# Experimental alteration of allanite at 200°C: the role of pH and aqueous ligands



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**Abstract:** Allanite is a major host of rare earth elements (REEs) in the continental crust. In this study, reaction mechanisms behind allanite alteration are investigated through batch experiment runs on natural allanite grains in carbonate-bearing hydrothermal fluids at  $200^{\circ}$ C, with initial acidic (pH = 4) or alkaline (pH = 8) conditions and with different aqueous ligands (120 mmol kg<sup>-1</sup> of F, Cl, P or S). Time-series experiment runs in F-doped systems at different durations between 15 and 180 days reached a steady state at 120 days. The pH efficiently controls the allanite alteration process, with initial high pH, alkaline conditions being more reactive (75% alteration compared with 25% under acidic conditions). The ligand also significantly influences the alteration process under initial acidic conditions with the P-doped system (70%) almost non-reactive for the Cl- and S-doped systems (<5%). In the alteration rim, REEs are mainly redistributed in REE-bearing phases either as carbonates (F-doped) or phosphates (P-doped). The relatively flat REE-normalized patterns of the recovered experimental fluids suggest a fractionation of light rare earth elements (LREEs) over heavy rare earth elements (HREEs) during the course of the alteration reactions. It is proposed that secondary REE mineral precipitation at the reaction front creates a local disequilibrium in the solution and a steep chemical gradient promoting allanite dissolution and thus its alterability.

**Supplementary material:** Tables S1, S2, S3 corresponding to EMP data and analytical conditions, Figure S4 showing BSE images of the starting allanite material and Figure S5 presenting EMP compositions (REE versus Ca) of the Calcite and BGM experimental products are available at https://doi.org/10.6084/m9.figshare.c. 6699992

Allanite, a mineral of the epidote group with the ideal formula CaREEFe<sup>2+</sup>(Al, Fe<sup>3+</sup>)<sub>2</sub>( $Si_2O_7$ )(SiO<sub>4</sub>)O (OH), is a major REE carrier mineral in the continental crust, with preferential incorporation of the light REEs (LREEs: La to Gd) over the heavy REEs (HREEs: Tb to Lu + Y). Primary allanite occurs as an accessory phase in magmatic and metamorphic rocks (Gieré and Sorensen 2004 and references therein). It is a good petrological proxy and geochronometer for metamorphic processes (e.g. Engi 2017), magma sourcing (e.g. Anenburg et al. 2015) or mineralization under hydrothermal conditions (e.g. Pal et al. 2011). Allanite has also been described as the main primary REE and U source in supergene and hydrothermal systems (Caruso and Simmons 1985; Berger et al. 2008; Ichimura et al. 2020), reaching economic levels (Chabiron and Cuney 2001; Corriveau et al. 2007). Hydrothermal alteration of allanite is common (Poitrasson 2002) and often occurs as partial replacement of primary allanite by secondary REE minerals. These include fluorocarbonates (e.g. Middleton et al.

2013), phosphates (Berger *et al.* 2008) and silicates (Smith *et al.* 2002). Frequently, secondary Th-minerals are also described in association with allanite replacement (Middleton *et al.* 2013). As a main REE host, these alteration reactions are thus important for understanding REE mass transfer, with their economic implications as strategic metals. Furthermore, understanding associated actinide mobility in REE-rich hydrothermal systems is also crucial, because it can be decisive for REE mining (as by-products or nuclear waste).

It is widely accepted that the greater sensitivity of allanite to alteration, compared with that of epidote (Price *et al.* 2005), is partly due to its metamict state, which is caused by  $\alpha$ -particle bombardment damaging the structure, even for a low Th and U content (Ewing *et al.* 1987; Ercit 2002). The role of other inherent factors, such as the crystal chemistry of the allanite and the physicochemical properties of the fluid, remains poorly understood. While numerous examples of natural allanite alteration have been reported, its experimental reactivity in the presence

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59 of hydrothermal fluids has received little attention, 60 only at high pressure and high temperature condi-61 tions (Krenn et al. 2012) or as a product of monazite 62 and xenotime alteration (Budzyń et al. 2011, 2017). 63 In order to fill this gap, allanite alteration experi-64 ments have been conducted on natural homogeneous 65 crystalline grains in the presence of carbonate-66 bearing hydrothermal fluids doped with various 67 ligands (120 mM of F, Cl, P, S) under initial acidic 68 and high-pH alkaline conditions at 200°C and Psat 69 for durations of 15 to 180 days. The role of added 70 ligands was investigated for initial acidic conditions 71 (pH around 4 at room temperature) common under 72 hydrothermal conditions (Seward et al. 2014). The 73 investigated ligands are elements of importance for 74 REE mobility in hydrothermal systems due to strong 75 aqueous complexation at 200°C (Gammons et al. 76 1996). The kinetics of the alteration reactions were 77 investigated through time-dependent experiments 78 using both acidic and high-pH alkaline fluids (pH 79 = 8 at room temperature) in the presence of F. In 80 this study, the experimental alteration of allanite is strongly controlled by the fluid composition and 81 82 the precipitation of secondary REE minerals in the 83 form of fluorocarbonates and phosphates. 84

# Analytical methods and experimental procedure

# Starting material

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91 All experiments were performed using fragments 92 from a monocrystal of allanite-Ce (henceforth allanite) 93 from the Frontenac Formation in the Central Metase-94 dimentary Belt of the Greenville Orogen (Ontario, 95 Canada). Crystallization ages, based on associated 96 titanite U-Pb geochronology, are around 1157-97 1178 Ma (Mezger et al. 1993). The composition, 98 determined by electron probe microanalyser 99 (EPMA), is homogeneous and corresponds to an inter-100 mediate composition between ferriallanite and allanite 101 (general formula:  $Ca_{1-1.2}REE_{0.6-0.8}Al_{1.5-1.7}Fe^{3+}_{0.1-}$  $_{0.5}$ Fe<sup>2+</sup> $_{0.8-1.1}$ Mg<sub>0.1</sub>Si<sub>3.1-3.3</sub>O<sub>12</sub>(OH)) (Table S1, 102 103 supp. mat.). The content of radionuclides (such as 0. 104 36-0.79 wt% ThO2 and UO2) ranges mostly below 105 the detection limit (DL).

106The crystal was crushed manually and then 107 ground mechanically using a planetary micromill 108 Fritsch Pulverisette 7. To ensure maximized kinetics 109 and yet a suitable grain size for post-experimental 110 characterization, we selected an initial grain size of 111 20-50 µm after sieving. Traces of REE-carbonates in microcracks (observed by scanning electron 112 113 microscope but not detected on the X-ray diffraction 114 pattern) were removed by soaking the allanite pow-115 der in a 1 M acetic acid solution in an ultrasonic 116 bath for 10 min. After centrifugation (3500 rpm, 10 min), the solid residue was filtered through a  $2.7 \,\mu\text{m}$  glass fibre filter and dried overnight at  $50^{\circ}$  C. The material was stored in spectroscopic plastic tubes in the dark at ambient temperature.

# Experimental procedure

Experiments were conducted by reacting 150 mg of powdered allanite (Fig. S4, supp. mat.) with 1.5 ml of the aqueous solution (fluid/solid ratio = 10) in 3 ml Teflon cell reactors sealed into a steel autoclave without agitation ('static batch reactor') and placed in a multi-oven at 200°C ( $P_{sat} \approx 16$  bar or 16 bar  $+ pCO_2$ , when  $CO_2$  was added). However,  $pCO_2$ varies during alteration and these variations were not quantified. Acidic solutions with an initial pH = 4 were obtained by adding to ultrapure water 99. 9% certified pure carbonic ice (around 30 mg). For alkaline systems, ultrapure water was replaced by 1.5 ml of a 1 M NaHCO<sub>3</sub> solution (pH = 8.7, Lafay et al. 2014). These solutions were mixed with 120 mM (equivalent to the REE molar content in allanite) of F (introduced as solid NaF), P (as Na<sub>3</sub>-PO4, 12H2O), S (as Na2SO4) or Cl (as NaCl). An initial time series of experiments using NaF as ligand in acidic and alkaline systems was performed (15, 30, 60, 120 and 180 days) to investigate the kinetics of the reaction processes (Table 1). Experiments with other ligands were run for 120 days. At the end of each experiment, the sealed reactor was rapidly quenched in cold water. Recovered solutions were carefully collected with a syringe, filtered to remove solid residue (0.2 µm), diluted 5 times in ultrapure water slightly acidified with nitric acid and immediately stored at 4°C in an ion-free tube for further characterization. The residual solid was collected, dried at 60°C overnight, weighted and stored at ambient temperature. A fraction of each solid run product was mounted in epoxy resin and finely polished (mirror surface) for microscopic and electron microprobe analyses.

# Solid characterization methods

*X-ray diffraction and Rietveld refinement.* Mineral modal abundances of initial and post-experimental solids were characterized by X-ray diffraction (XRD) at ISTerre (Grenoble, France). Samples were ground in ethanol using a McCrone micronizing mill, oven-dried overnight and prepared as a randomly oriented mount. The XRD patterns were recorded with a Bruker D8 powder diffractometer equipped with a SolXE Si(Li) solid-state detector from Baltic Scientific Instruments using CuK $\alpha_1$  + 2 radiation. Intensities were recorded at 0.026°  $2\theta$  step intervals from 5 to 90° (10 s counting time per step). Eva Bruker software associated with the International Centre for Diffraction Data (ICDD)

Set	Exp.	kp. Carbonate source Initial Ligands (120 mm $pH$ kg <sup>-1</sup> )		Ligands (120 mmol $kg^{-1}$ )	Duration Aln (days) (%)		Secondary solid products				
B1	B1015	B1015 Carbonic ice <sup>1</sup> 4		NaF	15 93		Bsn (1.2%); Syn (1.5%); Flr (2.0%); Hem (2.1%)				
	B1030	Carbonic ice <sup>1</sup>	4	NaF	30	92	Bsn (2.2%); Syn (1.0%); Flr (2.5%); Hem (2.0%)				
	B1060	Carbonic ice <sup>1</sup>	4	NaF	60	95	Bsn (3.2%); Flr (3.6%); Hem (2.4%); Ana (4.9%)				
	B1120	Carbonic ice <sup>1</sup>	4	NaF	120	76	Bsn (5.1%); Syn (<1%); Flr (4.3%); Hem (2.2%); Ana (12%)				
	B1180	Carbonic ice <sup>1</sup>	4	NaF	180	77	Bsn (5.6%); Flr (5.8%); Hem (4.7%); Ana (7.3%)				
B2	B2015	$NaHCO_3^- 1M 1.5 ml$	8.7	NaF	15	36	Bsn (2.0%); Syn (1.0%); Pst (6.6%); BGM (8.9%); Cal (4.5%);				
							Hem (8.9%); Ana (22%); Sme (6.7%); Nsd (3.1%)				
	B2030	$NaHCO_3^- 1M 1.5 ml$	8.7	NaF	30	29	Bsn (3.1%); Syn (1.0%); Pst (8.9%); BGM (5.7%); Cal (4.5%);				
							Hem (8.4%); Ana (26%); Sme (7.7%); Nsd (4.1%)				
	B2060	$NaHCO_3^- 1M 1.5 ml$	8.7	NaF	60	31	Bsn (3.1%); Syn (1.7%); Pst (8.9%); BGM (9.4%); Cal (8.4%);				
							Hem (9.1%); Ana (24%); Sme (7.6%); Nsd (1.8%)				
	B2120	$NaHCO_3^- 1M 1.5 ml$	8.7	NaF	120	23	Bsn (5.2%); Syn (<1%); Pst (3.3%); BGM (5.9%); Cal (9.5%);				
							Hem (9.9%); Ana (31%); Sme (7.2%); Nsd (3.8%)				
B3	B3P120	Carbonic ice <sup>1</sup>	4	Na <sub>3</sub> PO <sub>4</sub> .12H <sub>2</sub> O	120	27	Mnz (15%); Hap (13%); Hem (6.8%); Ana (31%); Sme (6.3%)				
	B3S120	Carbonic ice <sup>1</sup>	4	Na <sub>2</sub> SO <sub>4</sub>	120	97	Anh (1.6%); Ana (1.6%)				
	B3C1120	Carbonic ice <sup>1</sup>	4	NaĈl	120	98	HI (2.0%)				

Table 1. Experimental conditions and solid products

<sup>1</sup>Carbonic ice is certified 100% pure CO<sub>2</sub> – around 30 mg (after the epoxy reactor closure). Estimated standard deviation is <2% for values >10% and does not exceed 10% for lower quantification. Aln, allanite; Ana, analcime; Anh, anhydrite; BGM, burbankite-group mineral; Bsn, bastnäsite; Cal, calcite; Chl, chlorite; Flr, fluorite; Hap, hydroxyapatite; Hem, hematite; Hl, halite; Mnz, monazite; Nsd, nordstrandite; Pst, parisite; Sme, smectite; Syn, synchysite. For a better reading comprehension with Aln (allanite), Ana designate analcime instead of the common abbreviation Anl. Source: abbreviations from Warr L.N. (2021).

175 Powder Diffraction File (PDF) database was used to 176 determine the modal composition of the powder on a 177 significant part of the recovered solid product for all 178 alteration experiments. This enables distinguishing 179 between the different REE minerals in the solid prod-180 uct. Rietveld refinement with Profex/BGMN soft-181 ware was then performed to precisely quantify mineral abundances. The quality of the Rietveld 182 refinement is assessed by the  $\chi^2$  factor, which lies 183 between 2.5 and 4 for all experiments. 184

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186 Scanning electron microscopy. The mineral distribu-187 tion and microstructure of the experimental solids were investigated by using a ZEISS Gemini 500 188 189 scanning electron microscope (SEM). The measure-190 ments were carried out in high-vacuum mode using a 191 high tension (EHT) of 3 kV for a working distance 192 (WD) between 3.4 and 4.8 mm. Samples were sput-193 tered with a 15 nm thick cover of Au-Pd. Comple-194 mentary investigations were performed using the 195 conventional environmental SEM Tescan Vega 196 3. The measurements were carried out in highvacuum mode ( $9.9 \times 10^{-9}$  bar), using an accelerat-197 198 ing voltage of 16 kV, with 90 nm spot size and 199 15 mm WD. Samples were sputtered with 20 nm of 200 carbon. The microscope was equipped with a 30 mm<sup>2</sup> Energy Dispersive X-Ray Spectroscopy 201 202 (EDS) manufactured by Rayspec with SamX's elec-203 tronic system and software. 204

205 Electron probe microanalyser. Quantitative chemi-206 cal analyses of initial and post-experimental allanite 207 and secondary products (when the grain size was suit-208 able) were carried out using a JEOL JXA-8230 209 EPMA equipped with five wavelength-dispersive 210 spectrometers (WDS) at ISTerre (Grenoble, France). 211 Analytical conditions were 15 kV acceleration volt-212 age, 12 nA beam current and 1 to 5 µm beam size 213 (details in Table S3, supp. mat.). The ZAF (atomic 214 number, absorption and fluorescence) correction pro-215 cedure was applied using the JEOL software for quan-216 titative analysis. The DLs range between 0.01 and 0. 217 04 wt% using the  $2\sigma$  criterion (Batanova *et al.* 2018). 218

219 Trace element analysis. Trace element analysis of 220 allanite was performed at the Institute of Geological 221 Sciences (University of Bern) using laser ablation 222 inductively-coupled plasma mass spectrometry 223 (LA-ICP-MS), which consisted of a Geolas Pro 224 193 nm ArF excimer laser coupled to an Elan 225 DRC-e quadrupole ICP-MS. A He-H2 gas mixture 226 (1 and 0.008 L/min, respectively) was used as the 227 aerosol transport gas. Allanite trace element analyses 228 were performed with laser beam diameters of 16, 24 229 and 32 µm, frequencies of 9 and 7 Hz and energy densities on the sample of  $5.0 \text{ J/cm}^2$ . Sample analy-230 ses were calibrated using GSD-1Gg and accuracy 231 232 was monitored using a reference glass NIST SRM 612 (Jochum *et al.* 2005, 2011). Data reduction was performed using the SILLS software package (Guillong *et al.* 2008) and LOD values obtained with the method of Pettke *et al.* (2011).

# Fluid characterization methods

Inductively-coupled plasma spectrometry. All recovered solutions were stored using metal-free tubes (from VWR). For an accurate quantification of trace elements, measurements were performed by ICP-MS using a Thermo Scientific XSERIES 2 spectrometer. Recovered solutions were diluted 3 times with 2% HNO<sub>3</sub> solution to a volume of 6 ml. Finally, 0.5 ml of an In solution was systematically added as an internal standard to correct for the drift of the ICP-MS. Collision cell technology (CCT) was used for some elements (Ca, Fe and Mn) in order to reduce polyatomic interferences with 5% H<sub>2</sub> in He gas. Measurement quality was evaluated by duplicating the measurement of standards that were analysed 5 times on the ICP-MS. Calculations to extract concentrations from the integration of peak signals were performed off-line. Reproducibility depends on the nature of the analysed element. It ranges from 1% to 19% for the REEs and from 3% to 30% for other trace elements. The DLs are defined as 3 times the average of the blank measurements. All data below the DL were excluded. Because the torch for ICP-MS was sheathed in guartz, the concentration of Si was then determined by atomic emission spectrometry (ICP-AES) using a Perkin Elmer Optima 3000 DV ICP-AES. Solutions were diluted 5 times using a 2% HNO<sub>3</sub> solution providing the minimum analysable volume. The same HNO3 solution was used to prepare standards and blanks. The analytical error for Si is 8%.

Capillary electrophoresis. The anionic content  $(Cl^{-}, SO_4^{2-}, F^{-}, PO_4^{3-}, HCO_3^{-})$  in the recovered solutions was quantified using a capillary electrophoresis (CE) system by WATERS<sup>®</sup>. The CE apparatus was equipped with a fuse capillary (75 µm i.d.  $\times$  60 cm total length) and a diode detector. The CE was operated at 20°C and at a voltage of 20 kV. Electrophoregrams were recorded with indirect mode detection at 254 nm using an Hg lamp. The background electrolyte (BGE) was composed of 4.6 mmol/LNa<sub>2</sub>CrO<sub>4</sub> solution, 0.5 mmol/LOFMOH<sup>TM</sup> from WATERS<sup>TM</sup> and an H<sub>3</sub>BO<sub>4</sub> solution (pH = 8.0). Prior to each measurement series, the capillary was conditioned by flushing with 1 mol/L NaOH and 0.1 mol/L NaOH (5 min each) followed by a 10 min flush with deionized water and a BGE solution (15 min flush). The capillary was preconditioned prior to each measurement by flushing the BGE for 1 min. All samples were measured in duplicate using hydrostatic injection mode.

#### Results

Allanite alteration as a function of the initial pH

The role of initial pH was investigated by time-series experiments in order to evaluate, together with the final alteration extent, the kinetics of the reaction. The experiments were performed for an F-doped system at a duration of between 15 and 180 days under initial acidic and high-pH alkaline conditions (Table 1).

The recovered experimental solids, characterized by XRD, displayed alteration evidence with secondary phases in the run products (Fig. 1). The extent of alteration was estimated on the basis of remaining allanite in the recovered samples. The constancy of the allanite composition between the final and initial materials (Table S1 - Supp. Mat) attested to no secondary allanite/epidote precipitation. The reaction progress was estimated from the allanite abundance. The run products' modal composition showed that the kinetics and extent of alteration greatly varied with the initial pH (Fig. 1). The alteration rate was much higher in the high-pH alkaline system, with 65% alteration reached within the first 15 days and a rapid stabilization at around 70-75% alteration from 30 to 120 days. In contrast, the extent of alteration in the acidic experiments was scarce after 15 days and only achieved 25% alteration for the longest durations (120 and 180 days). However, under both the acidic and high-pH alkaline conditions, with an F-doped solution, the same mineral phases grew at the expense of allanite (Fig. 1): analcime (Na-Al silicate), hematite (Fe<sub>2</sub>O<sub>3</sub>), and REE-bearing carbonates (Table 2). The REE-bearing carbonates, determined from XRD analyses, changed depending on the initial pH of the solution. They consisted of: (1) bastnäsite (general formula: LREECO3F) and synchysite (general formula: CaLREE(CO<sub>3</sub>)<sub>2</sub>F) under acidic conditions; and (2) a burbankite-group mineral (BGM, with general formula:  $(Na,Ca)_3(Sr,Ba,Ce)_3(CO_3)_5)$ and REE-fluorocarbonates with parisite (general formula:  $CaLREE_2(CO_3)_2F_2$ ) associated with bastnäsite and minor synchysite in the high-pH alkaline system. Besides these phases, fluorite (CaF<sub>2</sub>) appeared in the acidic experiments, while calcite (CaCO<sub>3</sub>), smectite and minor nordstrandite (general formula: Al(OH)<sub>3</sub>) crystallized in the high-pH alkaline system. High REE contents up to 2 wt% and 8 wt% (REE + Y)<sub>2</sub>O<sub>3</sub> were measured in fluorite and calcite, respectively (Table 2; Table S2 supp. mat.).

The microstructures of the recovered solids differed depending on the initial pH, which can be attributed to the reaction progress. In acidic systems, due to low alteration rate (15 days), the initial shape of the allanite grains, characterized by typical conchoidal edges, was mostly preserved while fluorite and analcime crystals grew around allanite from the bulk fluid (Fig. 2a). The allanite surface was pitted and covered by smectite. At this stage, REE-(fluoro)carbonates were restricted to inherited fractures in the allanite. A higher reaction extent (25%) in the acidic system (120 days) resulted in alteration rims surrounding some of the allanite grains. Their surfaces were characterized by a



**Fig. 1.** Evolution of the proportion of the starting material and run products, utilizing Rietveld refinement (in %) for (**a**) initial acidic and (**b**) high-pH alkaline F-doped systems. The group of REE-carb (REE-carbonate minerals) represents bastnäsite + synchysite in acidic system and parisite + bastnäsite + synchysite + the burbankite-group mineral in the high-pH alkaline system. These REE-carbonate minerals were identified by X-ray diffraction (XRD) analyses. Full lines represent the maximum allanite replacement in a state close to equilibrium. Numerical values are presented in Table 1. Aln, allanite; Ana, analcime; Cal, calcite; Fl, fluorite; Hem, hematite; Nrd, nordstrandite; Sme, smectite.

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System	Ana	Calcite		BGM		Fluorite		Anhydrite	
	$HCO_3^- + F^-$	$\mathrm{CO}_2 + \mathrm{PO_4}^{2-}$	$HCO_3^- + F^-$		$HCO_3^- + F^-$		$\rm CO_2 + F^-$		$\mathrm{CO}_2 + \mathrm{SO_4}^{2-}$
Days	120	120	120	120	120	120	120	180	120
SiO <sub>2</sub>	49.1	49.0							
$Al_2O_3$	24.5	24.1					0.22	0.32	
FeO	0.09	0.13	0.23	0.32	0.54		0.09	0.21	0.10
CaO			51.2	53.0	21.08	6.07	66.35	67.05	41.75
Na <sub>2</sub> O	15.8	15.2	0.62	0.39	0.37	1.66	0.5	0.51	0.05
$P_2O_5$		0.15	0.12				0.14	0.18	
$SO_3$									47.47
F			0.30		0.18	0.57	48.02	47.75	
$La_2O_3$			1.90	0.90	14.69	15.17	0.68	0.35	0.17
$Ce_2O_3$			4.13	2.30	23.51	30.52	1.20	0.69	0.51
$Pr_2O_3$			0.46	0.24	1.68	2.57	0.19	-	0.14
$Nd_2O_3$			1.16	0.60	3.56	6.35	0.23	0.12	0.16
$Sm_2O_3$									
$Gd_2O_3$		0.13	0.21						
$Dy_2O_3$					0.23				
$Y_2O_3$			0.12	0.11	1.00	0.00	0.12	1.50	0.61
SrO			0.25	0.26	1.02	0.68	1.62	1.59	0.61
ThO <sub>2</sub>			0.09	0.15	0.84	0.90	0.27		
PbO	00.50	00.00	(0.(2	50.07	(7 (2	0.13	00.41	00.00	00.04
$\Gamma_{\text{OEE}}$	89.50	88.00	00.03	38.27	07.03	04.37 54.60	99.41	98.08	90.94
$\sum (\text{KEE})^{\dagger}$	nd	0.15 nd	1.99	4.10	43.08 nd	34.00 nd	2.42	1.1/ nd	0.9/ nd
La/I Ca/Ca*+	n.a.	n.d.	1/.4	8./9 1.10	n.a. 1.14	n.u. 1 1 9	0.02	11.U. 2.84	11.d. 0.82
Ce/Ce·‡	n.a.	n.u.	1.07	1.19	1.14	1.10	0.0	2.04	0.02

**Table 2.** *Microprobe selected analyses of major run products (wt%)* 

Notes: Values in italic (%) column are mean relative errors, and  $2\sigma$  is the standard deviation; n.d. not determined.

\*Total is corrected for  $-O = F_2$  values.

 $\dagger \sum \text{REE}$  refers to the sum of  $(\text{REE} + \text{Y})_2 \text{O}_3$ .

 $\pm Ce/Ce^* CeN/(LaN*PrN)^{1/2}$ . Empty cells are concentrations below detection; n.d. not determined.

325 pervasive sawtooth-shaped reaction front, highlight-326 ing more extensive dissolution (Fig. 2b). Reaction 327 rims were sequentially composed of discontinuous 328 layers of hematite followed by nanocrystals with 329 the granular and acicular shape of REE-fluorocar-330 bonates penetrating through the dissolving allanite at the reaction front and filling newly-opened frac-331 332 tures (Fig. 2c).

333 In the high-pH alkaline run products, the allanite 334 grain shape is preserved on the microscale, sur-335 rounded by layers of complex microtextures. The 336 morphologies and textures described for the run 337 product from the 15-day experiment do not signifi-338 cantly change compared with the longer duration experiments. Allanite has penetrative reaction rims 339 340 that can reach up to 10 µm thick (Fig. 2d). They 341 were delimited by complex microstructures at the 342 reaction front, such as nanoscale etch pits or saw-343 tooth surfaces (Fig. 2e). Close to the reaction front, 344 REE-fluorocarbonates also precipitated at the sur-345 face, within the etch pits or in inherited microfrac-346 tures, with nanogranular, acicular or prismatic 347 shapes (Fig. 2e). The submicron size of these phases 348 prevented quantitative chemical analyses by EMPA.

The allanite surface was overlain with a thin layer of hematite crystals of around 10 to 500 nm in size. Smectites were also ubiquitous and clearly identifiable by their fibrous (honeycomb) morphology and platelet growth oriented towards the fluid. The BGMs occur as microscale euhedral crystals that randomly precipitated from the reactive bulk fluid (decoupled from the allanite replacement products). They are mainly prismatic and more or less elongated with a size generally varying from c. 5 to 30 µm in size (Fig. 2f). The BGM crystals commonly display a zonation with respect to the REE content which is anti-correlated with respect to Ca (Fig. S5, supp. mat.). They have a higher LREE content than the initial allanite, but with Sm and Y below the DL (Table 2). Calcite precipitates as aggregates of euhedral crystals 10 to 20 microns in size or intergrown with relic allanite (Fig. 2f).

# Allanite alteration as a function of ligands

To investigate the effects of ligands on the alteration of allanite, experiments were run under the initial acidic conditions with P-doped, S-doped and

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**Fig. 2.** Scanning electron microscopy images using backscattered electron (BSE) imaging of allanite and secondary products from acidic (a, b and c) and high-pH alkaline (d, e and f) F-doped runs for different times. (a) Relatively unaltered allanite with fluorite and analcime growing along the allanite grain rims. (b) Relatively unaltered allanite (top left) with internal fractures filled by REE phases along with more reacted allanite (bottom right) with sawtooth-shaped grain rims after 120 days. (c) Magnification of (b) showing reaction interface with allanite composed of granular nanometric REE-fluorocarbonates replacing allanite. (d) Allanite grain displaying edge pitting with a porosity that progresses anisotropically to the grain centre. Edges are rimmed by saponite whiskers, which probably formed during quenching. (e) Detail of an allanite and needle-like shape, along with hematite and saponite. Porous cavities are filled with REE-fluorocarbonates. (f) Cluster of burbankite-group minerals with a large crystal of calcite growing in the interstitial space between the minerals. Aln, allanite; Ana, analcime; Bgm, burbankite-group mineral; Cal, calcite; FIr, fluorite; Hem, hematite; REE-FCb, REE-fluorocarbonates (bastnäsite, parisite, synchysite); Sap, saponite; Sme, smectite.

Cl-doped solutions for 120 days (Table 1). Similar to that observed for the pH, the reaction progress was also significantly affected by the ligands (Fig. 3). The most reactive system was the P-doped one, which achieved 73% allanite alteration. This reaction extent was similar to that seen in the F-doped system under high-pH alkaline conditions (75% of reaction), but much higher than that obtained under similar acidic conditions (23% of reaction) over the same duration (120 days). The S- and Cl-bearing systems were less reactive compared with the others, with less than 5% secondary minerals.

In the reactive P-doped experiments, analcime and hematite were present in major proportions in the recovered solid, as for the F-doped system. Smectite was also an alteration product of allanite, as in the high-pH alkaline system. The main difference between the P- and F-doped systems was the nature of the mineral phases that accommodated REEs and Ca, such as monazite (general formula: LREEPO<sub>4</sub>, 21% of solid product) and hydroxyapatite (general formula: Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, 18% of solid product). The alteration microstructures were similar to those previously described in the F-bearing system. Allanite was largely affected by dissolution, as illustrated by the numerous etch pits scattered on the surface (Fig. 4a). Allanite alteration resulted in thick reaction rims made up of a nanomixture of monazite-hematite and hydroxylapatite with an apparent microscale spatial distribution from the reaction front towards the reactive fluid (Fig. 4b). Submicron monazite crystals precipitated directly at the interface with the allanite (Fig. 4c). Similar to the F-doped systems, hematite occurred as a thin, quasi-continuous corona around the allanite grains. Finally, euhedral micrometric-sized grains

100 Aln 90  $\square$ Ana Modal composition (%) 80 Hem Nrd 70 **REE-carb** 60 Mnz 50 FI · · · ] 40 ... Cal 30 Hap <del>+</del> + 20 Anh ...... 10 ΗI Sme  $\bigtriangledown$ 0 F-doped F-doped P-doped S-doped Cl-doped Alkaline Acidic

**Fig. 3.** Comparison of mineral modal compositions after 120 days for the F-doped high-pH alkaline systems and the F-, P-, S- and Cl-doped systems (respectively shown in columns), which were identified by X-ray diffraction (XRD) and Rietveld refinement (in %). Aln, allanite; Ana, analcime; Anh, anhydrite; Cal, calcite; Fl, fluorite; Hl, halite; Hap, hydroxylapatite; Hem, hematite; Mnz, monazite; Nrd, nordstrandite; REE-Carb, REE-fluorocarbonates; Sme, smectite.

of hydroxylapatite, mixed with smectite filaments which probably formed during the quench, are seen along the outer edge of the alteration rim (Fig. 4b, c). Analcime remains the major alteration phase, and takes the form of large grains embedding relict allanite along the allanite reaction rims (Fig. 4a).

# Recovered fluid chemistry

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Beside solid product characterization, the fluid composition was also analysed for each experiment (Table 3; Fig. 5). While the fluid compositions can be modified by internal and external factors through the course of the reaction (water consumption by alteration products, permeability limits of the Teflon reactors, quenching effects), the reproducibility of the results supports the general qualitative significance of the fluid chemistry dataset.

In time-series experiments, the final fluid compositions indicated that the experiments under high-pH alkaline conditions were already in a steady-state (approaching constant concentrations of all measured elements with time) after 15 days (Fig. 5b), which is in agreement with the mineralogical results. In the initially acidic system, elemental concentrations of Ca, REE, Th and U evolved until reaching a near plateau only after 120 days (Fig. 5a). At that stage, Si, Al and Ca reached similar concentrations in the F-doped acidic and high-pH alkaline systems, whereas REEs, U, and Th were lower in the acidic



Fig. 4. Secondary electron (SE) and backscattered electron (BSE) images of allanite alteration in an acidic P-doped system. (a) Typical allanite grain with eroded grain boundaries and with large crystals of analcime partially embedding the other secondary minerals. (b) Continuous reaction front composed of monazite replacing allanite and a thin (<200 nm) rim of hematite outlining the original shape of the allanite. Outwards from the reaction front is rimmed by euhedral hydroxyapatite (Hap) that precipitated in the interstitial space between filaments of saponite (Sap). (c) Detail from (b) showing that the abundance of the nanosize monazite increases in the vicinity of the eroded allanite. Aln, allanite; Ana, analcime; Cal, calcite; Hem, hematite Mnz, monazite; Sme, smectite.</li>

							Experime	ntal set				
System	$CO_2 + F^-$					$NaHCO_3 + F^-$				$\mathrm{CO}_2 + \mathrm{PO_4}^{2-}$	$\mathrm{CO}_2 + \mathrm{SO_4}^{2-}$	$CO_2 + Cl^-$
<b>Experiment</b> <b>Days</b> $mol/kg \times 10^{-4}$	B1015 15	B1030 30	B1060 60	B1120 120	B1180 180	B2015 15	B2030 30	B2060 60	B2120 120	B3P120 120	B3S120 120	B3Cl120 120
<sup>1</sup> Si Al Fe Ca	38.0 1.20	15.8 1.35	13.1 0.51	16.8 5.88 0.11	16.0 5.76 0.069	19.4 2.40 0.21 0.14	22.3 2.06 0.20 0.14	25.4 1.50 0.16 0.16	43.0 0.50 0.12 0.17	62.1 2.48 0.045 0.082	14.9 0.35	27.4 0.11 0.077
Respective ligands HCO <sub>3</sub> <sup>-</sup> $mol/kg \times 10^{-8}$	950	976	869	668	598	1781 10 980	10 791	1412 7132	1211 6604	2489	14//	2877
Y La Ce Pr Nd Sm Eu Gd Tb	0.07	0.25 0.25	0.40 0.35 0.033	4.34 4.49 6.48 0.48 1.97 0.24 0.21 0.45 0.0031	0.20 1.51 5.28 0.23 0.52 0.037 0.077	140 30.3 81.4 9.50 37.2 9.26 1.69 9.80 1.70	175 24.8 73.5 11.3 45.6 11.4 2.10 12.1 2.15	227 41.6 94.2 12.5 49.1 11.8 2.22 13.8 2.54	297 52.9 75.1 14.8 55.6 12.7 2.59 15.3 2.85	4.85 15 8.04 1.14 5.23 0.44 0.36 0.76 0.013	0.26 4.90 1.92 0.27 0.94 0.04 0.02 0.06 0.0022	1.27 2.88 0.93 0.25 4.26 0.19 0.20 0.25 0.0035
Dy Ho Er Tm Yb Lu Th	16.0	0.0077	0.033	1.13 2.25 3.26 0.24 8.76	0.24	10.9 2.45 8.89 1.64 13.6 2.69 349 2795	14.0 3.15 11.7 2.12 17.6 3.47 216 2972	16.7 3.84 13.5 2.33 17.6 3.31 304 2570	19.6 4.55 16.6 2.59 20.2 3.59 193 3120	1.21 2.15 2.67 0.30 6.54	0.045 0.073 0.094 0.025	0.38 0.67 1.05

**Table 3.** Composition of fluids after allanite batch experiments

Respective ligands refer to the anion initially used for the experiments (measured as  $F^-$ ,  $PQ_4^{3-}$ ,  $SQ_4^{2-}$ ,  $CI^-$ ). Maximum analytical error is <4% for Si, La, Ce, Pr, Ho, Tm; <8% for Al, Fe, Eu, Lu, Y, Th; 9% for U; <15% for Nd, Sm, Yb; <19% for Gd, Eu; 34% for Ca. Empty cells are concentrations below detection.



**Fig. 5.** Major elements, REE and actinide concentrations (log) in experimental fluids for the time-series F-doped experiments in the acidic system (**a**), high-pH alkaline system (**b**), and in the 120 day experiments for the P-, S- and Cl-doped systems (**c**).

system compared with the high-pH alkaline system by 2 to 4 orders of magnitude.

In the P-doped system, which was the most reactive system under acidic conditions, elemental concentrations are similar to the concentrations of the F-doped in the acidic system at 120 days (Fig. 5c). In the unreactive Cl- and S-doped systems, Si and REE concentrations are comparable with those measured in the F- and P-doped systems under acidic conditions. The other elements were generally at lower concentrations.

In terms of REEs, the chondrite-normalized patterns plot relatively flat for the high-pH alkaline systems (Fig. 6). In acidic fluids, patterns plot also relatively flat but with a slight depletion in Sm, Gd and Dy, with no dependence on the ligand.

# Discussion

# Allanite alteration mechanisms

572 In the batch experiment runs (Table 1), the alteration 573 of allanite ranges from a limited (<5%) up to an 574 extensive (77%) degree, depending on the fluid chem-575 istry after 120 days. The pH has the first effect on the 576 alteration of allanite, as the kinetics for the high-pH 577 alkaline system are fastest (65%) after 15 days, and 578 the more advanced (70-75%) after 120 days in the 579 two time-series experiment runs conducted in an 580 F-doped system. Under acidic conditions, the nature of the ligand significantly affects the extent of alteration. The presence of P enhances the allanite alterability, reaching 73% of the reaction rate after 120 days, while allanite reactivity is minor in the Cl- or S-doped systems (<5%). F-doped systems display moderate alteration at the same duration (25%).



Fig. 6. Chondrite-normalized REE spectra of fluids after 120 days from the slightly acidic, F-doped, Pdoped, S- doped, Cl-doped and time-series, high-pH alkaline, F-doped experiments. The HREEs with odd numbers are below the detection limits (DLs) or have been removed from the diagram because of artificial anomalies due to being close to the DLs (Table 1). The lanthanide tetrad effect is discernible within the LREEs for the slightly acid experiments (dashed lines).

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Higher allanite reactivity in a high-pH alkaline fluid shows that high-pH fluids efficiently promote silicate dissolution rates, while dissolution is more limited in near neutral fluids (Hellmann 1994). This effect is also demonstrated for epidote group minerals (Rose 1991). Phosphorus seems to have a similar effect on allanite, though with a lower extent of alteration.

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588 In the most reactive systems (high-pH alkaline 589 and P-doped conditions), the alteration of allanite 590 is promoted by increasing dissolution coupled with 591 the precipitation of other minerals. On the one 592 hand, dissolution can be promoted due to a solubility 593 change for the dissolving elements in the bulk solu-594 tion, by modifying element complexation, the con-595 centration in the solution and the chemical affinity 596 per the dissolution reaction between allanite and 597 the fluid. On the other hand, the mineral microstruc-598 tures evidenced here also point to the crucial role of 599 secondary precipitation on the alteration rate. Alter-600 ation microstructures from highly altered experiment 601 products show well-developed dissolution features 602 (etch pits, fractures, porosity) with a penetrative replacement by an alteration rim made up of second-603 604 ary minerals with a complex mineralogical zonation. 605 General preservation of the initial pristine shape of 606 allanite suggests a mechanism of replacement by 607 interfacially-coupled dissolution-precipitation (Put-608 nis 2002; Putnis and Putnis 2007; Harlov et al. 609 2011; Hellmann et al. 2012), which indicate disequi-610 librium between the solid and the fluid (Putnis 2009; 611 Ruiz-Agudo et al. 2014). Such alteration processes can lead to an apparent incongruent dissolution due 612 to a preferential precipitation of low solubility 613 614 phases (with different composition than the altered phase) at the alteration interface (Ruiz-Agudo et al. 615 616 2012). Such apparent incongruent dissolution has 617 already been demonstrated for epidote dissolution 618 (Kalinowski et al. 1998), and seems also to apply 619 here to allanite alteration as seen by the mineralogi-620 cal gradation from the reaction front to the bulk sol-621 ution. In the reaction rim, the precipitation of 622 submicron, low-solubility secondary phases takes 623 in elements from the solution and changes their con-624 centration at the reaction interface. This is the case 625 for hematite, which nucleates as a thin rim at the 626 interface with the allanite. This is particularly true 627 for REE mineral phases (REE-fluorocarbonates or 628 monazite, depending on the ligand), which also 629 occur as a discontinuous rim of nanoscale crystallites 630 propagating anisotropically inwards into the pristine 631 grain and along fractures in the allanite. The growth 632 of other main phases with a higher solubility in the 633 solution, e.g. analcime, fluorite and calcite, is spatially decoupled from the alteration interface with 634 635 precipitation from the bulk solution as larger euhe-636 dral crystals. Such precipitation from the bulk fluid 637 away from the rim of the dissolving mineral have 638 been described in other alkaline systems (Lafay

*et al.* 2014, 2018). In the batch experiment runs, the preferential precipitation of REE phases at the reaction front is proposed to efficiently maintain significant dissolution rates by producing steep concentration gradients in the fluids close to the reactive surface, which act to renew the solutions (Frugier *et al.* 2008; Ruiz-Agudo *et al.* 2016).

Coupled with the chemical gradient at the interface, the precipitation of REE mineral phases will further strongly modify the geometry of the reaction front. The complex microstructures at the reaction interface, with etch pits, indentations and secondary fractures, are the result of reaction-induced fracturing due to molar volume change and the force of crystallization during the replacement of allanite by secondary phases (e.g. Jamtveit *et al.* 2009; Lafay *et al.* 2018). This increase of the reactive surface also enhances allanite dissolution.

In the two non-reactive systems (Cl- and Sdoped), there was limited precipitation of secondary phases (<5%). In batch experiment runs, this drop in the dissolution rates can occur when element concentrations progressively approach saturation in the fluid or when precipitation of an inert passivation layer isolates the reacting mineral from the reactive fluid (Montes-Hernandez et al. 2012). In unreactive systems, secondary precipitation observed at the grain surface is sufficiently low such that allanite remains accessible to the fluid throughout the experiment runs. In contrast, concentrations in fluids similar to those of reactive systems indicate that they reach conditions approaching saturation. Since precipitation of analcime and hematite is not chemically restricted, the only limiting factor here appears to concern the stability of the REE phases.

In the investigated reactive systems, the precipitation of secondary REE phases is thus proposed to be the main driving force behind allanite alteration by lowering the activities of REEs in the interfacial fluid. In the absence of efficient REE mineral precipitation (Cl- and S-doped) at the allanite interface, 'steady state' concentrations measured in the bulk fluid are assumed to be more readily reached, thus decreasing reaction rates. Therefore, allanite alteration remains low. These results are in good agreement with natural observations. The secondary, experimental REE mineral phases, i.e. REE-fluorocarbonates and/or REE-phosphates, are typical of low-temperature alteration products (e.g. Berger *et al.* 2008; Ondrejka *et al.* 2018).

# REEs, Th, and U mobility and fractionation during allanite alteration

In all reactive systems, comparison between a simple mass balance calculation from the low REE concentrations in the recovered fluid and the allanite composition and alteration rates indicate that the REEs 639 released during alteration are mostly in secondary 640 phases. An allanite alteration of 70% would provide 641 100 µmol of the REE released in high-pH alkaline 642 experiment runs. However, the REE content in the 643 final fluids are 4 orders of magnitude below. The 644 main REE minerals (REE-carbonates or REE-645 phosphates identified by XRD) occur as submicronic 646 crystals in the alteration rim, preventing accurate 647 determination of their REE content. Based on the 648 theoretical compositions of REE-fluorocarbonates 649 and monazite, along with their XRD modal abun-650 dance, rough mass balance calculations confirm that they are a major sink for the REEs released by 651 allanite. In the P-doped system, the hydroxylapatite 652 653 grains are also too small to determine their REE con-654 tent, though it could be up to a few wt% (Budzyń 655 et al. 2017).

656 While the composition of secondary phases in the 657 altered rim cannot be analysed precisely for their 658 REE content, minerals precipitating from the bulk 659 fluid are large enough for evaluating their REE con-660 tent by EPMA. In F-doped systems, fluorite represents 25% of the secondary products and can 661 662 incorporate up to 1-2 wt% REE<sub>2</sub>O<sub>3</sub>. The REE con-663 tent in fluorite has been extensively studied in hydro-664 thermal systems (Möller et al. 1998; Schwinn and 665 Markl 2005; Schönenberger et al. 2008; Gob et al. 666 2011), in economical REE deposits, such as the 667 Bayan Obo Complex (Xu et al. 2012) or by thermodynamic modelling (Kolonin and Shironosova 668 669 2007). It shows that REEs in fluorite, while 670 extremely variable, can reach up to >10 wt% in 671 yttrofluorite (Pekov et al. 2009). Although a coupled 672 substitution involving Na is often considered preponderant for incorporating the REEs in fluorite, i.e.  $\text{REE}^{3+} + \text{Na}^+ \leftrightarrow 2 \text{ Ca}^{2+}$  (Möller *et al.* 1998), 673 674 675 there is no real correlation between the REE and 676 Na contents in the fluorite from these experiments, 677 despite the high Na concentrations. The BGM (iden-678 tified from XRD) precipitating from the bulk fluid 679 also accommodates significant REEs, but with Na 680 concentrations that are significantly lower compared 681 with burbankite sensu stricto (Belovitskaya and Pekov 2004). The BGM grains are zoned with a typ-682 683 ical hourglass sector zoning, suggesting crystallo-684 graphic control on REE incorporation (Fig. 2f). 685 Integration of the REEs is directly correlated to the 686 size and geometry of the crystallographic sites, 687 which favours the LREEs in calcic minerals such 688 as tourmaline (van Hinsberg et al. 2010). Burbankite is a hydrothermal mineral encountered in alkaline 689 690 pegmatites and associated carbonatites (Zaitsev 691 et al. 2002). In experiments, the precipitation of BGMs is probably favoured by the Na concentration 692 693 in the fluid. Finally, the REE concentrations in the 694 calcite are considerably higher than those normally 695 encountered in nature (Stipp et al. 2006) but are ther-696 modynamically stable (Rimstidt et al. 1998), as has been experimentally demonstrated (Toyama and Terakado 2014; Gabitov *et al.* 2017). In calcite, two coupled substitution mechanisms are proposed (Perry and Gysi 2018): REE<sup>3+</sup> + Na<sup>+</sup>  $\leftrightarrow$  2Ca<sup>2+</sup> and 2REE<sup>3+</sup> +  $\Box \leftrightarrow$  3Ca<sup>2+</sup> (square represents site vacancies). The composition of the calcite produced in these experiments indicates that both mechanisms occur under the experimental conditions of this study (Fig. S5, supp. mat.).

# REE fractionation between fluid and solid

Though the REEs are mainly stored in secondary phases, minor REE concentrations have been recovered in the fluids. Though precise quantitative fluid concentrations are limited by the batch experimental setup, our qualitative results clearly indicate a significant difference in REE fractionation between the solid and the fluid, whatever the pH and the complexing ligands. Experimental fluids display relatively flat chondrite-normalized REE spectra, indicating that the experimental alteration of allanite ultimately produces a fluid enriched in HREEs relative to the initial LREE-rich allanite composition. This implies in turn the preferential fractionation of LREEs over HREEs in the secondary mineral precipitates relative to the fluid. This is in good agreement with the limited incorporation of HREEs in fluorocarbonates and monazite, as demonstrated for T <450°C (Heinrich et al. 1997; Poitrasson et al. 2000; Janots et al. 2008; Budzyń et al. 2010, 2017; Grand'Homme et al. 2018). Also, secondary minerals that precipitate from the bulk fluid (calcite, fluorite, BGM) are enriched in LREEs over HREEs but with lower La/Y compared with allanite, again supporting the fractionation of the LREEs over the HREEs in the bulk fluid compared with fluid at the reaction front. In these secondary mineral phases, the Y values are typically at the same level as in allanite, which suggests that the HREEs are more mobile compared with the LREEs, as seen in numerous natural environments, e.g. during monazite alteration (Hentschel et al. 2020).

The fluid compositions measured in this study have numerous implications for REE deposits. Here the flat or gently incurved REE-normalized pattern indicates that REEs are not released congruently, but that speciation in the fluids or precipitation of secondary products favours HREE fractionation over LREEs in the fluid compared with the initial allanite composition.

# Th and U behaviour during allanite alteration

Actinides seem to mostly partition into the fluid as opposed to secondary minerals. Simplified qualitative calculations show that virtually all the U released by allanite accumulates in the fluid under

697 these conditions. Actinide concentrations are higher 698 in the high-pH alkaline system (with higher carbon-699 ate activities) than in the acidic system. This agrees 700 well with studies that show that the solubility of acti-701 nides increases with the concentration of the aqueous 702 carbonate or phosphate ligands (Rai et al. 1994; San-703 dino and Bruno 1998). Recent studies also show that 704 actinides can be highly mobile in the presence of 705 ligands such as S-, Cl- or F-complexes for tempera-706 tures close to 200°C (Nisbet et al. 2018, 2019; Mig-707 disov et al. 2019). In the experimental runs under 708 initial acidic conditions, U release is at least 1 to 2 709 orders of magnitude lower than that under high-pH 710 alkaline conditions. Regardless of the chemical sys-711 tem, Th is systematically lower in the fluid compared 712 with U, while it is higher in the starting allanite, indi-713 cating U/Th fractionation during allanite alteration. 714 According to Rai et al. (1994), ThO<sub>2</sub> solubility is 715 higher than that of UO<sub>2</sub>, suggesting that tetravalent 716 U is likely oxidized in its hexavalent state during 717 the allanite alteration reaction. Preferential incorpo-718 ration of tetravalent Th in secondary REE mineral 719 phases may in turn enhance Th/U fractionation 720 between the fluid and secondary products, as 721 observed in natural monazite and allanite precipi-722 tated from hydrothermal systems (Janots et al. 2012). 723

# Conclusions

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Allanite has a complex composition and its experimental alteration under low temperature conditions results in a high diversity of mineralogical assemblages and microstructures. Allanite can be highly reactive in certain fluids, reaching more than 75% of alteration at 200°C and  $P_{sa} \approx 16$  bar, after only 15 days. The pH and the nature of the complexing ligand added to the fluid will strongly affect the alteration rate of the allanite, with the high-pH alkaline system being the most reactive. In carbonate-bearing fluids, F and P will promote allanite alteration, while allanite shows negligible alteration in the presence of Cl and S. The main driving force behind the alteration of allanite resides in the precipitation at a reactive front of secondary REE minerals, whose chemistry depends on the complexing ligands. These precipitated minerals maintain a local disequilibrium close to the reaction interface between the fluid and the solid, thus sustaining allanite dissolution. Though REEs are mostly stored in the secondary mineral phases, there is a preferential fractionation of the LREEs over the HREEs into the solid compared with the fluid, while U is strongly partitioned into the fluid.

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Author contributions AD: data curation (lead), formal analysis (lead), investigation (lead), writing – original draft (lead); A-LA: supervision (equal), writing – review and editing (equal); EJ: supervision (equal), writing – review and editing (equal); GM-H: conceptualization (supporting); NF: data curation (supporting); PL: data curation (equal); VM: data curation (supporting).

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