01–1.2 to ~0.7 g cm–3 with increasing temperature to 400–500 °C. Thus, the Eh values were considered to be directly proportional to REE concentration for such conditions and the average Eh value of ~0.0881 for the 200 ppm Gd + Yb solution was used to estimate Gd concentration in the carbonate-bearing solutions at 100–400 °C (400–600 ppm). The Eh value for the La solution at T > 450 °C could not be estimated due to the onset of brine-vapor separation. In the case of the Gd and Yb solutions, Eh values dropped significantly as the density decreases toward 0.5 g cm–3 (supercritical conditions). The decrease of Eh is however time-dependent at both 400 and 450 °C, suggesting a decrease of Gd and Yb solubility associated with precipitation of Gd and Yb solids, rather than a direct effect of density on the fluorescence signal. While an increase of fluorescence signal under supercritical conditions such as those we report for La in carbonate-bearing fluids is most likely related to an increase in their concentration, it remains difficult to assess the effect of decreasing density below 0.6 g cm–3 on the fluorescence signal. Thus, we do not provide an estimation for La concentration at T ≥ 400 °C.

Speciation analyses. The stability of Gd and Yb hydroxyl-carbonate complexes in 0.7 m Na2CO3 and 0.7 m Na2CO3–0.35 m NaF solutions was investigated simultaneously to solubility.

The XAS spectra were collected from ~200 to ~800–1000 eV across the corresponding RE LIII–edges (6.716 and 9.844 keV). XANES and EXAFS data were analyzed using the HORAE package83, using FEFF version 9. After normalization and background removal, the EXAFS oscillations were fitted, using a starting model of Gd and Yb(CO3)(OH)84. The k4-weighted data were fitted in the range 2 to 9 Å–1. The fitting was done in R-space over the range 1.0 to 4 Å. EXAFS transmission signals were noisy and thus fluorescence data were used for the analyses. Aqueous references of Gd3+ and Yb3+ in 0.1 m HCl were used to determine the amplitude reduction factor S02 (1 for both elements). Fitted structural parameters include the coordination number Nc, interatomic distances Rf, and Debye–Wallner factor σf. The energy shift δE0. The fits were performed simultaneously with k-weighting of 1–3 so as to diminish correlations between N and σf.

ADF calculations. The geometries of the Gd cluster proposed in Fig. 4 were optimized by static quantum mechanical calculations using the ADF program48. The ADF program implements density functional theory. ß Atoms were described optimized by static quantum mechanical calculations using the ADF program85. The raw XAS spectra for Yb and Gd in 0.7 m Na2CO3 solutions at 200 °C and 80 MPa are available in the H2O20 European SSShade Solid Spectroscopy database (https://www.ssshade.de).

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