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

3

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12

13

## 14 **Abstract**

15 Allanite is a major host of rare earth elements (REE) in the continental crust. In this study, reaction  
16 mechanisms behind allanite alteration are investigated through batch experiment runs on natural  
17 allanite grains in carbonate-bearing hydrothermal fluids at 200 °C, with initial acidic (pH=4) or  
18 alkaline (pH=8) conditions and with different aqueous ligands (120 mM of F, Cl, P or S). Time-  
19 series experiment runs in F-doped systems at different durations between 15 and 180 days reached  
20 a steady state at 120 days. The pH efficiently controls the allanite alteration process, with initial  
21 high pH, alkaline conditions being more reactive (75% alteration compared to 25% under acidic  
22 conditions). The ligand also significantly influences the alteration process under initial acidic  
23 conditions with P-doped system (70%) almost non-reactive for the Cl- and S-doped systems (<  
24 5%). In the alteration rim, REE are mainly redistributed in REE-bearing phases either as  
25 carbonates (F-doped) or phosphates (P-doped). The relatively flat REE-normalized patterns of the  
26 recovered experimental fluids suggest a fractionation of LREE over HREE during the course of  
27 the alteration reactions. It is proposed that secondary REE-mineral precipitation at the reaction  
28 front creates a local disequilibrium in the solution and a steep chemical gradient promoting allanite  
29 dissolution and thus its alterability.

30

31 **Keywords:** allanite; hydrothermal alteration; rare earth elements (REE); batch experiment;  
32 mineral replacement; REE-fluorocarbonate; monazite

## 33 **1 Introduction**

34           Allanite, a mineral of the epidote group with the ideal formula  $\text{CaREEFe}^{2+}(\text{Al},$   
35  $\text{Fe}^{3+})_2(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$ , is a major REE-carrier mineral in the continental crust, with  
36 preferential incorporation of the light REE (LREE: La to Gd) over the heavy REE (HREE: Tb to  
37 Lu + Y). Primary allanite occurs as an accessory phase in magmatic and metamorphic rocks (Gieré  
38 and Sorensen, 2004 and references therein). It is a good petrological proxy and geochronometer  
39 for metamorphic processes (e.g. Engi et al., 2017), magma sourcing (e.g. Anenburg et al., 2015),  
40 or mineralisation under hydrothermal conditions (e.g. Pal et al., 2011). Allanite has also been  
41 described as the main primary REE and U source in supergene and hydrothermal systems (Caruso  
42 and Simmons, 1985; Berger et al., 2008; Ichimura et al., 2020), reaching economic levels  
43 (Chabiron and Cuney, 2001; Corriveau et al., 2007). Hydrothermal alteration of allanite is  
44 common (Poitrasson et al., 2002) and often occurs as partial replacement of primary allanite by  
45 secondary REE-minerals. These include fluorocarbonates (e.g. Middleton et al., 2013),  
46 phosphates (Berger et al., 2008), and silicates (Smith et al., 2002). Frequently, secondary Th-  
47 minerals are also described in association with allanite replacement (Buda and Nagy, 1995;  
48 Middleton et al., 2013). As a main REE-host, these alteration reactions are thus important for  
49 understanding REE mass transfer, with their economic implications as strategic metals.  
50 Furthermore, understanding associated actinide mobility in REE-rich hydrothermal systems is  
51 also crucial, because it can be decisive for REE-mining (as by-products or nuclear waste).

52           It is widely accepted that the greater sensitivity of allanite to alteration, compared to that  
53 of epidote (Price et al., 2005), is partly due to its metamict state, which is caused by  $\alpha$ -particle  
54 bombardment damaging the structure, even for a low Th and U content (Ewing et al., 1987; Ercit,

55 2002). The role of other inherent factors, such as the crystal chemistry of the allanite and the  
56 physicochemical properties of the fluid, remains poorly understood. While numerous examples  
57 of natural allanite alteration have been reported, its experimental reactivity in the presence of  
58 hydrothermal fluids has received little attention, only at high pressure and high temperature  
59 conditions (Krenn et al., 2012) or as a product of monazite and xenotime alteration (Budzyń et  
60 al., 2011; 2017). In order to fulfil this gap, allanite alteration experiments have been conducted  
61 on natural homogeneous crystalline grains in the presence of carbonate-bearing hydrothermal  
62 fluids doped with various ligands (120 mM of F, Cl, P, S) under initial acidic and high pH alkaline  
63 conditions at 200 °C and  $P_{\text{sat}}$  for durations from 15 to 180 days. The role of added ligands was  
64 investigated for initial acidic conditions, (pH around 4 at room temperature), common under  
65 hydrothermal conditions (Seward et al., 2014). The investigated ligands are elements of  
66 importance for REE mobility in hydrothermal systems due to strong aqueous complexation at 200  
67 °C (Gammons et al., 1996; Migdisov and Williams-Jones, 2002, 2008; Migdisov et al., 2009).  
68 The kinetics of the alteration reactions were investigated through time-dependent experiments  
69 using both acidic and high pH alkaline fluids, (pH = 8 at room temperature), in the presence of F.  
70 In this study, the experimental alteration of allanite is strongly controlled by the fluid composition  
71 and the precipitation of secondary REE-minerals in the form of fluorocarbonates and phosphates.

72

## 73 2 Analytical methods and experimental procedure

### 74 2.1 Starting material

75 All experiments were performed using fragments from a monocrystal of allanite (~~20 mm~~  
76 Ce (henceforth allanite)) from the Frontenac formation in the Central Metasedimentary Belt of the  
77 Greenville Orogen (Ontario, Canada). Crystallisation ages, based on associated titanite U-Pb  
78 geochronology, ~~range from~~ are around 1157 - 1178 to 1157 Ma (Mezger et al., 1993). The  
79 composition, determined by EPMA, is homogeneous, and corresponds to an intermediate  
80 composition between ferriallanite and allanite, with a general formula:  $\text{Ca}_{1-1.2}\text{REE}_{0.6-0.8}\text{Al}_{1.5-}$   
81  $_{1.7}\text{Fe}^{3+}_{0.1-0.5}\text{Fe}^{2+}_{0.8-1.1}\text{Mg}_{0.1}\text{Si}_{3.1-3.3}\text{O}_{12}(\text{OH})$  (Table S1, supp. mat.). Radionuclides contents ~~are~~ range  
82 such as 0.5336-0.79 wt.% ThO<sub>2</sub> and ~~0.06 wt.%~~ UO<sub>2</sub> mostly below detection limit.

83 The crystal was crushed manually and then grinded mechanically using a planetary micro-  
84 mill Fritsch Pulverisette 7. To ensure maximized kinetics and yet a suitable grain size for post-  
85 experimental characterization, we selected an initial grain size of 20-50 μm after sieving. Traces  
86 of REE-carbonates in micro-cracks (observed by SEM but not detected on X-ray diffraction  
87 pattern) were removed by soaking the allanite powder in a 1M acetic acid solution in an  
88 ultrasonic bath for 10 min. After centrifugation (3500 rpm, 10 min), the solid residue was filtered  
89 through a 2.7 μm glass fibre filter and dried overnight at 50°C. The material was stored in  
90 spectroscopic plastic tubes in the dark at ambient temperature.

91

## 92 2.2 Experimental procedure

93 Experiments were conducted by reacting 150 mg of powdered allanite (Fig. S4, supp. mat.)  
94 with 1.5 mL of the aqueous solution (fluid/solid ratio = 10) in 3 mL Teflon cell reactors sealed  
95 into a steel autoclaves without agitation (“static batch reactor”) and placed in a multi-oven at  
96 200 °C ( $P_{\text{sat}} \approx 16$  bar or 16 bar +  $p\text{CO}_2$ , when  $\text{CO}_2$  was added). However,  $p\text{CO}_2$  varies during  
97 alteration and these variations were not quantified. Acidic solutions with an initial pH = 4 were  
98 obtained by adding to ultrapure water 99.9% certified pure carbonic ice (around 30 mg). For  
99 alkaline systems, ultrapure water was replaced by 1.5 mL of a 1 M  $\text{NaHCO}_3$  solution (pH = 8.7,  
100 Lafay et al., 2014). These solutions were mixed with 120 mM<sub>7</sub> (equivalent of the REE molar  
101 content in allanite<sub>7</sub>) of F<sub>7</sub> (introduced as solid NaF), P (as  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ), S (as  $\text{Na}_2\text{SO}_4$ ) or  
102 Cl (as NaCl). A first time series of experiments using NaF as ligand in acidic and alkaline  
103 systems was performed (15, 30, 60, 120, and 180 days) to investigate the kinetics of the reaction  
104 processes (**Table 1**). Experiments with other ligands were run for 120 days. At the end of each  
105 experiment, the sealed reactor was rapidly quenched in cold water. Recovered solutions were  
106 carefully collected with a syringe, filtered to remove solid residue (0.2  $\mu\text{m}$ ), diluted 5 times in  
107 ultra-pure water slightly acidified with nitric acid and immediately stored at 4 °C in a ion-free-  
108 ion tube for further characterization. Residual solid was collected, dried at 60 °C for one night,  
109 weighted and stored at ambient temperature. A fraction of each solid run product was mounted  
110 in epoxy resin and finely polished (mirror surface) for microscopic and electron microprobe  
111 analyses.

## 112 **2.3 Solid characterization methods**

### 113 **2.3.1 X-Ray Diffraction (XRD) and Rietveld refinement**

114 Mineral modal abundances of initial and post-experimental solids were characterized by  
115 XRD at ISTERre (Grenoble, France). Samples were grounded in ethanol using a McCrone  
116 micronizing mill, oven-dried overnight and prepared as a randomly oriented mount. The XRD  
117 patterns were recorded with a Bruker D8 powder diffractometer equipped with a SolXE Si(Li)  
118 solid state detector from Baltic Scientific Instruments using  $\text{CuK}\alpha_{1+2}$  radiation. Intensities were  
119 recorded at  $0.026^\circ$   $2\theta$  step intervals from  $5$  to  $90^\circ$  (10 s counting time per step). Eva Bruker  
120 software associated with the ICCD pdf database was used to determine the modal composition of  
121 the powder on a significant part of the recovered solid product for all alteration experiments. This  
122 enables to distinguish between the different REE-minerals in the solid product. Rietveld  
123 refinement with Profex/BGMN software was then performed to precisely quantify mineral  
124 abundances. The quality of the Rietveld refinement is assessed by the  $\chi^2$  factor, which lies between  
125 2.5 and 4 for all experiments.

126

### 127 **2.3.2 Scanning Electron Microscopy (SEM)**

128 The mineral distribution and microstructure of the experimental solids were investigated  
129 by using a ZEISS Gemini 500 SEM. The measurements were carried out in high-vacuum mode  
130 using a high tension (EHT) of 3 kV for a working distance (WD) between 3.4 and 4.8 mm.  
131 Samples were sputtered with a 15 nm thick cover of Au-Pd. Complementary investigations were  
132 performed using the conventional environmental SEM Tescan Vega 3. The measurements were



133 carried out in high-vacuum mode ( $9.9 \times 10^{-9}$  bar), using an accelerating voltage of 16 kV, with  
134 90 nm spot size and 15 mm working distance. Samples were sputtered with 20 nm of carbon.  
135 The microscope is equipped with a 30 mm<sup>2</sup> Energy Dispersive X-Ray Spectroscopy (EDS)  
136 manufactured by Rayspec with SamX's electronic system and software.

137

### 138 **2.3.3 Electron probe micro-analyser (EPMA)**

139 Quantitative chemical analyses of initial and post-experimental allanite and secondary  
140 products (when the grain size was suitable) were carried out using a JEOL JXA-8230 electron  
141 probe micro-analyser (EPMA) equipped with five wavelength-dispersive spectrometers (WDS)  
142 at ISTERre (Grenoble, France). Analytical conditions were 15 kV acceleration voltage, 12nA beam  
143 current, and 1 to 5  $\mu\text{m}$  beam size (details in Table S3, supp. mat.). The ZAF correction procedure  
144 was applied using the JEOL software for quantitative analysis. The detection limits range between  
145 0.01 and 0.04 wt% using the  $2\sigma$  criterion (Batanova et al., 2018).

146

### 147 **2.3.4 Trace element analysis (LA-ICP-MS)**

148 Trace element analysis of allanite was performed at the Institute of Geological Sciences  
149 (University of Bern) using a laser ablation inductively-coupled plasma mass spectrometry (LA-  
150 ICP-MS), which consisted of a Geolas Pro 193 nm ArF excimer laser coupled to an Elan DRC-e  
151 quadrupole ICP-MS. A He-H<sub>2</sub> gas mixture (1 and 0.008 L/min respectively) was used as the  
152 aerosol transport gas. Allanite trace element analyses were performed with laser beam diameters  
153 of 16, 24, and 32  $\mu\text{m}$ , frequencies of 9 and 7 Hz, and energy densities on the sample of 5.0 J/cm<sup>2</sup>.

154 Sample analyses were calibrated using GSD-1Gg and accuracy was monitored using a reference  
155 glass NIST glass SRM 612 (Jochum et al., 2005, 2011). Data reduction was performed using the  
156 SILLS software package (Guillong et al., 2008) and LOD values obtained with the method of  
157 Pettke et al. (2011).

158

## 159 **2.4 Fluid characterization methods**

### 160 **2.4.1 Inductively-coupled Plasma Spectrometry**

161 All recovered solutions were stored using metal-free tubes (VWR). For an accurate  
162 quantification of trace elements, measurements were performed by ICP-MS using a Thermo  
163 Scientific XSERIES 2 spectrometer. Recovered solutions were diluted 3 times with 2% HNO<sub>3</sub>  
164 solution to a volume of 6 mL. Finally, 0.5 mL of an In solution was systematically added as an  
165 internal standard to correct for the drift of the ICP-MS. Collision Cell Technology (CCT) was  
166 used for some elements (Ca, Fe, and Mn) in order to reduce polyatomic interferences with 5% H<sub>2</sub>  
167 in He gas. Measurements quality was evaluated by duplicating the measurement of standards that  
168 were analysed five times on the ICP-MS. Calculations, to extract concentrations from the  
169 integration of peak signals, were performed off-line. Reproducibility depends on the nature of the  
170 analysed element. It ranges between 1 and 19% for the REE and from 3 to 30% for other trace  
171 elements. The detection's limits (D.L.) are defined as 3 times the blanks average. All data below  
172 the detection limit were excluded. Because the torch for ICP-MS was sheathed in quartz, Si was  
173 then determined by atomic emission spectrometry (ICP-AES) using a Perkin Elmer Optima 3000  
174 DV ICP-AES. Solutions were diluted five times using a 2% HNO<sub>3</sub> solution providing the

175 minimum analysable volume. The same HNO<sub>3</sub> solution was used to prepare standards and blanks.  
176 The analytical error for Si is 8 %.

177

#### 178 **2.4.2 Capillary electrophoresis (CE)**

179 The anionic content (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HCO<sub>3</sub><sup>-</sup>) in the recovered solutions was quantified  
180 using a capillary electrophoresis (CE) system by WATERS®. The CE apparatus was equipped  
181 with a fused capillary (75 μm i.d. × 60 cm total length) and a diode detector. The CE was operated  
182 at 20 °C and at a voltage of 20 kV. Electrophoregrams were recorded with the indirect mode  
183 detection at 254 nm using an Hg lamp. The background electrolyte (BGE) was composed of 4.6  
184 mmol/L Na<sub>2</sub>CrO<sub>4</sub> solution, 0.5 mmol/L OFMOH™ from WATERS™, and an H<sub>3</sub>BO<sub>4</sub> solution (pH  
185 = 8.0). Prior to each measurement series, the capillary was conditioned by flushing with 1 mol/L  
186 NaOH and 0.1 mol/L NaOH (5 min each) followed by a 10 min flush with deionized water and a  
187 BGE solution (15 min flush). The capillary was preconditioned prior to each measurement by  
188 flushing the BGE for 1 min. All samples were measured in duplicate using hydrostatic injection  
189 mode.

## 190 **3 Results**

### 191 **3.1 Allanite alteration as a function of the initial pH**

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

196 The recovered experimental solids, characterized by X-ray diffraction, displayed alteration  
197 evidence with secondary phases in the run products (Fig 1). The extent of alteration was estimated  
198 on the basis of remaining allanite in the recovered samples. The constancy of the allanite  
199 composition between the final and initial materials (Table S1 - Supp. Mat) attested to no secondary  
200 allanite/epidote precipitation. The reaction progress was estimated from the allanite abundance.  
201 The run products modal composition showed that the kinetics and extent of alteration greatly  
202 varied with the initial pH (Fig. 1). The alteration rate was much higher in the high pH alkaline  
203 system, with 65% alteration reached within the first 15 days and a rapid stabilisation at around 70  
204 to 75% alteration from 30 to 120 days. In contrast, the extent of alteration in the acidic experiments  
205 was scarce after 15 days and only achieved 25% alteration for the longest durations (120 and 180  
206 days). However, under both the acidic and high pH alkaline conditions, with a F-doped solution,  
207 the same mineral phases grew at the expense of allanite (Fig. 1): analcime (Na-Al silicate),  
208 hematite ( $\text{Fe}_2\text{O}_3$ ), and REE-bearing carbonates (Table 2). The REE-bearing carbonates,  
209 determined from XRD analyses, changed depending on the initial pH of the solution. They  
210 consisted of (1) bastnäsite (general formula:  $\text{LREECO}_3\text{F}$ ) and synchysite (general formula:

211 CaLREE(CO<sub>3</sub>)<sub>2</sub>F) under acidic conditions and (2) a burbankite-group mineral (thereafter referred  
212 as BGM, with the general formula: (Na,Ca)<sub>3</sub>(Sr,Ba,Ce)<sub>3</sub>(CO<sub>3</sub>)<sub>5</sub>) and REE-fluorocarbonates with  
213 parisite (general formula: CaLREE<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>F<sub>2</sub>) associated with bastnäsite and minor synchysite in  
214 the high pH alkaline system. Besides these phases, fluorite (CaF<sub>2</sub>) appeared in the acidic  
215 experiments, while calcite (CaCO<sub>3</sub>), smectite, and minor nordstrandite (general formula:  
216 Al(OH)<sub>3</sub>) crystallized in the high pH alkaline system. High REE contents up to 2 wt% and 8 wt%  
217 (REE+Y)<sub>2</sub>O<sub>3</sub> were measured in fluorite and calcite, respectively (Table 2; Table S2 supp. mat.).

218 The microstructures of the recovered solids differed depending on the initial pH, which  
219 can be attributed to the reaction progress. In acidic system, due to low alteration rate (15 days),  
220 the initial shape of the allanite grains, characterized by typical conchoidal edges, was mostly  
221 preserved while fluorite and analcime crystals grew around allanite from the bulk fluid (Fig. 2a).

222 The allanite surface was pitted, ~~however,~~ and covered by smectite ~~in a typical honeycomb~~  
223 ~~structure~~ (Fig. 4b). At this stage, REE-(fluoro)carbonates were restricted to inherited fractures in  
224 the allanite. A higher reaction extent (25%) in the acidic system (120 days), resulted in alteration  
225 rims surrounding some of the allanite grains. Their surfaces were characterized by a pervasive  
226 saw-tooth shaped reaction front, highlighting more extensive dissolution (Fig. 2b). Reaction rims  
227 were sequentially composed of discontinuous layers of hematite followed by nanocrystals with  
228 the granular and acicular shape of REE-fluorocarbonates penetrating through the dissolving  
229 allanite at the reaction front and filling newly-opened fractures (Fig. 2c).

230 In the high pH alkaline run products, the allanite grain shape is preserved on the micro-  
231 scale, surrounded by layers of complex micro-textures. The morphologies and textures described  
232 for the run product from the 15-days experiment do not significantly change compared to the

233 longer duration experiments. Allanite has penetrative reaction rims that can reach up to 10  $\mu\text{m}$   
234 thick (Fig. 2d). They were delimited by complex microstructures at the reaction front, such as  
235 nanoscale etch pits or saw-tooth surfaces (Fig. 2e). Close to the reaction front, REE-  
236 fluorocarbonates also precipitated at the surface, within the etch pits or in inherited microfractures,  
237 with nano-granular, acicular, or prismatic shapes (Fig. 2e). The sub micron size of these phases  
238 prevented quantitative chemical analyses by EMPA. The allanite surface was overlain with a thin  
239 layer of hematite crystals of around 10 to 500 nm in size. Smectites were also ubiquitous and  
240 clearly identifiable by their fibrous (honeycomb) morphology and platelet growth oriented  
241 towards the fluid. The burbankite-group minerals (BGM) occur as microscale euhedral crystals  
242 that randomly precipitated from the reactive bulk fluid (decoupled from the allanite replacement  
243 products). They are mainly prismatic and more or less elongated with a size generally varying  
244 from ca. 5 to 30  $\mu\text{m}$  in size (Fig. 2f). The BGM crystals commonly display a zonation with respect  
245 to the REE content which is anti-correlated with respect to Ca (Fig. S5, supp. mat.). They have a  
246 higher LREE than the initial allanite, but with Sm and Y below the detection limit (Table 2).  
247 Calcite precipitates as aggregates of euhedral crystals 10 to 20 microns in size or intergrown with  
248 relic allanite (Fig. 2f).

### 249 **3.2 Allanite alteration as a function of ligands**

250 To investigate the effects of ligands on the alteration of allanite, experiments were run under the  
251 initial acidic conditions with P-doped, S-doped and Cl-doped solutions for 120 days (Table 1).  
252 Similar to that observed for the pH, the reaction progress was also significantly affected by the  
253 ligands (Fig. 3). The most reactive system was the P-doped one, which achieved 73% allanite  
254 alteration. This reaction extent was similar to that seen in the F-doped system under high pH

255 alkaline conditions (75%,% of reaction), but much higher than that obtained under similar acidic  
256 conditions (23%,% of reaction) over the same duration (120 days). The S- and Cl-bearing systems  
257 were not less reactive compared to the others with less than 5% secondary minerals.

258 In the reactive P-doped experiments, analcime and hematite were present in major proportions in  
259 the recovered solid, as for the F-doped system. Smectite was also an alteration product of allanite,  
260 as in the high pH alkaline system. The main difference between the P- and F-doped systems was  
261 the nature of the mineral phases that accommodated REE and Ca, such as monazite (general  
262 formula  $\text{LREEPO}_4$ , 21% of solid product) and hydroxyapatite (general formula  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ,  
263 18% of solid product). The alteration microstructures were very similar to those previously  
264 described in the F-bearing system. Allanite was largely affected by dissolution, as illustrated by  
265 the numerous etch pits scattered on the allanite surface (Fig. 4a). Allanite alteration resulted in  
266 thick reaction rims made up of a nano-mixture of monazite-hematite and hydroxylapatite with an  
267 apparent microscale spatial distribution from the reaction front towards the reactive fluid (Fig 4b).  
268 Sub-micron monazite crystals precipitated directly at the interface with the allanite (Fig. 4c).  
269 Similar to the F-doped systems, hematite occurred as a thin, quasi-continuous corona around the  
270 allanite grains. Finally, euhedral micrometric-sized grains of hydroxylapatite, mixed with smectite  
271 filaments, which probably formed during the quench, are seen along the outer edge of the  
272 alteration rim (Fig. 4b and c). Analcime remains the major alteration phase, and takes the form of  
273 large grains embedding relict allanite along the allanite reaction rims (Fig. 4a).

274

### 275 3.3 Recovered fluid chemistry

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

281 In time-series experiments, the final fluid compositions indicated that the experiments  
282 under high pH alkaline conditions were already in a steady-state (approaching constant  
283 concentrations of all measured elements with time) after 15 days (Fig. 5b), which is in agreement  
284 with the mineralogical results. In the initially ~~acid~~acidic system, elemental concentrations of Ca,  
285 REE, Th, and U evolved until reaching a near plateau only after 120 days (Fig. 5a). At that stage,  
286 Si, Al, and Ca reached similar concentrations in the F-doped acidic and high pH alkaline systems,  
287 whereas REE, U, and Th were lower in the acidic system compared to the high pH alkaline system  
288 by 2 to 4 orders of magnitude.

289 In the P-doped system, which was the most reactive system under acidic conditions,  
290 elemental concentrations are similar to the concentrations of the F-doped in the acidic system at  
291 120 days (Fig. 5c). In the unreactive Cl- and S-doped systems, Si and REE concentrations are  
292 comparable with those measured in the F- and P-doped systems under acidic conditions. The other  
293 elements were generally at lower concentrations.

294 In terms of REE, the chondrite-normalized patterns plot relatively flat for the high pH  
295 alkaline systems (Fig. 6). ~~There is~~In acidic fluids, patterns plot also relatively flat but with a



296 ~~MREEs~~light depletion ~~compared to LREE in Sm, Gd and HREE in acidic fluids~~<sub>Dy</sub>, with no  
297 dependence on the ligand.

298

## 299 **4. Discussion**

### 300 **4.1 Allanite alteration mechanisms**

301 In the batch experiment runs (Table 1), the alteration of allanite ranges from a very limited  
302 (< 5%) up to a very extensive (77%) degree depending on the fluid chemistry after 120 days. The  
303 pH has the first effect on the alteration of allanite, as the kinetics for the high pH alkaline system  
304 are fastest (65%) after 15 days, and the more advanced (70–75%) after 120 days in the two time-  
305 series experiment runs conducted in an F-doped system. Under acidic conditions, the nature of  
306 the ligand significantly affects the extent of alteration. The presence of P enhances the allanite  
307 alterability, reaching 73% of the reaction rate after 120 days, while allanite reactivity is minor in  
308 the Cl- or S-doped systems (< 5%). F-doped systems display moderate alteration at the same  
309 duration (25%). Higher allanite reactivity in a high pH alkaline fluid shows that high pH fluids  
310 efficiently promote silicate dissolution rates, while dissolution is more limited in near neutral  
311 fluids (Hellmann, 1994). This effect is also demonstrated for epidote group minerals (Rose, 1991).  
312 Phosphorus seems to have a similar effect on allanite, though with a lower extent of alteration.

313 In the most reactive systems (high pH alkaline and P-doped conditions), the alteration of allanite  
314 is promoted by increasing dissolution coupled with the precipitation of other minerals. On one  
315 hand, dissolution can be promoted due to a solubility change for the dissolving elements in the  
316 bulk solution, by modifying element complexation, the concentration in the solution, and the

317 chemical affinity per the dissolution reaction between allanite and the fluid. On the other hand,  
318 the mineral microstructures evidenced here also point to the crucial role of secondary precipitation  
319 on the alteration rate. Alteration microstructures from highly altered ~~run~~experiment products show  
320 well-developed dissolution features (etch pits, fractures, porosity) with a penetrative replacement  
321 by an alteration rim made up of secondary minerals with a complex mineralogical zonation.  
322 General preservation of the initial pristine shape of allanite suggests a mechanism of replacement  
323 by interfacially coupled dissolution-precipitation (Putnis, 2002; Putnis and Putnis, 2007;  
324 Hellmann et al., 2012), which indicate disequilibrium between the solid and the fluid (Putnis,  
325 2009; Ruiz-Agudo et al., 2014). Such alteration processes can lead to an apparent incongruent  
326 dissolution due to a preferential precipitation of low solubility phases (with different composition  
327 than the altered phase) at the alteration interface (Ruiz-Agudo et al., 2012). Such apparent  
328 incongruent dissolution has already been demonstrated for epidote dissolution (Kalinowski et al.,  
329 1998), and seems also to apply here to allanite alteration as seen by the mineralogical gradation  
330 from the reaction front to the bulk solution. In the reaction rim, the precipitation of submicron,  
331 low-solubility secondary phases takes in elements from the solution and changes their  
332 concentration at the reaction interface. This is the case for hematite, which nucleates as a thin rim  
333 at the interface with the allanite. But this is particularly true for REE-mineral phases, (REE-  
334 fluorocarbonates or monazite depending on the ligand), which also occur as a discontinuous rim  
335 of nano-scale crystallites propagating anisotropically inward into the pristine grain and along  
336 fractures in the allanite. The growth of other main phases with a higher solubility in the solution,  
337 e.g. analcime, fluorite, and calcite, is spatially decoupled from the alteration interface with  
338 precipitation from the bulk solution as larger euhedral crystals. Such precipitation from the bulk  
339 fluid away from the rim of the dissolving mineral have been described in other alkaline systems

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

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

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

360 In the investigated reactive systems, the ~~precipitated~~precipitation of secondary REE-  
361 phases is thus proposed to be the main driving force behind allanite alteration by lowering the

362 activities of REE in the interfacial fluid. In the absence of efficient REE-mineral precipitation (Cl-  
363 and S-doped) at the allanite interface, “steady state” concentrations measured in the bulk fluid are  
364 assumed to be more readily reached, thus decreasing reaction rates. Therefore, allanite alteration  
365 remains low. These results are in good agreement with natural observations. The secondary,  
366 experimental REE-mineral phases, i.e., REE-fluorocarbonates and/or REE-phosphates ~~associated~~  
367 ~~with~~ are typical of low-temperature alteration products (e.g. Berger et al., 2008; Ondrejka et al.,  
368 2018).

369

## 370 **4.2 REE, Th, and U mobility and fractionation during allanite alteration**

371 In all reactive systems, comparison between a simple mass balance calculation from the  
372 low REE concentrations in the recovered fluid and the allanite composition and alteration rates  
373 ~~indicate~~ indicates that the REE released during alteration are mostly in secondary phases. Seventy  
374 percent allanite alteration would provide 100  $\mu\text{mol}$  of the REE released in high pH alkaline  
375 experiment runs. However, the REE contents in the final fluids are 4 orders of magnitude below.  
376 The main REE-minerals (REE-carbonates or REE-phosphates identified by XRD), occur as  
377 submicronic crystals in the alteration rim, preventing accurate determination of their REE  
378 contents. Based on the theoretical compositions of REE-fluorocarbonates and monazite, along  
379 with their XRD modal abundance, rough mass balance calculations confirm that they are a major  
380 sink for the REE released by allanite. In the P-doped system, the hydroxylapatite grains are also  
381 too small for determining their REE content though it could be up to a few wt.% (Budzyń et al.,  
382 2017).

383 While the composition of secondary phases in the altered rim cannot be analysed precisely  
384 for their REE ~~compositions~~contents, minerals precipitating from the bulk-fluid are large enough  
385 for evaluating their REE content by EPMA. In F-doped systems, fluorite represents 25% of the  
386 secondary products, and can incorporate up to 1-2 wt.% ~~REEREE~~REE<sub>2</sub>O<sub>3</sub>. The REE content in fluorite  
387 has been extensively studied in hydrothermal systems (Möller et al., 1998; Schwinn and Markl,  
388 2005; Schönenberger et al., 2008; Gob et al., 2011), in economical REE-deposits, such as the  
389 Bayan Obo complex (Xu et al., 2012), or by thermodynamic modelling (Kolonin and Shironosova,  
390 2007). It shows that REE in fluorite, while extremely variable, but can reach up to > 10 wt.% in  
391 yttrifluorite (Pekov et al., 2009). Although a coupled substitution involving Na is often considered  
392 preponderant for incorporating the REE within fluorite, i.e.  $REE^{3+} + Na^{+} \leftrightarrow 2 Ca^{2+}$  (Möller et  
393 al., 1998), there is no real correlation between the REE and Na contents in the fluorite from these  
394 experiments, despite the high Na concentrations. The BGM (identified from XRD) precipitating  
395 from the bulk-fluid also accommodate significant REE, but with Na concentrations that are ~~too~~  
396 lowsignificantly lower compared to burbankite *sensu stricto* (Beloviskaya and Pekov, 2004). The  
397 BGM are zoned with a typical hourglass sector zoning suggesting crystallographic control on REE  
398 incorporation (Fig. 2f). Integration of the REE is directly correlated to the size and geometry of  
399 the crystallographic sites, which favour the LREE in calcic minerals, such as tourmaline (van  
400 Hinsberg et al., 2010). Burbankite is a hydrothermal mineral encountered in alkaline pegmatites  
401 and associated carbonatites (Zaitsev et al., 2002). In the experiments, the precipitation of BGM  
402 minerals is probably favoured by the Na concentration in the fluid. Finally, the REE  
403 concentrations in the calcite are considerably higher than those normally encountered in nature  
404 (Stipp et al., 2006) but are thermodynamically stable (Rimstidt et al., 1998) as has been  
405 experimentally demonstrated (Toyama and Terakado, 2014; Gabitov et al., 2017). In calcite, two

406 coupled substitution mechanisms are proposed as follow (Perry and Gysi, 2018), i.e.  $\text{REE}^{3+} + \text{Na}^+$   
407  $\leftrightarrow 2\text{Ca}^{2+}$  and  $2\text{REE}^{3+} + \square \leftrightarrow 3\text{Ca}^{2+}$ . The composition of the calcite produced in these experiments  
408 ~~indicate~~indicates that both mechanisms occur under the experimental conditions of this study (Fig.  
409 S5, supp. mat.).

410

### 411 **4.3 REE fractionation between fluid and solid**

412         Though the REE are mainly stored in secondary phases, minor REE concentrations have  
413 been recovered in the fluids. Though precise quantitative fluid concentrations are limited by the  
414 batch experimental setup, our qualitative results clearly indicate a significant difference in REE  
415 fractionation between the solid and the fluid whatever the pH and the complexing ligands.  
416 Experimental fluids display relatively flat chondrite normalized REE spectra, indicating that the  
417 experimental alteration of allanite ultimately produces a fluid enriched in HREE relative to the  
418 initial LREE-rich allanite composition. This implies in turn the preferential fractionation of LREE  
419 over HREE in the secondary mineral precipitates relative to the fluid. This is in good agreement  
420 with the limited incorporation of HREE in fluorocarbonates and monazite, as demonstrated for T  
421  $< 450\text{ }^\circ\text{C}$  (Heinrich et al., 1997; Poitrasson et al., 2000; Janots et al., 2008; Budzyń et al., 2010;  
422 2017; Grand'Homme et al., 2018). Also, secondary minerals that precipitate from the bulk-fluid  
423 (calcite, fluorite, BGM) are enriched in LREE over HREE but with lower La/Y compared to  
424 allanite, again supporting the fractionation of the LREE over the HREE in the bulk fluid compared  
425 to fluid at the reaction front. In these secondary mineral phases, the Y values are typically at the

426 same level as in allanite, which suggests that the HREE are more mobile compared to the LREE,  
427 as seen in numerous natural environments, e.g. during monazite alteration (Hentschel et al., 2020).

428 The fluid compositions measured in this study have numerous implications for REE  
429 deposits. Here the flat or gently incurved REE normalized pattern indicates that REE are not  
430 released congruently but that speciation in the fluids or precipitation of secondary products favour  
431 HREE fractionation over LREE in the fluid compared to the initial allanite composition.

432

#### 433 **4.4 Th and U behaviour during allanite alteration**

434 Actinides seem to mostly partition into the fluid as opposed to secondary minerals.  
435 Simplified qualitative calculations show that virtually all the U released by allanite goes into the  
436 fluid under these conditions. Actinide concentrations are higher in the high pH alkaline system  
437 (with higher carbonate activities) than in the acidic system. This agrees rather well with studies  
438 that show that the solubility of actinides increases with the concentration of the aqueous carbonate  
439 or phosphate ligands (Rai et al., 1994; Sandino and Bruno, 1998). Recent studies also show that  
440 actinides can be highly mobile in the presence of ligands such as S-, Cl-, or F-complexes for  
441 temperatures close to 200 °C (Nisbet et al., 2018, 2019; Migdisov et al., 2019). In the experimental  
442 runs under initial acidic conditions, U release is however at least 1 to 2 orders of magnitude lower  
443 than that under high pH alkaline conditions. Regardless of the chemical system, Th is  
444 systematically lower in the fluid compared to U while it is higher in the starting allanite, indicating  
445 U/Th fractionation during allanite alteration. According to Rai et al. (1994), ThO<sub>2</sub> solubility is  
446 higher than that of UO<sub>2</sub>, suggesting that tetravalent U is likely oxidized in its hexavalent state  
447 during the allanite alteration reaction. Preferential incorporation of tetravalent Th in secondary

448 REE-mineral phases may in turn enhance Th/U fractionation between the fluid and secondary  
449 products as observed in natural monazite and allanite precipitated from hydrothermal systems  
450 (Janots et al., 2012).

451

## 452 **5. Conclusions**

453 Allanite has a complex composition and its experimental alteration under low temperature  
454 conditions results in a high diversity of mineralogical assemblages and microstructures. Allanite  
455 can be highly reactive in certain fluids, reaching more than 75% of alteration at 200 °C and  $P_{\text{sat}} \approx$   
456 16 bar, after only 15 days. The pH and the nature of the complexing ligand added to the fluid will  
457 strongly affect the alteration rate of the allanite, with the high pH alkaline system being the most  
458 reactive. In carbonate-bearing fluids, F and P will promote allanite alteration, while allanite shows  
459 negligible alteration in the presence of Cl and S. The main driving force behind the alteration of  
460 allanite resides in the precipitation at a reactive front of secondary REE-minerals, whose  
461 chemistry depends on the complexing ligands. These precipitated minerals maintain a local  
462 disequilibrium close to the reaction interface between the fluid and the solid, thus sustaining  
463 allanite dissolution. Though REE are mostly stored in the secondary mineral phases, there is a  
464 preferential fractionation of the LREE over the HREE into the solid compared to the fluid while  
465 U is strongly partitioned into the fluid.

466

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477

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686

687



## 688 **Figure Captions**

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

696

697 **Figure 2.** Scanning electron microscopy images using backscattered electron (BSE) imaging of  
698 allanite and secondary products from acidic (a, b, and c) and high pH alkaline (d, e, and f) F-doped  
699 runs for different times. **a.** Relatively unaltered allanite with fluorite and analcime growing along  
700 the allanite grain rims. **b.** Relatively unaltered allanite (top left) with internal fractures filled by  
701 REE-phases along with more reacted allanite (bottom right) with sawtooth-shaped grain rims after  
702 120 days. **c.** Magnification of b showing reaction interface with allanite composed of granular  
703 nanometric REE-fluorocarbonates replacing allanite. **d.** Allanite grain displaying edge pitting  
704 with a porosity that progresses anisotropically to the grain center. Edges are rimmed by a saponite  
705 whiskers, which probably formed during quenching. **e.** Detail of an allanite edge showing a sharp  
706 eroded surface rimmed by REE-fluorocarbonates with a granular, prismatic, and needle-like  
707 shape, along with hematite and saponite. Porous cavities are filled with REE fluorocarbonates **f.**  
708 Cluster of Burbankite-group minerals with a large crystal of calcite growing in the interstitial  
709 space between the minerals. AIn = allanite; Ana = analcime; Bgm = burbankite-group mineral;  
710 Cal = calcite; Fl = fluorite; Hem = hematite; REE-FCb = REE-fluorocarbonates (bastnäsite,  
711 parisite, synchysite); Sap = saponite; Sme = smectite.

712

713 **Figure 3.** Comparison of mineral modal compositions after 120 days for the F-doped high pH  
714 alkaline systems and the F-, P-, S-, and Cl-doped systems (respectively shown in columns), which

715 were identified by X-ray diffraction (XRD) and Rietveld refinement (in %). Aln = allanite; Ana  
716 = analcime; Anh = anhydrite; Cal = calcite; Fl = fluorite; Hal = halite; Hap = hydroxylapatite;  
717 Hem = hematite; Mnz = monazite; Nrd = nordstrandite; Sme = smectite.

718  
719 **Figure 4.** Secondary electron (SE) and backscattered electron (BSE) images of allanite alteration  
720 in an acidic P-doped system. **a.** Typical allanite grain with eroded grain boundaries and with large  
721 crystals of analcime partially embedding the other secondary minerals. **b.** Continuous reaction  
722 front composed of monazite replacing allanite and a thin (< 200 nm) rim of hematite outlining the  
723 original shape of the allanite. Outwards from the reaction front is rimmed by euhedral  
724 hydroxylapatite (Hap) that precipitated in the interstitial space between filaments of saponite (Sap).  
725 **c.** Detail from **b** showing that the abundance of the nano-size monazite increases in the vicinity  
726 of the eroded allanite. Aln = allanite; Ana = analcime; Cal = calcite; Hap = hydroxylapatite; Hem  
727 = hematite Mnz = monazite; Sap = saponite.

728  
729 **Figure 5.** Major elements, REE, and actinide concentrations (log) in experimental fluids for the  
730 time series F-doped experiments in the acidic system (**a**), high pH alkaline system (**b**), and in the  
731 120 day experiments for the P-, S-, and Cl-doped systems (**c**).

732  
733 **Figure 6.** Chondrite-normalized REE spectra of fluids after 120 days from the slightly acidic, F-  
734 doped, P- doped, S- doped, Cl-doped, and time series, high pH alkaline, F-doped experiments.  
735 The HREE with odd numbers are below the detection limits or have been removed from the  
736 diagram because of artificial anomalies due to being close to the detection limits (Table 1). The  
737 lanthanide tetrad effect is discernible within the LREE for the slightly acid experiments (dashed  
738 lines).

739

**Table 1.** Experimental conditions and solid products

| Set | Exp.    | Carbonate source               | Initial pH | Ligands (120 mM)                                    | Duration (days) | Aln (%) | Secondary solid products  |
|-----|---------|--------------------------------|------------|---|-----------------|---------|---|
| B1  | 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 (1.2%);   |
|     | 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 <sub>3</sub> 1M<br>1.5mL | 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 <sub>3</sub> 1M<br>1.5mL | 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 <sub>3</sub> 1M<br>1.5mL | 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 <sub>3</sub> 1M<br>1.5mL | 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%) |
|     | 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%)   |
| B3  | 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          | NaCl  | 120             | 98      | HI (2.0%)   |

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 = bastnäsäite; Cal = calcite; Chl = chlorite; Flr = fluorite; Hap = hydroxyapatite; Hem = hematite; HI = 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. Abbreviation from Warr L.N. (2021) IMA–CNMNC approved mineral symbols. Mineralogical Magazine 85, 291–320.

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

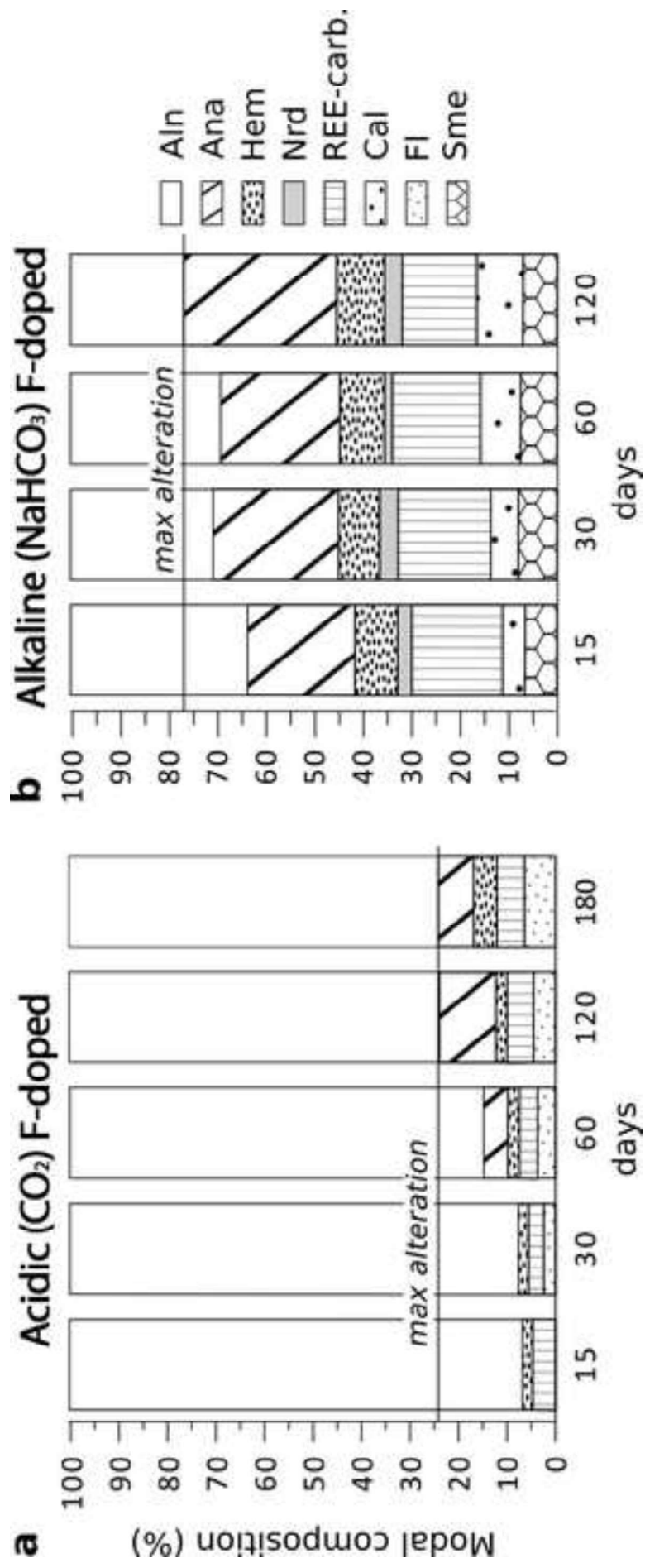
| System                         | Analcime  |  | Calcite  |       | BGM  |       | Fluorite                         |       | Anhydrite                                       |
|--------------------------------|---|--|--|-------|--|-------|----------------------------------|-------|---|
|                                | HCO <sub>3</sub> <sup>-</sup><br>+ F <sup>-</sup> | CO <sub>2</sub><br>+ PO <sub>4</sub> <sup>2-</sup> | HCO <sub>3</sub> <sup>-</sup> + F <sup>-</sup> |       | HCO <sub>3</sub> <sup>-</sup> + F <sup>-</sup> |       | CO <sub>2</sub> + F <sup>-</sup> |       | CO <sub>2</sub> + SO <sub>4</sub> <sup>2-</sup> |
| Days                           | 120   | 120  | 120  | 120   | 120  | 120   | 120                              | 180   | 120   |
| SiO <sub>2</sub>               | 49.1  | 49.0   |  |       |  |       |                                  |       |   |
| Al <sub>2</sub> O <sub>3</sub> | 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 <sub>2</sub> O <sub>5</sub>  |   | 0.15   | 0.12   |       |  |       | 0.14                             | 0.18  |   |
| SO <sub>3</sub>                |   |  |  |       |  |       |                                  |       | 47.47   |
| F                              |   |  | 0.30   |       | 0.18   | 0.57  | 48.02                            | 47.75 |   |
| La <sub>2</sub> O <sub>3</sub> |   |  | 1.90   | 0.90  | 14.69  | 15.17 | 0.68                             | 0.35  | 0.17  |
| Ce <sub>2</sub> O <sub>3</sub> |   |  | 4.13   | 2.30  | 23.51  | 30.52 | 1.20                             | 0.69  | 0.51  |
| Pr <sub>2</sub> O <sub>3</sub> |   |  | 0.46   | 0.24  | 1.68   | 2.57  | 0.19                             | -     | 0.14  |
| Nd <sub>2</sub> O <sub>3</sub> |   |  | 1.16   | 0.60  | 3.56   | 6.35  | 0.23                             | 0.12  | 0.16  |
| Sm <sub>2</sub> O <sub>3</sub> |   |  |  |       |  |       |                                  |       |   |
| Gd <sub>2</sub> O <sub>3</sub> |   | 0.13   | 0.21   |       |  |       |                                  |       |   |
| Dy <sub>2</sub> O <sub>3</sub> |   |  |  |       | 0.23   |       |                                  |       |   |
| Y <sub>2</sub> O <sub>3</sub>  |   |  | 0.12   | 0.11  |  |       | 0.12                             |       |   |
| 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                            |   |  |  |       |  | 0.13  |                                  |       |   |
| Total <sup>1</sup>             | 89.50   | 88.66  | 60.63  | 58.27 | 67.63  | 64.37 | 99.41                            | 98.68 | 90.94   |
| Σ(REE) <sup>2</sup>            |   | 0.13   | 7.99   | 4.16  | 43.68  | 54.60 | 2.42                             | 1.17  | 0.97  |
| La/Y                           | n.d.  | n.d.   | 17.4   | 8.79  | n.d.   | n.d.  | 6.02                             | n.d.  | n.d.  |
| Ce/Ce* <sup>3</sup>            | n.d.  | n.d.   | 1.07   | 1.19  | 1.14   | 1.18  | 0.8                              | 2.84  | 0.82  |

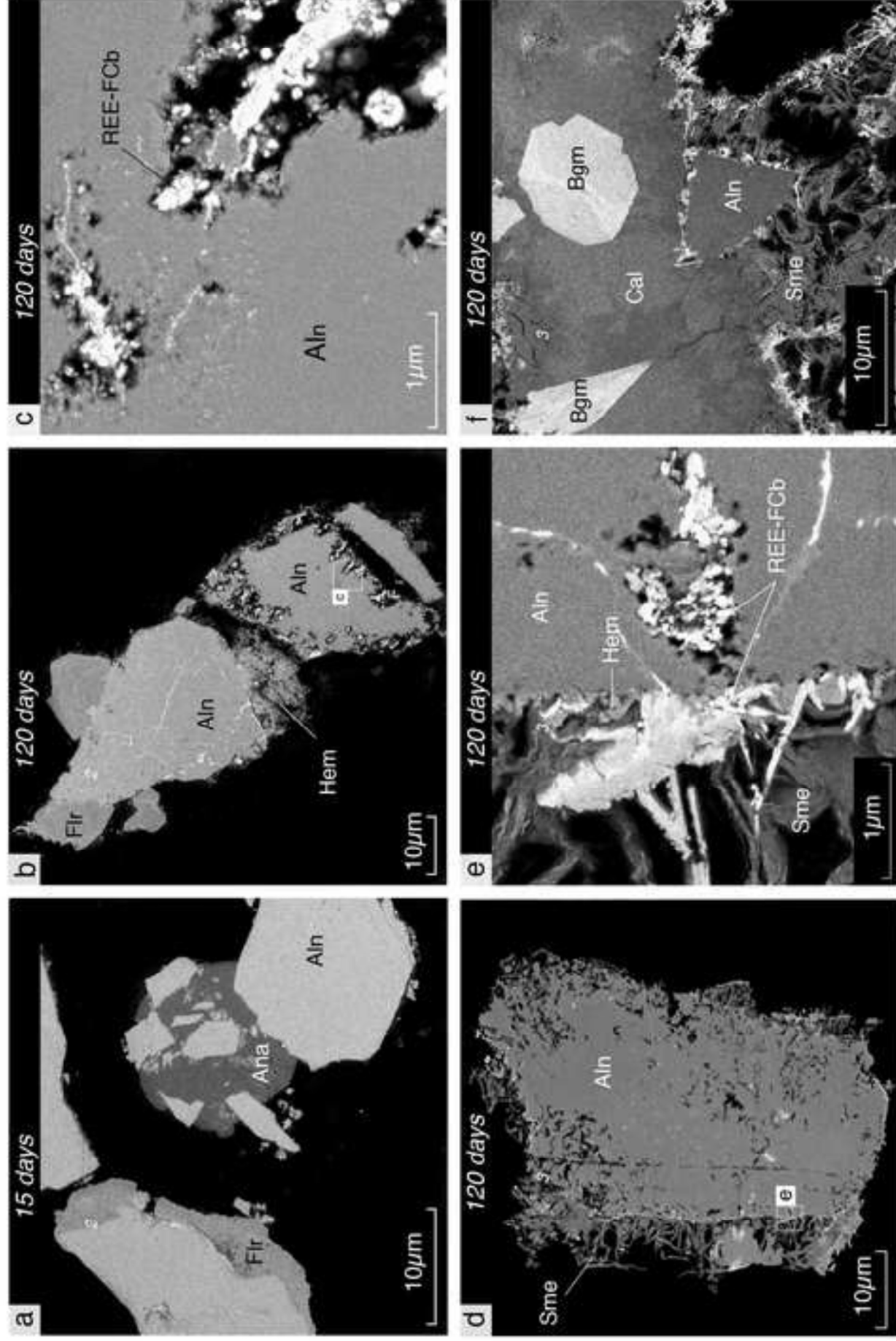
Notes: Values in *italic (%)* column are mean relative errors, and 2σ is the standard deviation; n.d. not determined; <sup>1</sup> Total is corrected of -O=F<sub>2</sub> values; <sup>2</sup> ΣREE refers to the sum of (REE+Y)<sub>2</sub>O<sub>3</sub>; <sup>3</sup> Ce/Ce\* CeN/(LaN\*PrN)<sup>1/2</sup>. Empty cells are concentrations below detection. n.d. not determined

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

| Experimental set              |                                  |        |       |                                     |       |       |   |       |       |   |        |         |                                   |     |     |     |
|-------------------------------|----------------------------------|--------|-------|-------------------------------------|-------|-------|---|-------|-------|---|--------|---------|-----------------------------------|-----|-----|-----|
| System                        | CO <sub>2</sub> + F <sup>-</sup> |        |       | NaHCO <sub>3</sub> + F <sup>-</sup> |       |       | CO <sub>2</sub> + PO <sub>4</sub> <sup>2-</sup> |       |       | CO <sub>2</sub> + SO <sub>4</sub> <sup>2-</sup> |        |         | CO <sub>2</sub> + Cl <sup>-</sup> |     |     |     |
| Experiment                    | B1015                            | B1030  | B1060 | B1120                               | B1180 | B2015 | B2030   | B2060 | B2120 | B3P120  | B3S120 | B3Cl120 | Days                              | 120 | 120 | 120 |
| <sup>1</sup> Si               | 38.0                             | 15.8   | 13.1  | 16.8                                | 16.0  | 19.4  | 22.3  | 25.4  | 43.0  | 62.1  | 14.9   | 27.4    |                                   |     |     |     |
| /kg Al<br>x10 <sup>-4</sup>   | 1.20                             | 1.35   | 0.51  | 5.88                                | 5.76  | 2.40  | 2.06  | 1.50  | 0.50  | 2.48  | 0.35   | 0.11    |                                   |     |     |     |
| Fe                            |                                  |        |       |                                     |       | 0.21  | 0.20  | 0.16  | 0.12  | 0.045   |        |         |                                   |     |     |     |
| Ca                            |                                  |        |       | 0.11                                | 0.069 | 0.14  | 0.14  | 0.16  | 0.17  | 0.082   |        |         |                                   |     |     |     |
| Respective ligands            | 950                              | 976    | 869   | 668                                 | 598   | 1781  | 1661  | 1412  | 1211  |   |        |         |                                   |     |     |     |
| HCO <sub>3</sub> <sup>-</sup> |                                  |        |       |                                     |       | 10980 | 10791   | 7132  | 6604  | 2489  |        |         |                                   |     |     |     |
| mol Y                         |                                  |        |       | 4.34                                | 0.20  | 140   | 175   | 227   | 297   | 4.85  | 0.26   | 1.27    |                                   |     |     |     |
| /kg La<br>x10 <sup>-8</sup>   |                                  | 0.25   | 0.40  | 4.49                                | 1.51  | 30.3  | 24.8  | 41.6  | 52.9  | 15  | 4.90   | 2.88    |                                   |     |     |     |
| Ce                            | 0.07                             | 0.25   | 0.35  | 6.48                                | 5.28  | 81.4  | 73.5  | 94.2  | 75.1  | 8.04  | 1.92   | 0.93    |                                   |     |     |     |
| Pr                            |                                  |        | 0.033 | 0.48                                | 0.23  | 9.50  | 11.3  | 12.5  | 14.8  | 1.14  | 0.27   | 0.25    |                                   |     |     |     |
| Nd                            |                                  |        |       | 1.97                                | 0.52  | 37.2  | 45.6  | 49.1  | 55.6  | 5.23  | 0.94   | 4.26    |                                   |     |     |     |
| Sm                            |                                  |        |       | 0.24                                | 0.037 | 9.26  | 11.4  | 11.8  | 12.7  | 0.44  | 0.04   | 0.19    |                                   |     |     |     |
| Eu                            |                                  |        |       | 0.21                                |       | 1.69  | 2.10  | 2.22  | 2.59  | 0.36  | 0.02   | 0.20    |                                   |     |     |     |
| Gd                            |                                  |        |       | 0.45                                | 0.077 | 9.80  | 12.1  | 13.8  | 15.3  | 0.76  | 0.06   | 0.25    |                                   |     |     |     |
| Tb                            |                                  |        |       | 0.0031                              |       | 1.70  | 2.15  | 2.54  | 2.85  | 0.013   | 0.0022 | 0.0035  |                                   |     |     |     |
| Dy                            |                                  |        |       | 1.13                                |       | 10.9  | 14.0  | 16.7  | 19.6  | 1.21  | 0.045  | 0.38    |                                   |     |     |     |
| Ho                            |                                  |        |       | 2.25                                |       | 2.45  | 3.15  | 3.84  | 4.55  |   |        |         |                                   |     |     |     |
| Er                            |                                  |        |       |                                     |       | 8.89  | 11.7  | 13.5  | 16.6  | 2.15  | 0.073  | 0.67    |                                   |     |     |     |
| Tm                            |                                  |        |       | 3.26                                |       | 1.64  | 2.12  | 2.33  | 2.59  |   |        |         |                                   |     |     |     |
| Yb                            |                                  |        |       |                                     |       | 13.6  | 17.6  | 17.6  | 20.2  | 2.67  | 0.094  | 1.05    |                                   |     |     |     |
| Lu                            |                                  |        |       |                                     |       | 2.69  | 3.47  | 3.31  | 3.59  |   |        |         |                                   |     |     |     |
| Th                            |                                  | 0.0077 | 0.033 | 0.24                                | 0.24  | 349   | 216   | 304   | 193   | 0.30  | 0.025  |         |                                   |     |     |     |
| U                             | 16.0                             | 18.1   | 4.89  | 8.76                                | 12.4  | 2795  | 2972  | 2570  | 3120  | 6.54  |        |         |                                   |     |     |     |

Respective ligands refer to the anion initially used for the experiments (measured as F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>). 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.

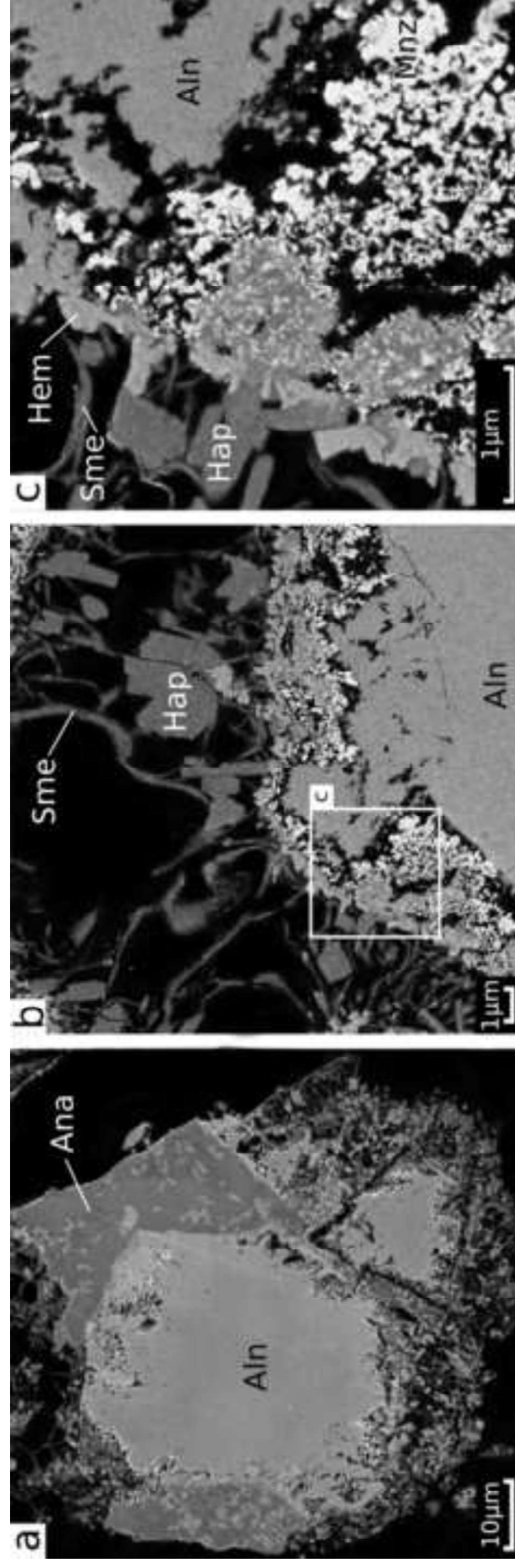


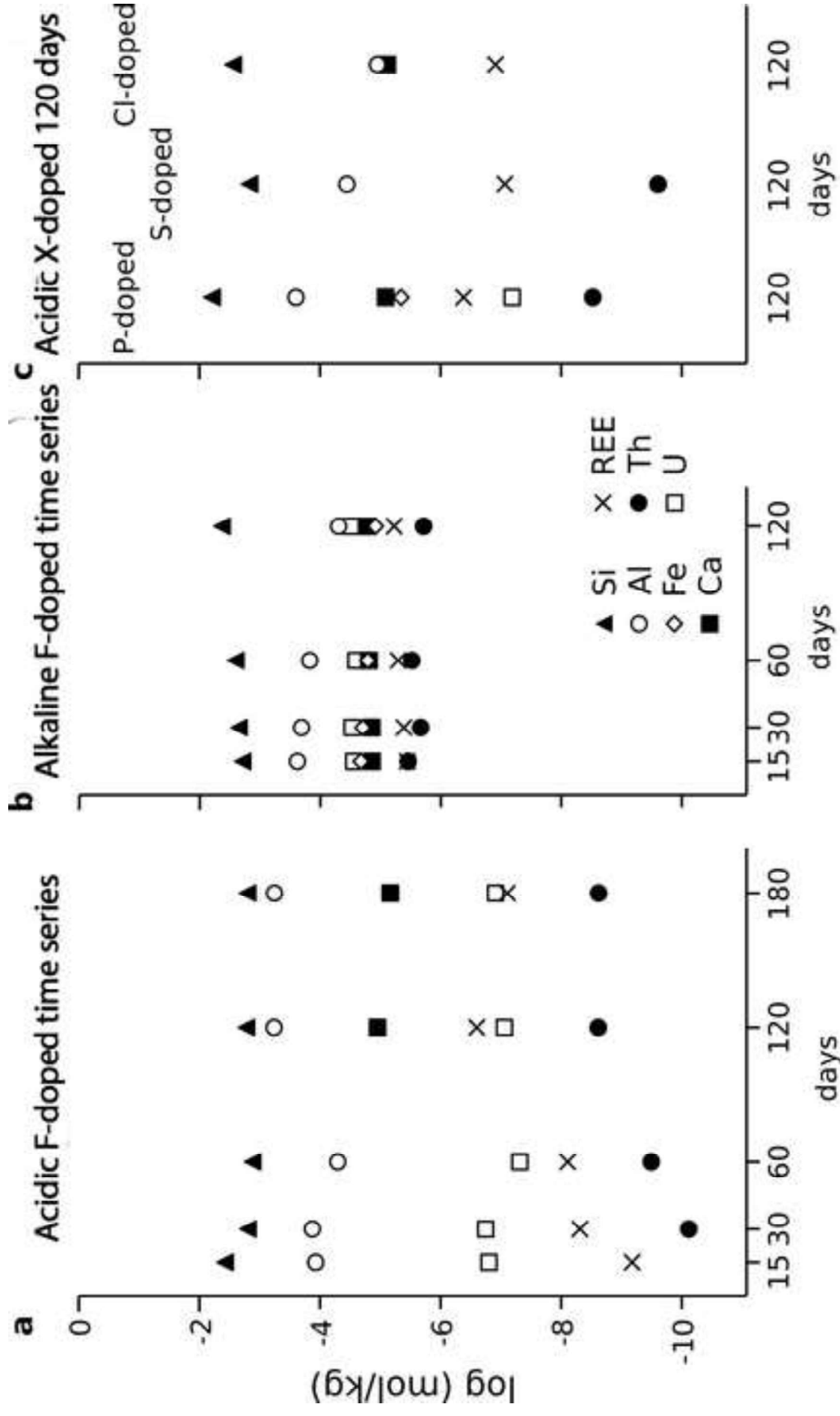












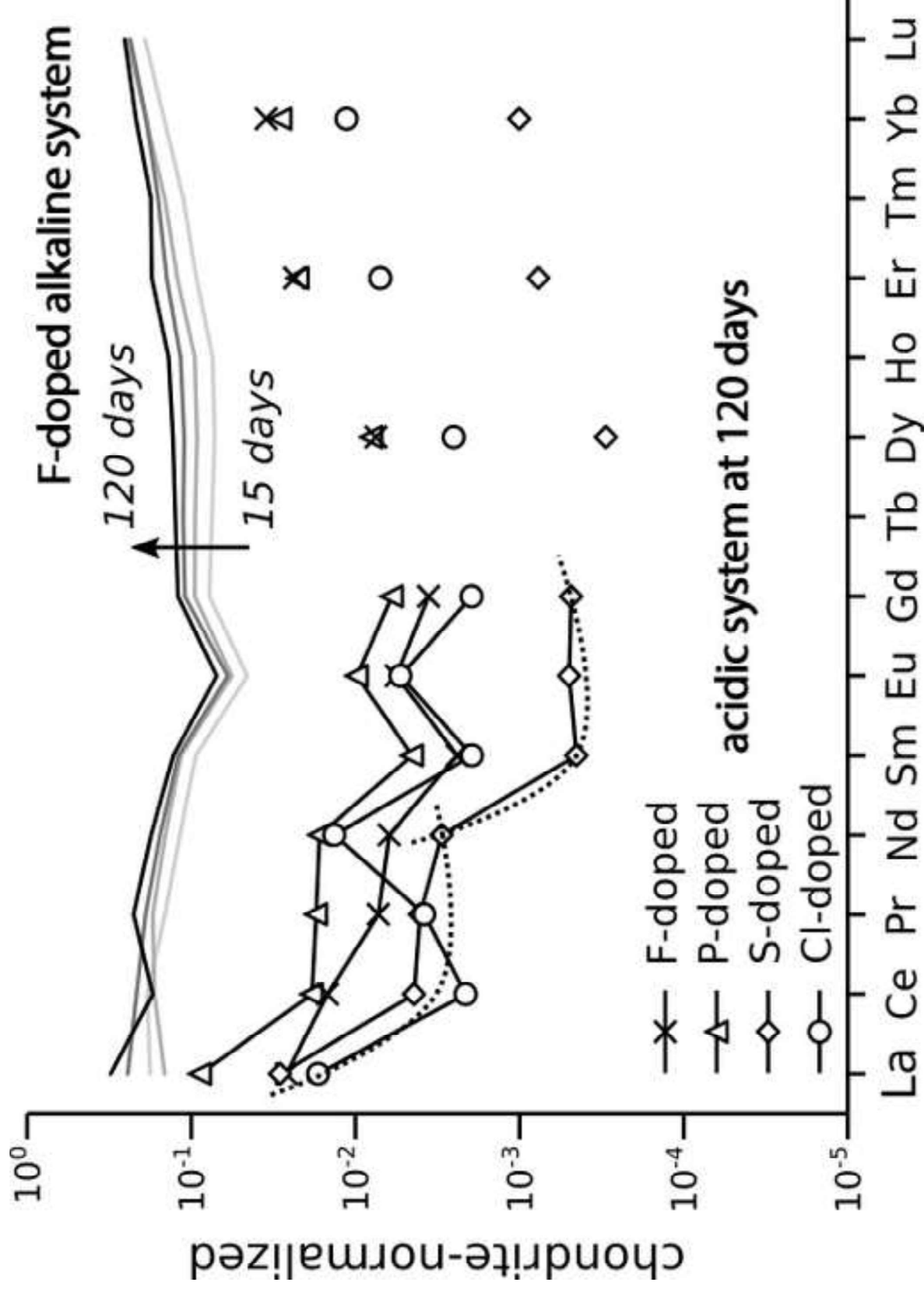
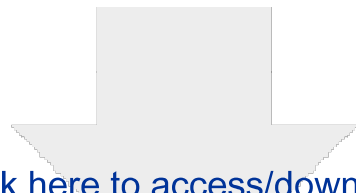
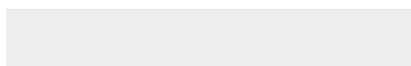
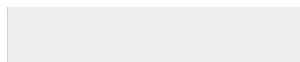


figure 6



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**supplementary material**  
Supp-data\_S4-S5\_R2.docx

