

Highlights

Hydrothermal fluorite solubility experiments and mobility of REE in acidic to alkaline solutions from 100 to 250 °C

Revision 1

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- Experimental investigation of fluorite solubility and REE mobility in acidic, mildly acidic and alkaline solutions
- Reaction textures of fluorite are dissolution-controlled between 100 and 250 °C
- Addition of NaCl enhances fluorite dissolution and mobilizes REE in acidic and alkaline fluids
- Mass balance indicates REE-depleted fluorite and REE fluorides precipitation control variations in fluid chemistry
- Fluorite solubility constants are derived between 25 and 250 °C

Hydrothermal fluorite solubility experiments and mobility of REE in acidic to alkaline solutions from 100 to 250 °C

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Abstract

Fluorite is a common vein mineral in critical mineral deposits that are overprinted by hydrothermal processes. Its chemistry potentially reflects the mobilization conditions of rare earth elements (REE) in these hydrothermal fluids. However, the controls of temperature and fluid chemistry (i.e. pH and salinity) on fluorite solubility and coupled REE mobilization is still uncertain. In this study, batch-type experiments were conducted to investigate REE mobility in aqueous fluids controlled by the solubility of fluorite at temperatures between 100 and 250 °C. Natural fluorite crystals from Cooke's Peak (New Mexico) were equilibrated with aqueous solutions of variable starting pH (2–10), salinities (0 and 15 wt.% NaCl), and initial REE concentrations (0 and 0.5 ppm). Reacted fluorite crystals display dissolution-controlled reaction textures (i.e., etch pits and dissolution channels along fluorite cleavage

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planes), which are most pronounced in experiments conducted in acidic fluids and at elevated temperature. Addition of NaCl enhances considerably fluorite dissolution, in both acidic and alkaline solutions, which is also reflected by the compositions of the reacted solutions displaying an increase in Ca, F, and REE concentrations. The overall fluorite solubility is controlled by the association behavior of HF^0 at acidic conditions, and by the formation of Ca chloride, Ca hydroxyl, and Na fluoride complexes, which become enhanced by addition of NaCl, including in mildly acidic and alkaline solutions. Mass balance calculations were used to compare the REE stoichiometry of unreacted fluorite crystals with measured REE concentrations in the reacted solutions, which reveal several possible controls on REE mobility: i) stoichiometric release of REE upon fluorite dissolution; ii) precipitation of secondary REE-depleted fluorite; and/or iii) precipitation of secondary light REE fluorides, which were observed to form on fluorite crystals surfaces in the REE-doped experiments. Fluorite solubility constants (K_{sp}) were regressed with available low temperature solubility data using the equation $\log K_{\text{sp}} = A + BT + C/T + D\log(T)$ (T , temperature in K) valid between 25–250 °C. Fitted coefficients yield: $A = 171.180$, $B = 0.01477$, $C = -7794.10$, $D = -64.6634$. The experimental results have important implications for geochemical modeling of natural systems, where fluorine controls the mobility of REE, and can be enhanced by addition of NaCl in both acidic and alkaline solutions. Therefore, the salinity of magmatic-hydrothermal fluids plays a crucial role in mobilizing REE during the formation of hydrothermal fluorite veins.

Keywords: fluorite, rare earth elements, mineral deposits, solubility products, hydrothermal experiments

1. Introduction

The rare earth elements (REE) are considered critical minerals that are used for building components in the high-tech and green technology industries, such as for instance, permanent magnets in wind turbines and electronic components in computers and cellphones (Hatch, 2012; Goodenough et al., 2018). Carbonatites and (per)alkaline igneous complexes are host to the largest REE mineral deposits, and while their emplacement is largely magmatic, hydrothermal aqueous fluids commonly play a significant role in the mobilization of REE in their final evolution stages (Gysi and Williams-Jones, 2013; Gysi et al., 2016; Elliott et al., 2018; Walter et al., 2021). Prominent examples include the giant Bayan Obo carbonatite deposit in China (Smith and Henderson, 2000; Smith et al., 2000, 2015) and the world class Strange Lake peralkaline granitic REE-Zr-Nb deposit in Canada (Salvi and Williams-Jones, 1990; Gysi and Williams-Jones, 2013; Gysi et al., 2016; Vasyukova and Williams-Jones, 2018, 2019).

To date, most of the fluid-rock interaction models of hydrothermal REE transport have focused on the role of aqueous speciation and REE-ligand complexes (Kolonin and Shironosova, 2002; Gysi and Williams-Jones, 2013; Migdisov and Williams-Jones, 2014; Migdisov et al., 2016; Perry and Gysi, 2018). Another factor that influences the mobility of REE includes the solubility of REE-bearing minerals, such as the REE fluorides, fluorocarbonates, and phosphates, some of which have only recently been determined experimentally (Gysi and Williams-Jones, 2015; Voigt et al., 2016; Gysi et al., 2018; Gysi and Harlov, 2021).

Fluorite veins are commonly observed in association with critical min-

26 eral deposits and other magmatic-hydrothermal systems, and their chemical
 27 signatures are useful indicators of fluid-rock interaction (Möller et al., 1998;
 28 Gagnon et al., 2003; Schwinn and Markl, 2005; Schönenberger et al., 2008;
 29 Nadoll et al., 2018). However, we do not yet have a solid understanding of
 30 the factors controlling the REE signatures in fluorite and the effect of dis-
 31 solved fluorine on REE mobility in carbonatite and peralkaline systems. The
 32 substitution of REE into the fluorite crystal structure is generally thought to
 33 be correlated with the difference in ionic radii between REE^{3+} and Ca^{2+} ; the
 34 light (L)REE (e.g. La^{3+} with 1.16 Å) are preferentially incorporated into
 35 fluorite over the heavy (H)REE (e.g. Lu^{3+} with 0.98 Å) when comparing
 36 their ionic radii with Ca^{2+} (1.12 Å) in 8-fold coordination (Shannon, 1976).
 37 Hydrothermal REE-doped fluorite synthesis experiments by Van Hinsberg
 38 et al. (2010) have shown that at 60 °C the REE partitioning behavior can
 39 be explained by the lattice strain model (Blundy and Wood, 2003, 1994),
 40 and is less influenced by the presence of different ligands (i.e., Cl^- , NO_3^- and
 41 SO_4^{2-}). In contrast, recent REE-doped calcite synthesis experiments at 200
 42 °C (Perry and Gysi, 2020) have shown that pH and fluid chemistry can affect
 43 the REE fluid-mineral partitioning behavior and substitution mechanisms in
 44 hydrothermal minerals. The same was observed by Curti et al. (2005) for
 45 the precipitation of Eu^{3+} in calcite at ambient temperature. To our knowl-
 46 edge, hydrothermal fluorite solubility experiments are sparse >100 °C (e.g.
 47 Strübel, 1965; Richardson and Holland, 1979; Kurovskaya and Malinin, 1983;
 48 Tropper and Manning, 2007; Zhang et al., 2017), and none of these studies
 49 have investigated the mobility of REE.

50 Here, we investigate the effects of temperature, pH and fluid compositions

(NaCl and REE concentration) on the solubility of fluorite and the consequent release of REE in hydrothermal fluids, and present a series of fluorite dissolution experiments conducted in batch reactors between 100 and 250 °C. The experimental data are evaluated using the GEMS code package (Kulik et al., 2013; Miron et al., 2015) and the MINES thermodynamic database (Gysi, 2017) for determining aqueous speciation, saturation of secondary REE minerals, and retrieving fluorite solubility products. This approach provides new insight into how fluid chemistry and fluorite solubility both affect REE mobility in hydrothermal aqueous fluids.

2. Methods

2.1. Starting materials

Natural fluorite crystals were collected from the Surprise mine in the Cooke’s Peak Pb-Zn-Cu-Au sulfide carbonate replacement and fluorite historic mining district in New Mexico (North and Tuff, 1986; Simmons, 2019). Three generations of transparent fluorite zones were identified, including a green, purple, and blue fluorite with distinct REE signatures (Fig. 1 and Table 1). The green fluorite displays the highest chondrite-normalized LREE values (>10 – 100) and is occasionally intergrown with minor purple fluorite which shows an overall REE depletion. The blue fluorite displays a LREE depletion and HREE enrichment in comparison to the green fluorite. The green fluorite was selected for the experiments due to its inclusion-free transparent crystals and relatively high REE concentrations (Table 1). Fluorite crystals were hand-picked for the experiments, cleaved into millimeter-sized fragments and ultrasonically cleaned in a 0.5% HCl solution for 15 minutes.

75 The fluorite crystals were then transferred into MilliQ water ($18\text{ M}\Omega\cdot\text{cm}$),
76 ultrasonically cleaned for 20 minutes, and dried in an oven.

77 Acidic stock solutions of pH 2 and 4 were prepared by titrating trace metal
78 grade HCl (Inorganic Ventures, $0.1001 \pm 0.0005\text{ M}$) into MilliQ water to ad-
79 just the pH values. Alkaline stock solutions of pH 10 were prepared using
80 trace metal grade NaOH (Inorganic Ventures, $0.1002 \pm 0.0005\text{ M}$) and titrated
81 into MilliQ water. The pH values in the stock solutions were measured at
82 room temperature using a Thermo Scientific Orion Star A111 benchtop pH
83 meter and a 9157BNMD Orion Triode combined pH-temperature electrode.
84 The electrode was calibrated using Fisher Scientific commercial buffer solu-
85 tions (pH of 2, 4, 7, 10; accuracy of ± 0.01). Saline stock solutions of 15
86 wt.% NaCl (Alfa Aesar, 99.998% metals basis) were prepared by dissolving
87 15 grams NaCl in 100 grams of previously prepared pH 2, 4, and 10 stock so-
88 lutions. The REE-doped stock solutions were prepared using a REE custom
89 standard (SCP Science, 10 ppm; NIST traceable certified standard), which
90 was first diluted in MilliQ water to a concentration of 0.5 ppm total REE
91 followed by a titration of NaOH/HCl to reach the desired starting pH val-
92 ues of 2 and 4, respectively. The alkaline stock solution of pH 10 was not
93 doped with REE due to precipitation of REE at room temperature. The
94 compositions of the starting experimental solutions are listed in Table 2.

95 *2.2. Experimental method*

96 Hydrothermal fluorite solubility experiments were carried out for up to 14
97 days in 45 mL Teflon-lined stainless steel batch-type reactors (Parr Instru-
98 ments Company[®], 4744) between 100 and 250 °C at saturated water vapor
99 pressure. A series of kinetic experiments were sequentially quenched between

100 1 and 14 days to determine approach to steady state Ca and F concentra-
101 tions. These kinetic runs were tested in the experiments with a starting
102 pH of 2 at 150 °C, pH of 4 at 150 °C, and pH of 10 at 250 °C. Duplicate
103 experiments were also conducted and quenched at various time periods to
104 determine experimental uncertainty.

105 Each reactor was first loaded with 25 g of the starting experimental solu-
106 tion and a single mm-sized fluorite crystal. The experimental starting condi-
107 tions (Table 2) were subdivided based on starting pH at room temperature
108 (i.e., acidic, mildly acidic, and alkaline), addition of NaCl, and/or doping
109 with REE. Masses of both the starting solution and fluorite crystal were de-
110 termined prior to loading the reactor and after quenching the experiments.
111 The sealed reactors were loaded into a furnace (ColeParmer[®], EW-33858-
112 70) and the temperature was maintained within 2 °C of the experimental set
113 point and monitored via an Omega[®] temperature logger and K-type thermo-
114 couple, located at the center of the furnace. At the end of an experiment, the
115 reactors were removed from the furnace and quenched in a cold water bath
116 in less than 20 minutes to minimize reaction upon cooling. The reacted fluo-
117 rite crystals were then removed and rinsed with MilliQ water. The quenched
118 solutions were then pipetted into separate vials including a 5 mL sample for
119 F analysis and a 20 mL acidified sample (2% HNO₃, Fisher Scientific, trace
120 metal grade) for REE, Ca, and Na analysis. The Teflon liners were then
121 rinsed with MilliQ water, followed by a 24-hour soak in a concentrated nitric
122 acid solution, a MilliQ water soak, and dried in an oven before starting a
123 new experiment.

124 2.3. Analytical methods

125 Prior to analysis, the unreacted and reacted fluorite crystals were mounted
126 in epoxy and polished, followed by carbon coating for analysis using scan-
127 ning electron microscopy (SEM). Crystal zoning, reaction textures, and sec-
128 ondary mineral precipitates were studied using a TESCAN MIRA3 LMH
129 Schottky field-emission SEM at the Mineral and Materials Characterization
130 Facility at the Department of Geology and Geological Engineering, Colorado
131 School of Mines. An accelerating voltage of 15 keV and a working distance of
132 ~ 10 mm were used for analysis. Backscattered electron (BSE) imaging was
133 performed using a TESCAN motorized retractable annular, single-crystal
134 yttrium aluminum garnet (YAG) detector. Semi-quantitative energy disper-
135 sive (EDS) analyses were conducted using a Bruker XFlash 6/30 silicon drift
136 X-ray spectrometer. Additional BSE imaging was conducted on a Cameca
137 4-spectrometer SX-100 electron microprobe at the New Mexico Bureau of
138 Geology and Mineral Resources, New Mexico Institute of Mining and Tech-
139 nology.

140 The REE compositions of the unreacted and reacted fluorite samples from
141 the Cooke's Peak mining district in New Mexico were measured using laser
142 ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the
143 United States Geological Survey (USGS) federal center in Denver, Colorado.
144 The following isotopes were quantified: ^{23}Na , ^{24}Mg , ^{29}Si , ^{31}P , ^{88}Sr , ^{89}Y , ^{139}La ,
145 ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm ,
146 ^{172}Yb , ^{175}Lu . The LA system consists of a Photon Machines Analyte G2 (193
147 nm, 4 ns excimer) with a HeLEX ablation cell. Ablation was carried out using
148 a 30 μm square spot size for a duration of 30 seconds, a laser energy density

149 of $\sim 10.5 \text{ J/cm}^2$, and a repetition rate of 5 Hz. Two cleaning ablation shots
150 were applied before collecting background and sample signal. The ablated
151 samples were then carried to an Agilent 8900 ICP-MS via a He carrier gas
152 mixed with argon. Dwell times were set to: 5 ms for Na, Si, P; 10 ms for
153 Mg, Ca, and Sr; 20 ms for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er,
154 Tm, Yb, Lu. Concentrations, drift, spikes, and detection limit calculations
155 were conducted using the protocol of Longerich et al. (1996) and the SILLS
156 software program developed by Guillong et al. (2008). Signals were calibrated
157 using the NIST 612 glass as an external standard, and ^{44}CaO was used as
158 the internal standard assuming ideal fluorite stoichiometry. Yttrium counts
159 were used to correct for drift. Additional standards measured include the
160 USGS synthetic basaltic glass reference materials (BCR-2g and BHVO-g) to
161 compare measured with standard values for method development.

162 Dissolved Ca and Na concentrations in the quenched experimental solu-
163 tions were measured in acidified (2% HNO_3 matrix) samples using an Agilent
164 7900 ICP optical emission spectrometry (OES) instrument at the Analytical
165 Chemistry Laboratory in the New Mexico Bureau of Geology and Mineral
166 Resources, New Mexico Institute of Mining and Technology. Analytical stan-
167 dards were prepared from single Ca (Inorganic Ventures, CGCA1, 1001 ± 3
168 ppm) and Na (Inorganic Ventures, CGNA1, 1002 ± 4 ppm) standards and
169 diluted with a 2% HNO_3 (Fisher Scientific, trace metal grade) blank matrix
170 solution. Based on repeated standard analysis, the analytical precision for
171 both Ca and Na were better than 3% in the concentration range of the ex-
172 perimental solutions. The analytical precision (95% confidence level) based
173 on repeated standard analysis was better than 1% for Ca at concentrations

174 between 2×10^{-6} and 5×10^{-4} mol/kg (0.1–20 ppm), and 2% for Na at con-
175 centrations between 2×10^{-5} and 2×10^{-3} mol/kg (0.5–50 ppm).

176 Dissolved REE concentrations were measured in acidified (2% HNO_3 ma-
177 trix) samples using an Agilent 7500 quadruple ICP-MS at the Analytical
178 Chemistry Laboratory in the New Mexico Bureau of Geology and Mineral
179 Resources, New Mexico Institute of Mining and Technology. An in-line he-
180 lium gas collision cell was used to reduce REE oxide formation. A series of di-
181 luted multi-REE standards (Inorganic Ventures, CMS-1, 10 ± 0.04 ppm) were
182 prepared for external calibration. Individual La, Ce, Nd, and Eu standards
183 (Inorganic Ventures, 1000 ± 5 ppm) were prepared, and if necessary, used to
184 correct for REE oxide formation using the same method as described by Gysi
185 et al. (2018) and Aries et al. (2000). Samples were spiked in-line with indium
186 (SCP Science, NIST traceable) as an internal standard for drift corrections.
187 The analytical precision (95% confidence level) based on repeated standard
188 analysis is 10% at concentrations between 1×10^{-10} and 1×10^{-9} mol/kg (0.01–
189 0.1 ppb), better than 3% at concentrations above 1×10^{-9} mol/kg (>0.1 ppb).
190 The detection limits were determined using repeated analysis of the proce-
191 dural blank (5σ) and range between 1 and 5 ppt.

192 Dissolved F concentrations were measured with a Dionex ion chromato-
193 graph (ICS-5000 DP-5) with an IonPac[®] AS22 analytical column, AG22
194 guard column, ASRS[®] 300 anion self-regenerating suppressor, and Thermo
195 Scientific conductivity detector. The standard current used for the self-
196 regenerating suppressor was 9 mA. The in-line eluent used was 4.5 mM
197 sodium carbonate and 1.4 mM sodium bicarbonate (Dionex AS22 Eluent
198 Concentrate). The injection volume was 50 μL . A series of dilute multi-

199 analyte (Inorganic Ventures, IC-FAS-1A, 19.98 ± 0.08 ppm F) IC standards
200 were prepared for calibration. The analytical precision (95% confidence level)
201 based on repeated standard analysis is 2.3% for F concentrations between
202 1×10^{-6} and 1×10^{-5} mol/kg (0.02–0.2 ppm), and 1.4% for concentrations
203 above 1×10^{-5} to 1×10^{-4} mol/kg (>0.2 –2 ppm).

204 *2.4. Data treatment*

205 Aqueous speciation, mineral saturation indices, and pH were calculated
206 at the experimental pressures and temperatures using the GEMS code pack-
207 age (Kulik et al., 2013) and GEMSFITS (Miron et al., 2015) from the mea-
208 sured cation and anion concentrations in the reacted experimental solutions.
209 Thermodynamic properties of aqueous species, gases and minerals in the
210 Ca-Na-REE-F-Cl-O-H component system were taken from the MINES ther-
211 modynamic database (<https://geoinfo.nmt.edu/mines-tdb/>). Aqueous REE
212 species of interest include the REE fluoride and chloride complexes deter-
213 mined experimentally by Migdisov et al. (2009) and the REE hydroxyl com-
214 plexes from Haas et al. (1995). The latter were theoretically extrapolated to
215 high temperatures, and need revision, but are currently the only available
216 internally consistent dataset for all of the REE hydroxyl species (Migdisov
217 et al., 2016). The thermodynamic properties of other aqueous species were
218 taken from the SUPCRT92 program and slop98.dat database (Helgeson et al.,
219 1981; Tanger and Helgeson, 1988; Johnson et al., 1992; Shock et al., 1997;
220 Sverjensky et al., 1997), which were implemented in the GEMS code package
221 and referred as Supcrt92 hereafter. This dataset was recently updated for
222 Na-, Ca-, and Cl-bearing aqueous species using the GEMSFITS optimization
223 program (Miron et al., 2015) and based on more recent experimental data

(Miron et al., 2016, 2017), which are included in the MINES database. The thermodynamic properties of fluorite were taken from Robie and Hemingway (1995) and data for solid REEF_3 and $\text{REE}(\text{OH})_3$ from Diakonov et al. (1998) and Navrotsky et al. (2015).

Activity models and equations of state are implemented in GEMS using the TSolMod library (Wagner et al., 2012). Activity coefficients for charged species were calculated using the extended Debye-Hückel equation (Robinson and Stokes, 1968) and corresponding background electrolyte models for NaCl, NaOH, and HCl (Helgeson et al., 1981; Wagner et al., 2012). The activity of neutral species was calculated from the osmotic coefficient. The thermodynamic properties of aqueous species were calculated at elevated temperature according to the revised Helgeson-Kirkham-Flowers (HKF) equation of state (Helgeson et al., 1981; Shock and Helgeson, 1988; Tanger and Helgeson, 1988; Shock et al., 1992). The equation of state used for gases was the Peng-Robinson-Stryjek-Vera with critical parameters from Frenkel et al. (1994), Proust and Vera (1989), and Stryjek and Vera (1986).

3. Results

3.1. Fluorite dissolution textures and secondary REE minerals

Representative BSE images of the fluorite crystals indicate alteration textures dominantly controlled by dissolution features and varying in intensity as a function of temperature, pH, and salinity of the experiments (Figs. 2–4). The effects of reacting the fluorite crystals with acidic and alkaline experimental solutions are compared in Figure 2. Dissolution textures are more prominent in the experiments conducted at acidic conditions, which are char-

acterized by irregular leached crystal surfaces, triangular etch pits, and etch
pit trails along fluorite cleavage planes (Fig. 2c-d). Dissolution textures in
alkaline solutions are characterized by the development of pitting along the
fluorite crystal cleavage planes near the crystal edges but only reaching about
50 to 100 μm into the fluorite (Fig. 2 e-f).

Temperature considerably increases the intensity of fluorite dissolution
textures, which is particularly pronounced by comparison of the 100 °C (Fig.
2) experiments versus the experiments conducted at 150 and 250 °C (Fig.
3). The dissolution textures are characterized by the development of etch pit
networks and irregular dissolution channels along fluorite cleavage planes,
which can reach hundreds of micrometers into the fluorite crystals. Differences
in dissolution textures observed in acidic and alkaline solutions appear
to be more pronounced in experiments conducted at 150 and 250 °C. Fluorite
crystals reacted in the acidic solutions develop strongly leached and irregular
rounded surfaces (Fig. 3a-b), whereas crystals reacted in the alkaline solutions
preserve straight crystal edges and elongate pit trails reaching about
20 to 50 μm into the fluorite crystals (Fig. 3c-d).

Addition of NaCl significantly increases the intensity of fluorite dissolution
textures with the formation of pervasively rounded crystal surfaces
in both acidic and alkaline pH solutions (Fig. 4). In these experiments,
triangular etch pits are absent. Fluorite reacted in saline mildly acidic solutions
displays similar textures but the rounded crystal rims preserve some of
the small-scale dissolution textures (i.e., etch pits and dissolution channels;
Supplementary Materials, Appendix B). Fluorite reacted in saline alkaline
experimental solutions display the development of interconnected dissolu-

tion channels reaching $\sim 100\text{--}200\text{ }\mu\text{m}$ into the altered fluorite crystal surfaces (Fig. 4d).

Minor secondary fluorite can be observed on the reacted fluorite surfaces with representative SEM images shown in Figure 5. This fluorite displays an anhedral habit and preferentially forms small ($1\text{--}5\text{ }\mu\text{m}$) crystals in etch pits, and was observed in experiments conducted in mildly alkaline and alkaline solutions. Secondary REE minerals were only identified in experiments initially doped with 0.5 ppm REE (Fig. 5). Backscattered electron images show bright REE minerals typically precipitated along the cleavage planes of the reacted fluorite. The secondary REE minerals were analyzed using SEM-EDS and are composed of La, Ce, Pr, Nd, Y, and F, with a stoichiometry corresponding to REE fluoride (REEF_3), i.e. fluocerite (Fig. 5).

Fluorite crystal fragments reacted with acidic to mildly acidic REE-doped experimental solutions display only minimal deviations from the REE concentrations of the unreacted green fluorite (Fig. 1; Supplementary Materials, Tables A1 and A2). The REE composition was therefore not significantly modified upon reaction of the fluorite crystals with the hydrothermal solutions. This also corroborates with the subtle zoning observed in BSE images of some fluorite crystal fragments that preserved their original compositions (Fig. 2).

3.2. Fluid chemistry

3.2.1. Kinetic experiments and fluorite solubility

Major element compositions of the quenched experimental solutions are listed in Table 3 and the results for each set of kinetic experiments are shown in Figure 6. The total dissolved Ca and F concentrations indicate an ap-

298 proach to steady state after 1–2 days of reaction. A significantly higher
 299 fluorite solubility is observed in the experiments with an acidic pH, with
 300 about 1 to 2 orders of magnitude higher concentrations in dissolved Ca and
 301 F in comparison to the mildly acidic and alkaline pH solutions. Addition of
 302 ~15 wt.% NaCl increases fluorite solubility, particularly in the mildly acidic
 303 to alkaline solutions (Fig. 6).

The ionic activities of $a\text{Ca}^{2+}$ and $a\text{F}^-$ were calculated at the experimental temperatures using measured Ca and F concentrations and the GEMS code package (full speciation listed in the Supplementary Materials, Table A4) to derive the reaction quotient (Q_{sp} , i.e. solubility products) for the fluorite dissolution reaction,



$$Q_{sp} = a\text{Ca}^{2+} \times (a\text{F}^-)^2 \quad (2)$$

The reaction quotients were then compared to calculated equilibrium constants (K_{sp}) of the fluorite dissolution reaction in order to calculate the fluorite saturation index (SI),

$$\text{SI} = \log(Q_{sp}/K_{sp}) \quad (3)$$

304 Calculated values for aqueous ion activities, Q_{sp} , and SI (Table 3 and Sup-
 305 plementary Materials, Table A3), and their variations as a function of tem-
 306 perature are shown in Figure 7. A plot of $\log Q_{sp}$ vs. temperature between
 307 100 and 250 °C (Fig. 7a) indicates a systematic retrograde solubility trend
 308 in the NaCl-free solutions. The highest $\log Q_{sp}$ values are found in the ex-
 309 periments with mildly acidic and alkaline solutions, both plotting close to
 310 the calculated fluorite saturation and suggesting approach to equilibrium in

311 these experiments. Variation of the solubility product at each temperature
 312 generally reflects the kinetic experiments and the experimental uncertainty
 313 based on duplicate runs; values cluster close together for experiments carried
 314 out for 2 days or longer. Departure from the calculated fluorite saturation
 315 is significant for experiments conducted in saline solutions and some of the
 316 acidic solutions as well as experiments conducted at 100 °C (Fig. 7a). Ex-
 317 periments in saline solutions display about an order of magnitude lower Q_{sp}
 318 values than in other experiments.

319 Departure from fluorite saturation can also be further investigated by
 320 inspecting the calculated fluorite saturation indices (Fig. 7b), which gen-
 321 erally corroborate with the pH of the starting experimental solutions. The
 322 alkaline solutions are close to saturation with fluorite with an average SI
 323 between 150 and 250 °C of -0.15 ± 0.17 ; the mildly acidic experiments dis-
 324 play slightly lower average SI values of -0.43 ± 0.21 ; and the experiments in
 325 acidic solutions were more undersaturated with average SI values of -0.96
 326 ± 0.14 . Experiments with ~ 15 wt.% NaCl have lower calculated SI values of
 327 -1.17 ± 0.46 . The calculated SI in the REE-doped experiments have values
 328 of -3.44 ± 1.54 (Supplementary Materials, Table A3) and indicate a strong
 329 undersaturation with fluorite possibly due to precipitation of secondary REE
 330 fluorides.

331 Kinetic experiments and calculated fluorite saturation indices indicate
 332 that experiments in mildly acidic and alkaline solutions provide the most
 333 reliable data to evaluate the solubility constants of fluorite as a function
 334 of temperature between 150 and 250 °C. The systematic shift in calculated
 335 $\log Q_{sp}$ and SI values for the saline experiments and some of the acidic HCl-

bearing solutions, indicate a possible need to revise data for the Ca chloride species (i.e., CaCl^+ and $\text{CaCl}_2(\text{aq})$) and NaF^0 involved in the speciation calculations, which can result in the lower calculated activities for Ca^{2+} (Table 3). The latter influence the calculated reaction quotients and saturation indices of fluorite (Eq. 2).

3.2.2. REE solubility

Measured REE concentrations in the quenched experimental solutions are summarized in Table 4. Kinetic runs indicate a rapid approach to steady state with REE concentrations leveling off after 1–2 days of reaction (Fig. 8), and minimal perturbation by precipitation of secondary REE fluorides (if present). These trends also indicate rapid equilibration between fluorite and the reacted solutions, corroborating the chemistry of Ca and F (Fig. 6)

Figure 9 shows a comparison of the REE concentrations measured in the experimental solutions as a function of temperature, salinity and pH. The REE concentrations are chondrite-normalized to eliminate the effects of crustal abundance (i.e., odd/even atomic numbers for each of the REE), allowing to make a comparison to REE profiles in the unreacted fluorite (Fig. 1). These plots indicate that pH and salinity play a major role in controlling the solubility of REE. In the absence of NaCl, the highest REE concentrations are found in the quenched fluids from experiments conducted in acidic solutions with chondrite-normalized values ranging between $\sim 1 \times 10^{-3}$ and 1×10^{-1} . Experiments conducted in mildly acidic and alkaline solutions had overall lower chondrite-normalized values ranging between $\sim 1 \times 10^{-5}$ and 1×10^{-3} .

Temperature has a minimal influence on the solubility of REE between

100 and 250 °C. Some of the variations shown in Figure 9 are related to reaction time as shown by a higher chondrite-normalized REE profiles. In the acidic solutions, some variations in LREE can be related to the initial fluorite crystals used the experiments (i.e., blue fluorite is depleted in LREE over the green fluorite); these can easily be distinguished by the small variations in REE profiles within one group of fluorite crystals. The overall LREE and HREE variations in the mildly acidic and alkaline solutions are very similar and display an overall flat REE profile in comparison to the experiments conducted in acidic solutions (Fig. 9b-c).

For all investigated pH, addition of NaCl results in a significant increase in REE concentrations by several orders of magnitude (Table 4). This increase is more pronounced in alkaline solutions, where the chondrite-normalized values increase from $\sim 1 \times 10^{-3}$ to $\sim 1 \times 10^0$ approaching values observed in the acidic solutions.

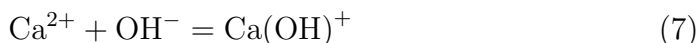
4. Discussion

4.1. Controls on fluorite solubility and derivation of solubility constants

Comparison of fluid chemistry (Fig. 6–7; Table 3) with fluorite reaction textures (Figs. 2–4) indicates that salinity and pH exert a stronger control on fluorite solubility than temperature between 100 and 250 °C. In turn, fluorite solubility has a primary control on the release of REE and availability of F for the formation of secondary REE fluorides and/or fluorite enriched/depleted in REE. The experiments indicate that the overall mobility of REE is fluorite dissolution-controlled. This contrasts to coupled dissolution-precipitation mechanisms (Putnis and Putnis, 2022) which have

385 been reported for the metasomatism of apatite and monazite in high tem-
 386 perature-pressure experiments (300–900 °C and 100–1000 MPa) and deduced
 387 from REE mineral textures in natural systems (Harlov et al., 2005, 2011;
 388 Betkowski et al., 2016; Harlov et al., 2016; Patel et al., 2022). This would
 389 be reflected, for example, by the replacement of apatite by secondary apatite
 390 plus xenotime and monazite, while preserving the overall crystal morphology
 391 (i.e., pseudomorphic replacement).

392 The control of fluid chemistry on fluorite solubility in our experiments can
 393 be described by the following sets of aqueous complex formation reactions:



394 Driving these reactions to the right will lower the Ca^{2+} and F^- activities
 395 in the fluid and drive fluorite solubility (Eq. 1). In acidic and mildly acidic
 396 solutions, fluorite solubility is controlled by Reactions 4–6 (see also Supple-
 397 mentary Materials Tables, calculated species activities), which explains why
 398 addition of HCl and NaCl enhances fluorite solubility. In alkaline solutions,
 399 the formation of Ca hydroxyl species becomes important with increased pH
 400 (Reaction 7). The formation of NaF^0 becomes important in the experiments
 401 with NaCl (Supplementary Materials, Table A4). A similar observation was
 402 made in the study by Richardson and Holland (1979), in which the solubility

403 of fluorite was measured at >100 °C in solutions containing variable amounts
404 of NaCl, CaCl_2 and other salts.

405 Fluorite solubility products derived from our experimental data (Eqs: 1–
406 3) are compared with available literature data between 25–350 °C in Figure
407 10. Based on the fluorite saturation indices presented earlier (Fig. 7), exper-
408 iments conducted at 100 °C and experiments with NaCl were excluded for
409 the derivation of the solubility constant (K_{sp}) of fluorite because their low
410 SI indicate that they may not have reached equilibrium.

411 The high temperature experiments by Richardson and Holland (1979)
412 (except their data at 100 °C), Strübel (1965), and fitted data by Nordstrom
413 and Jenne (1977), diverge considerably from our measured fluorite solubil-
414 ity products (Fig. 10). These literature data also display large discrepancies
415 with the predicted solubility products calculated from a combination of aque-
416 ous species (Ca^{2+} and F^-) from Sucprt92 (slop98.dat) recently optimized by
417 Miron et al. (2017), with the properties of fluorite from Robie and Hem-
418 ington (1995). These discrepancies can result from several factors. Firstly,
419 fluorine was analyzed using ion selective electrodes, which is less accurate
420 (i.e., formation of potentials) and has higher detection limits than IC used
421 in our study. Secondly, the experiments by Richardson and Holland (1979)
422 were carried out in gold capsules using a weight loss technique with only a
423 few mg solutions recovered in comparison to this study, where Ca was mea-
424 sured reliably using ICP-OES and about 25 g solution recovered. Finally, the
425 calculated activities of Ca^{2+} and F^- species need to be carefully evaluated
426 at elevated temperature. Species that may need to be re-evaluated include
427 some of the fluoride species (NaF^0 , CaF^+ , and HF^0) that strongly affect the

428 calculated F^- activities and fluorite solubility in saline and acidic solutions
 429 and hence can result in apparent strongly undersaturated solutions (Fig. 7).

The fluorite solubility products from Garand and Mucci (2004) and Henry (2018) at 25 °C closely approach each other, whereas the solubility constants derived by Zhang et al. (2017) are slightly higher (Fig. 10). Therefore, our experimental solubility products were only combined with the values from Garand and Mucci (2004) at 25 °C, Henry (2018) at 25–50 °C, Richardson and Holland (1979) at 100 °C, then fitted to the following equation to derive the solubility constants as a function of temperature:

$$\log K_{sp} = A + BT + C/T + D\log(T) \quad (9)$$

430 The fitted coefficients, solubility constants, and thermodynamic proper-
 431 ties are listed in Table 5. The fitted curve is shown in Figure 10. The
 432 solubility constant retrieved at 25 °C and 1 bar has a $\log K_{sp}$ value of -10.56,
 433 which is in excellent agreement with the recent fluorite solubility analysis
 434 by Nordstrom (2022) with a $\log K_{sp}$ value of -10.57 ± 0.08 . Further, the
 435 standard thermodynamic properties of reaction can be retrieved from the
 436 solubility constants and the fitted coefficients (Table 5):

$$\log K_{sp} = \frac{-\Delta_r G^\circ}{R \ln(10) T} \quad (10)$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad (11)$$

$$\Delta_r H^\circ = (R \ln(10) (BT^2 - C + DT/\ln(10))) / 1000 \quad (12)$$

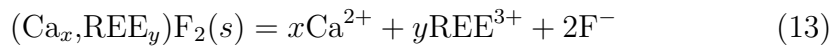
437 where $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ are the standard Gibbs energy, enthalpy
 438 and entropy of reaction (in Eq. 2); T is the temperature in Kelvin; R is the
 439 ideal gas constant. At reference temperature (298.15 K) and pressure (1 bar)

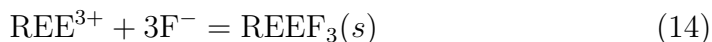
the retrieved values yield: $\Delta_r G^\circ_{298.15K} = 60.29 \text{ kJ mol}^{-1}$ and $\Delta_r H^\circ_{298.15K} = 14.05 \text{ kJ mol}^{-1}$. Combining these values with the properties of aqueous species (Table 5) yields the fluorite standard properties of formation from the elements at 298.15 K and 1 bar of: $\Delta_f G^\circ_{\text{fluorite}}$ of $-1176.6 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ_{\text{fluorite}}$ of $-1227.9 \text{ kJ mol}^{-1}$. For comparison, the thermodynamic properties for fluorite from Robie and Hemingway (1995) are listed with a $\Delta_f G^\circ_{\text{fluorite}}$ value of $-1175.3 \text{ kJ mol}^{-1}$ and a $\Delta_f H^\circ_{\text{fluorite}}$ value of $-1228.0 \text{ kJ mol}^{-1}$. Also, the standard entropy derived from the solubility data (Eq. 11) yields $72.3 \text{ J mol}^{-1}\text{K}^{-1}$, which is quite close to the value of $68.9 \text{ J mol}^{-1}\text{K}^{-1}$ from Robie and Hemingway (1995). This gives confidence in the fitted experimental data between 25–254 °C as presented in Table 5.

Including the solubility products from Zhang et al. (2017) or the higher temperature data (200–260 °C) by Richardson and Holland (1979) yields inconsistent regressed thermodynamic properties of reaction. Trying to add these values to the data regression yielded standard enthalpy of formation values diverging by 10–20 kJ/mol and entropy values diverging by 30–40 $\text{J mol}^{-1}\text{K}^{-1}$ in comparison to the values by Robie and Hemingway (1995). We therefore do not recommend combining these solubility data with our experimental data to derive fluorite solubility constants at elevated temperature.

4.2. Controls of secondary fluorite and REE minerals on REE mobility

The following two simplified reactions explain how the formation of secondary minerals further affects REE mobility and stoichiometry of the experimental solutions:





463 Reaction 13 represents the dissolution of fluorite and stoichiometric re-
 464 lease of REE when driven to the right, or precipitation of secondary fluorite
 465 with *a priori* unknown REE concentrations when driven to the left. Reac-
 466 tion 14 represents the solubility of REE fluorides. Minor precipitation of
 467 fluorite was observed on some of the reacted crystal surfaces, and secondary
 468 REE fluorides were identified using SEM-EDS but only in the REE-doped
 469 experiments (Fig. 5). Due to the small sizes and small abundance of sec-
 470 ondary fluorite, it is difficult to evaluate whether Reaction 13 or 14 control
 471 the mobility of REE upon release of REE and F during fluorite dissolu-
 472 tion. Comparison of chondrite-normalized LREE variations in the quenched
 473 experimental solutions (Fig. 9) with the REE profiles measured in the un-
 474 reacted fluorite crystals (Fig. 1), indicates a possible control by formation
 475 of secondary minerals. This is particularly pronounced for La, Ce, Pr, and
 476 Nd, that are depleted over heavier REE in many of the experiments (Fig.
 477 9). Two approaches are presented here to further evaluate the controls of
 478 secondary mineral formation on REE mobility including the calculation of
 479 mineral saturation indices and a mass balance approach.

480 The first approach consists of evaluating the potential for secondary REE
 481 mineral formation by calculating the saturation indices (SI) of REE fluo-
 482 rides and hydroxides. The SI were determined from calculated ion activities
 483 (Supplementary Materials, Tables A3 and A4), which were derived from the
 484 compositions of the quenched experimental solutions and the speciation cal-
 485 culations using the GEMS code package (Kulik et al., 2013). Calculated SI
 486 indicate that the experimental solutions are generally closer to saturation

487 with REE fluorides than with the REE hydroxides; the latter are mostly
 488 undersaturated except in a few of the alkaline and NaCl-bearing solutions
 489 (Supplementary Materials, Table A3). Experiments in acidic and mildly
 490 acidic solutions as well as experiments in NaCl-solutions are close to satura-
 491 tion with REE fluorides. This behavior corroborates with the higher fluorite
 492 solubility, and hence higher F^- activity in these solutions in comparison to
 493 experiments conducted in alkaline solutions. The LREE fluorides (i.e., LaF_3 ,
 494 CeF_3 , SmF_3 , and EuF_3) show typically the highest affinity for saturation in
 495 the experimental solutions, whereas the HREE fluorides are all undersatu-
 496 rated. Experiments in the REE doped solutions are also close to saturation
 497 with the LREE fluorides and some of the HREE fluorides, particularly in the
 498 high temperature experiments conducted at 250 °C (Supplementary Materi-
 499 als, Appendix B3).

The second approach consists of mass balance calculations to evaluate the stoichiometry of REE upon fluorite dissolution and potential for precipitation of secondary REE-bearing fluorite versus REE fluorides. Comparison of the measured Ca, F, and REE concentration ratios in the quenched experimental solutions (Tables 3–4) with measured LA-ICP-MS data of the unreacted fluorite (Table 1) allows determining the following logarithmic ratios:

$$\log \frac{(REE/Ca)_{fluid}}{(REE/Ca)_{solid}} \quad (15)$$

$$\log \frac{(REE/F)_{fluid}}{(REE/F)_{solid}} \quad (16)$$

500 where $(REE/Ca)_{fluid}$ and $(REE/F)_{fluid}$ are the molality ratios of REE,
 501 Ca and F measured in the quenched experimental solutions; $(REE/Ca)_{solid}$
 502 and $(REE/F)_{solid}$ are the ratios expected from the stoichiometric dissolution

503 of fluorite. For Equations 15 and 16, a value equal to 0 indicates a stoi-
 504 chometric REE release upon fluorite dissolution. A value greater than 0
 505 indicates that the REE remain in solution and an affinity for the formation
 506 of secondary REE-depleted fluorite (i.e., lowering Ca and F concentrations).
 507 Conversely, a value less than 0 indicates precipitation of secondary REE min-
 508 erals and sequestration of REE from solution due to either the formation of
 509 REE fluorides or REE-enriched fluorite. Distinction between the latter two
 510 can be made by comparing the REE/Ca and REE/F ratios as depicted in
 511 Figure 11.

512 In acidic solutions, the REE/Ca and REE/F ratios plot close to the sto-
 513 ichiometric dissolution line for fluorite (Figs. 11a,d). The LREE deviate
 514 from that trend, most notably La and Ce that plot above the stoichiometric
 515 line. In contrast, the HREE plot all close to the stoichiometric line, except
 516 Y. We interpret these trends to indicate the formation of LREE depleted
 517 and slightly Y enriched fluorite, with an overall lack of LREE fluoride pre-
 518 cipitation. These trends contrast with the predicted saturation indices for
 519 La- and Ce-fluorides that seem to overpredict the affinity for LREE fluo-
 520 ride precipitation in those experiments (Supplementary Materials, Appendix
 521 B3). Nevertheless, these observations are in line with some of the chondrite-
 522 normalized REE profiles depicted in Figure 9a. Lanthanum is enriched in
 523 the acidic solutions over other REE, whereas Y is present in similar con-
 524 centrations than Ho and Dy. Because Y presents a positive anomaly in the
 525 unreacted fluorite, the fluid chemistry indicates that some Y must have pre-
 526 cipitated into secondary fluorite to reach similar concentrations to Ho and
 527 Dy in the reacted solutions.

528 In mildly acidic and alkaline solutions (Figs. 11b-c and 11e-f), there is
529 a notable switch in REE/Ca and REE/F ratios with the La, Ce, Pr, and
530 Nd and some of the HREE (i.e., Dy, Y, and Ho) plotting below the stoichio-
531 metric line. Clear positive REE/Ca and REE/F ratios can be observed for
532 the experiments conducted at the highest temperature of 250 °C. We inter-
533 pret these trends to indicate the possible precipitation of LREE fluorides,
534 particularly at mildly acidic conditions, and precipitation of mostly HREE
535 depleted secondary fluorite at the higher experimental temperature. These
536 observations are in line with the calculated saturation indices for La- and Ce-
537 fluoride for the mildly acidic solutions (Supplementary Materials, Appendix
538 B3) as well as their chondrite-normalized REE profiles. The latter display
539 a depletion in La, Ce, Pr, and Nd over adjacent LREE such as Sm and Eu
540 (Fig. 9b), which is less pronounced in the alkaline solutions.

541 Overall these trends indicate that in alkaline solutions there is a higher
542 potential for REE fluoride precipitation, whereas in the acidic solutions the
543 measured REE mostly correspond to stoichiometric dissolution from fluo-
544 rite and possibly the precipitation of secondary LREE-depleted/Y-enriched
545 fluorite. While the mass balance calculations permit identifying the poten-
546 tial formation of secondary REE-bearing minerals, the measured variations
547 in F concentrations are too small to affect the calculated fluorite solubility
548 products, i.e. mildly acidic and alkaline solutions plot close to the fluorite
549 saturation line (Fig. 7).

550 4.3. Controls of aqueous speciation on REE mobility

551 The mobility of REE in natural hydrothermal fluids depends on the sta-
552 bility of REE complexes and the solubility of REE-bearing minerals. In

critical mineral deposits with acidic/mildly acidic fluids, chlorides and sulfates are considered major transporting ligands of REE, whereas fluorides and phosphates are considered depositional ligands due to the low solubility of fluorides and phosphates (Migdisov and Williams-Jones, 2014; Gysi et al., 2018). In near-neutral to alkaline solutions, the REE hydroxyl and/or carbonate complexes could potentially become important (Pourtier et al., 2010; Perry and Gysi, 2018; Louvel et al., 2022; Nisbet et al., 2022).

The speciation of REE was calculated using the GEMS code package (Kulik et al., 2013) to determine the dominant aqueous complexes controlling the solubility of REE in the experiments. Figure 12 shows an example of predominant (mole fractions) species for Ce (i.e., LREE) and Er (i.e., HREE) as a function of temperature, pH and salinity. In the NaCl-free experiments (Fig. 12a-b), the REE fluoride complexes are calculated to be predominant in both acidic and mildly acidic solutions, and the REE hydroxyl complexes in alkaline solutions. The dominant REE fluoride species include REEF^{2+} , and REEF_2^+ at 100–150 °C with the appearance of REECl^{2+} in the acidic and REE hydroxyl complexes (i.e., REEOH^{2+} and $\text{REE}(\text{OH})_2^+$) in the mildly acidic solutions at 250 °C. In the alkaline experimental solutions, $\text{REE}(\text{OH})_3^0$ and $\text{REE}(\text{OH})_4^-$ are predominant between 100–250 °C. Experiments conducted in NaCl solutions yield a significant increase in the calculated stability of REE chloride over the REE fluoride complexes, in both, acidic and mildly acidic solutions (Fig. 12c). This is particularly pronounced for the Ce species, for which, the fluoride complexes are negligible between 100–250 °C.

Here we carried out an additional series of acid/base titration simula-

578 tions using the GEMS code package to show the overall predicted stability
 579 of aqueous REE species and saturation of REE fluorides and hydroxides at
 580 150 °C for a REE-bearing fluid in equilibrium with fluorite at pH of 2 to
 581 10. Figure 13 illustrates the calculated pH–log a_{REE} diagram using currently
 582 available experimental data for REE aqueous complexes at 150 °C for a fluid
 583 saturated with fluorite and using the updated solubility products retrieved
 584 in our study (Table 5). In the simulations with no NaCl (Fig. 13a,c), the
 585 solubility of REE is controlled by the formation of REE fluorides and the
 586 formation of REE fluoride species at pH values between 2–6.5 and the sol-
 587 ubility of REE hydroxides and stability of REE hydroxyl complexes at pH
 588 values above 5.5–6.5. The predominance of REE fluoride complexes in the
 589 simulated acidic fluids is different from the observations by Migdisov and
 590 Williams-Jones (2014) who did not consider the availability of fluoride from
 591 fluorite dissolution in their model. Addition of 15 wt.% NaCl (Fig. 13b,d)
 592 increases the stability of REE chloride complexes, which predominate for Ce
 593 but not for Er. Further addition of chloride increases the predominance of
 594 REE chloride species, in agreement with the simulations by Migdisov and
 595 Williams-Jones (2014). The present simulations highlight the importance of
 596 considering additional sources and sinks of F[−] for REE mobility, which in-
 597 cludes the solubility of fluorite and the formation of fluoride complexes such
 598 as NaF⁰ (Eq. 8), which affect the solubility of REE-bearing fluoride minerals.

599 Thermodynamic modeling of REE mobility in F-rich natural systems is
 600 still hampered by several limitations that need to be pointed out. Simulated
 601 REE speciation in F-bearing hydrothermal fluids by Migdisov and Williams-
 602 Jones (2014) suggest that REE chloride complexes are primarily responsible

603 for the transport of REE in these fluids. In contrast to REE chloride, fluoride,
 604 and sulfate complexes for which thermodynamic properties are determined
 605 experimentally (Migdisov et al., 2009), our knowledge about the stability of
 606 REE hydroxyl and carbonate complexes is currently limited to the thermo-
 607 dynamic data derived by Haas et al. (1995). The latter have a high degree
 608 of uncertainty (Migdisov et al., 2016). Only a few experimental studies have
 609 been conducted recently on the REE speciation at near-neutral to alkaline
 610 conditions (e.g. Wood et al., 2002; Louvel et al., 2022). However, solubility
 611 experiments and molecular dynamic simulations are missing for those species
 612 and would be needed.

613 The formation of REE fluorides, such as fluocerite, is rather uncommon
 614 in natural systems but can be a precursor to more stable REE minerals
 615 (Strzelecki et al., 2022). Instead, fluorocarbonates (i.e., bastnäsité, parisite,
 616 synchysite, etc.) are commonly found in magmatic-hydrothermal critical
 617 mineral deposits including alkaline complexes and carbonatites (Smith et al.,
 618 2000; Williams-Jones et al., 2000; Gysi and Williams-Jones, 2013; Gysi et al.,
 619 2016; Wu et al., 2021; Beard et al., 2022; Patel et al., 2022; Verplanck et al.,
 620 2022). However, thermodynamic properties that permit modeling the stabil-
 621 ity of these minerals are still scarce (Gysi and Williams-Jones, 2015; Shiv-
 622 aramaiah et al., 2016; Voigt et al., 2016; Goncharov et al., 2022). Further,
 623 these simulations commonly use a set amount of REE added to the fluid
 624 to calculate REE speciation. The primary control of fluorite solubility on
 625 the mobility of the REE (Eq. 13) has until now not been predicted even
 626 though it is a common vein mineral in many REE mineral deposits where
 627 hydrothermal overprint has been documented (Smith and Henderson, 2000;

Smith et al., 2000; Samson et al., 2004; Gysi and Williams-Jones, 2013; Gysi et al., 2016).

5. Conclusions

In this experimental study we quantify the combined effects of pH, salinity and temperature on REE mobility upon fluorite dissolution at temperatures >100 °C. A major finding from the experiments is that the solubility of REE can be enhanced in alkaline solutions with the addition of NaCl, with concentrations in the fluids reaching similar levels to the acidic solutions (i.e., NaCl-free and NaCl solutions). The processes affecting REE mobility investigated here include the role of: 1) fluorite solubility; 2) aqueous REE speciation; 3) precipitation of secondary REE fluorides and REE-depleted fluorite under hydrothermal conditions. Fluorite reaction textures in conjunction with fluid chemistry were investigated in detail and indicate that the experiments represent a dissolution-controlled environment. Further, we derived a series of new fluorite solubility constants based on the experiments between 150 and 254 °C that match with previous low temperature solubility studies. The experiments also indicate that the Supcrt92 database overpredicts fluorite solubility between 25 and 250 °C.

Upon approach to equilibrium with fluorite, and in the absence of doping the experimental solutions with 0.5 ppm REE, the affinity to form secondary REE minerals was found to be generally low, except for the lighter REE (i.e., La, Ce, Pr, and Nd). The fluorite solubility was found to be controlled dominantly by the formation of Ca chloride and hydroxyl species, NaF^0 , and the association behavior of HF^0 (Eqs. 5-8). The overall REE mobility behavior is controlled by fluid chemistry (pH and salinity). The maximum

REE concentrations in the fluid range between $\sim 1 \times 10^{-5}$ and 1×10^{-7} mol/kg, and minimum concentrations between $\sim 1 \times 10^{-9}$ and 1×10^{-11} mol/kg (Table 4), with the highest concentrations found in the NaCl-bearing solutions (independent of pH) and the lowest concentrations in the alkaline NaCl-free solutions.

Based on a series of mass balance equations (Eqs. 15-16), the following conclusions can be made: 1) acidic fluid produces a REE signature that behaves stoichiometric with fluorite; 2) mildly acidic and alkaline fluids promote the formation of REE-depleted fluorite; 3) addition of NaCl promotes increased fluorite dissolution and saturation with secondary LREE fluorides. There is a need for high temperature precipitation experiments to study the REE incorporation mechanisms into hydrothermal fluorite, similar to the recent study by Perry and Gysi (2020) on REE-doped calcite. These next steps will allow deriving a thermodynamic solid solution model to simulate the mobility of REE and predict REE signatures in hydrothermal fluorite veins.

Acknowledgments

This project was supported by the National Science Foundation to APG (NSF CAREER grant EAR-2039674). We would like to thank B. Frey, D. Baca and H. Han from the New Mexico Bureau of Geology and Mineral Resources, New Mexico Tech Geochemistry laboratory, for assistance on the IC, ICP-OES and ICP-MS instruments. J. Thompson from the U.S. Geological Survey Federal Center in Denver, Colorado, provided assistance on the LA-ICP-MS instrument. K. Pfaff and K. Livingston provided assistance with

677 scanning electron microscope imaging in the Mineral and Materials Charac-
 678 terization Facility in the Department of Geology and Geological Engineering,
 679 Colorado School of Mines. We are grateful for access to the Surprise mine in
 680 New Mexico, and thank P. Simmons and his team for guidance in the field and
 681 for allowing us to collect fluorite crystals in the mine. This manuscript ben-
 682 efited greatly from the constructive reviews by M. Louvel and O. Vasyukova.
 683 We also thank Editor-in-Chief M. Böttcher for handling this manuscript.

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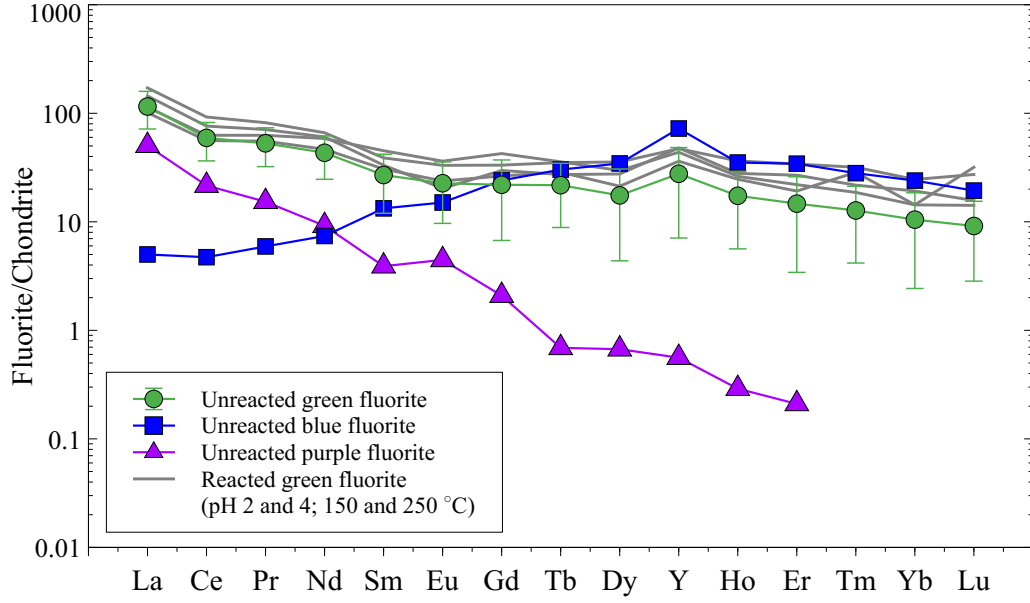


Figure 1: Chondrite-normalized (McDonough and Sun, 1995) fluorite composition measured using LA-ICP-MS and showing the mean REE profiles of the three different unreacted fluorite types and reacted green fluorite. The error bars for the green fluorite represent the standard deviation of the mean and indicate that the fluorite reacted rims with the REE doped experimental solutions displays limited variability in comparison to the core-to-rim variability observed in the unreacted fluorite. The full dataset is available in the Supplementary Materials (Tables A1 and A2).

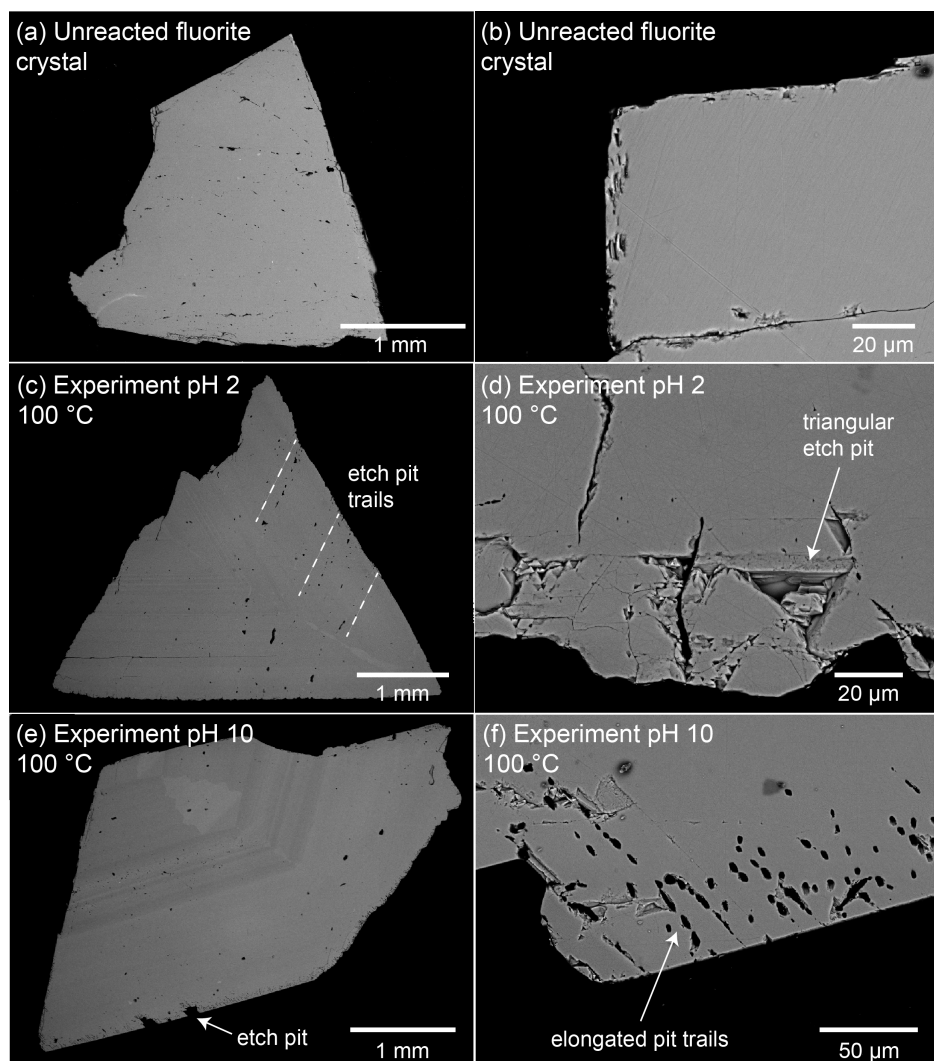


Figure 2: Backscattered electron images of unreacted and reacted fluorite crystal fragments presented as a function of starting pH of the experimental solutions. Overviews (a, c, e) and magnified views (b, d, f) are shown for each reaction texture. (a-b) Unreacted fluorite crystals display slight etching on the surface from crystal cleaning. (c-d) Fluorite crystals reacted with acidic solutions (pH 2) exhibit increased pitting in the crystal, leaching along crystal edges, and the formation of triangular etch pits along cleavage planes. (e-f) Fluorite crystals reacted with alkaline solutions (pH 10) exhibit dissolution networks ~ 50 - $100\ \mu\text{m}$ and elongated pit trails. Starting experimental conditions are listed in Table 2, and additional images for the pH 4 experiments are found in the Supplementary Materials (Appendix B).

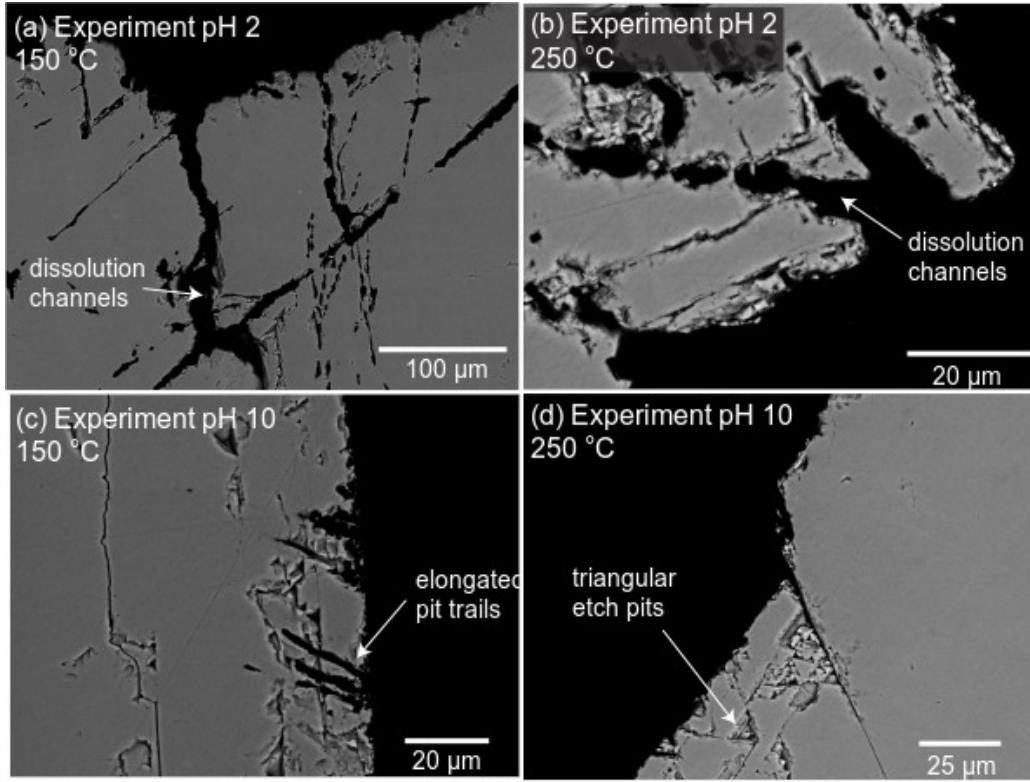


Figure 3: Backscattered electron images showing reacted fluorite crystal surfaces presented as a function of pH and experimental temperature of 150 and 250 °C. (a-b) Fluorite crystals reacted with acidic solutions (pH 2) display the formation of dissolution channels along cleavage planes and irregular leached crystal surfaces. (c-d) Fluorite crystals reacted with alkaline solutions (pH 10) display the formation of elongated pits trails along the crystal edges and the formation of triangular etch pits near the crystal edges. Dissolution textures are generally more pronounced with increased temperature in comparison to the 100 °C experiments (Fig. 2). Starting experimental conditions are listed in Table 2.

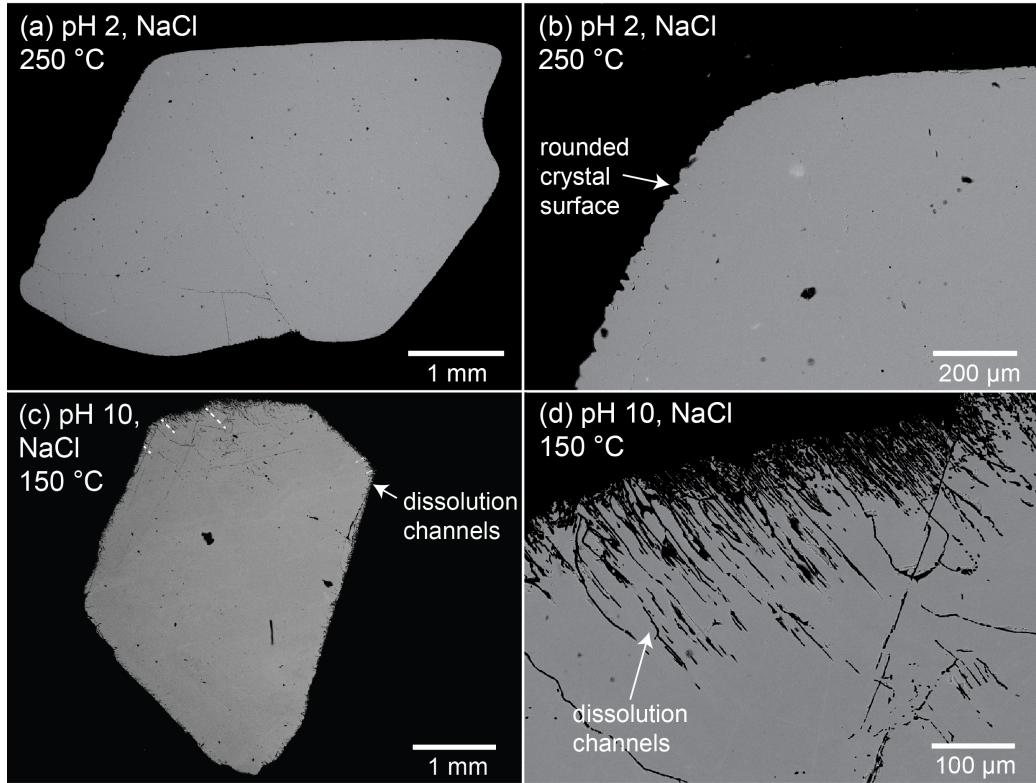


Figure 4: Backscattered electron images of fluorite crystal fragments reacted with saline (~15 wt.% NaCl) solutions with acidic (a-b) and alkaline (c-d) pH. (a-b) Addition of NaCl to acidic solutions (pH 2) results in increased intensity of fluorite dissolution textures with the development of leached rounded crystal surfaces. (c-d) Addition of NaCl to the alkaline solutions (pH 10) results in the development of >100 μm dissolution channels along cleavage planes. Starting experimental conditions are listed in Table 2.

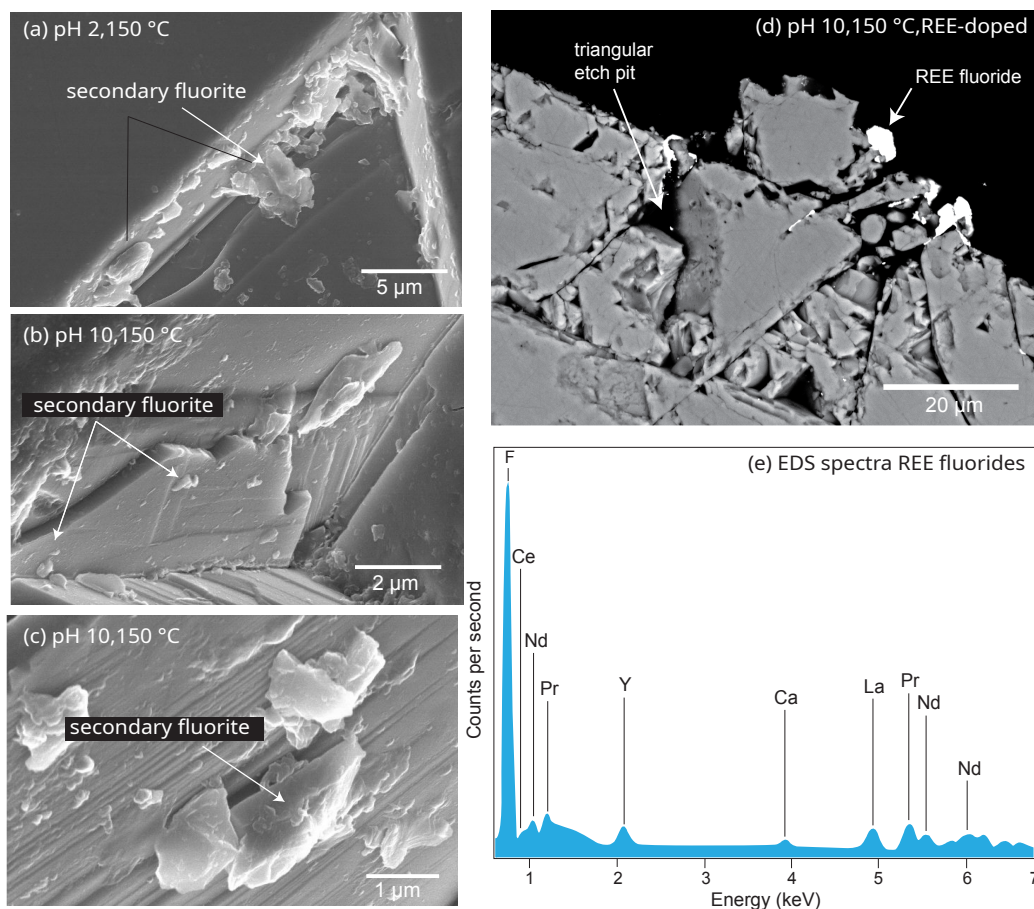


Figure 5: Scanning electron and BSE images of secondary minerals formed. (a-c) Small fluorite precipitates formed on the reacted fluorite surfaces. (d) BSE image and (e) SEM-EDS spectra of secondary REE fluorides precipitated on the fluorite crystal surface and along cleavage planes and etch pits formed in the REE doped (0.5 ppm) experiments conducted in mildly acidic (pH 4) solutions and a temperature of 250 °C. EDS spectra indicate the presence of the La, Ce, Pr, Nd, Y and F with minimal Ca.

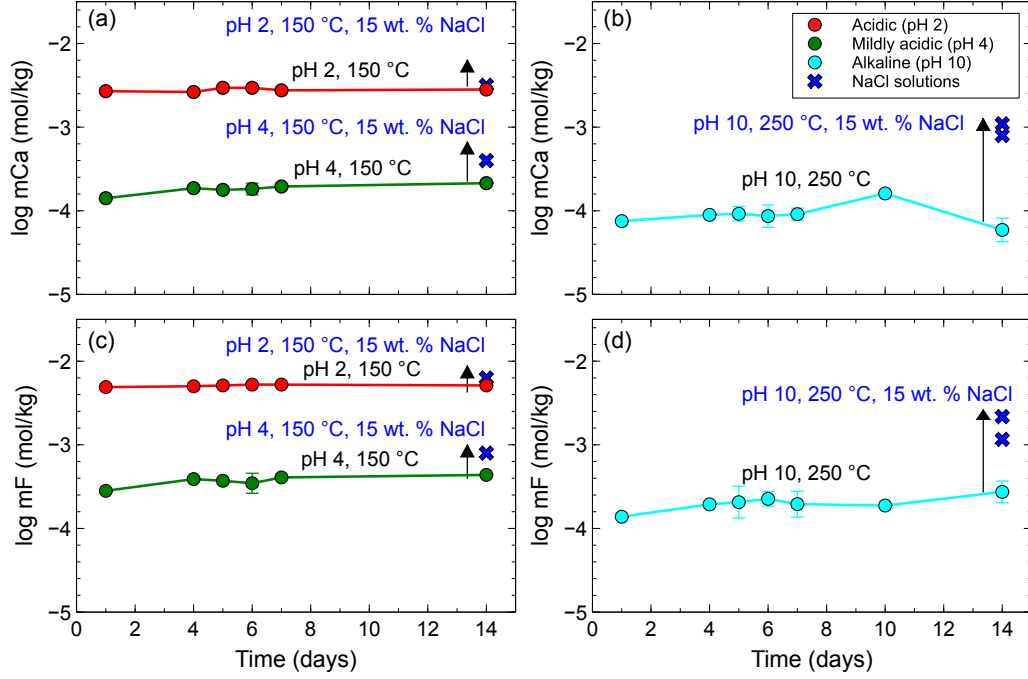


Figure 6: Kinetic experiments showing the logarithm of total dissolved Ca and F molalities (mol/kg) in the quenched experimental solutions as a function of time for experiments in acidic solutions and mildly acidic solutions at 150 °C (a, c), and for experiments in alkaline solutions at 250 °C (b, d). Addition of ~15 wt.% NaCl results in increased fluorite dissolution at each experimental condition (blue symbols). Error bars indicate the standard deviation (1σ) determined from duplicate experiments.

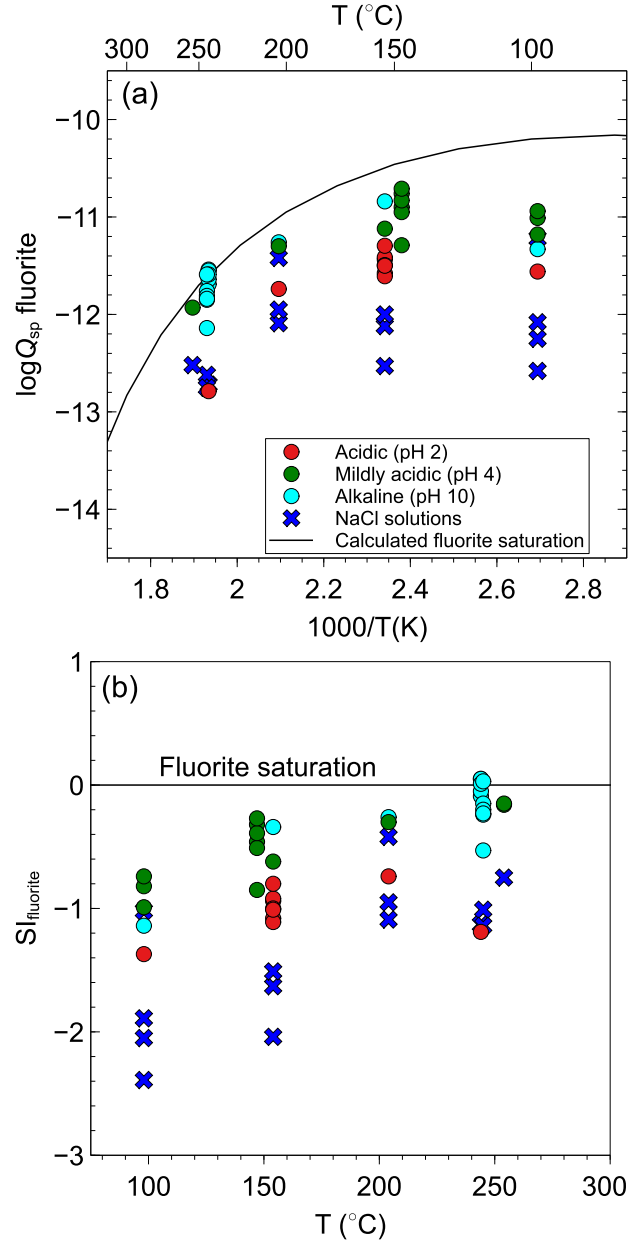


Figure 7: (a) Logarithm of fluorite solubility products (Q_{sp}) and (b) fluorite saturation index (SI) as a function of temperature for experiments conducted in acidic, mildly acidic and alkaline solutions. Fluorite saturation was calculated using thermodynamic properties from Robie and Hemingway (1995) for fluorite, from Miron et al. (2017) for Ca^{2+} , and Supcrt92 and for F^{-} . Calculated activities of aqueous species are found in the Supplementary Materials (Table A4).

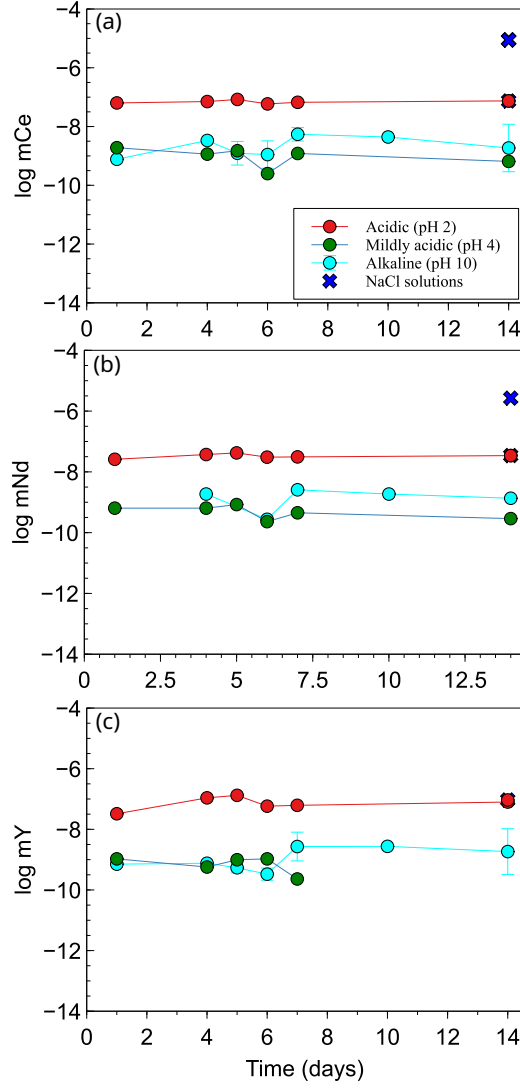


Figure 8: Kinetic experiments showing typical REE concentrations (mol/kg) in the quenched experimental solutions as a function of reaction time with fluorite. Experiments in acidic (pH 2) and mildly acidic (pH 4) solutions were conducted at 150 °C and experiments in alkaline (pH 10) solutions at 250 °C. Addition of ~15 wt.% NaCl to the experiments (blue dots) led to an overall increase in dissolved REE concentrations. Error bars indicate the standard deviation (1σ) determined from duplicate experiments.

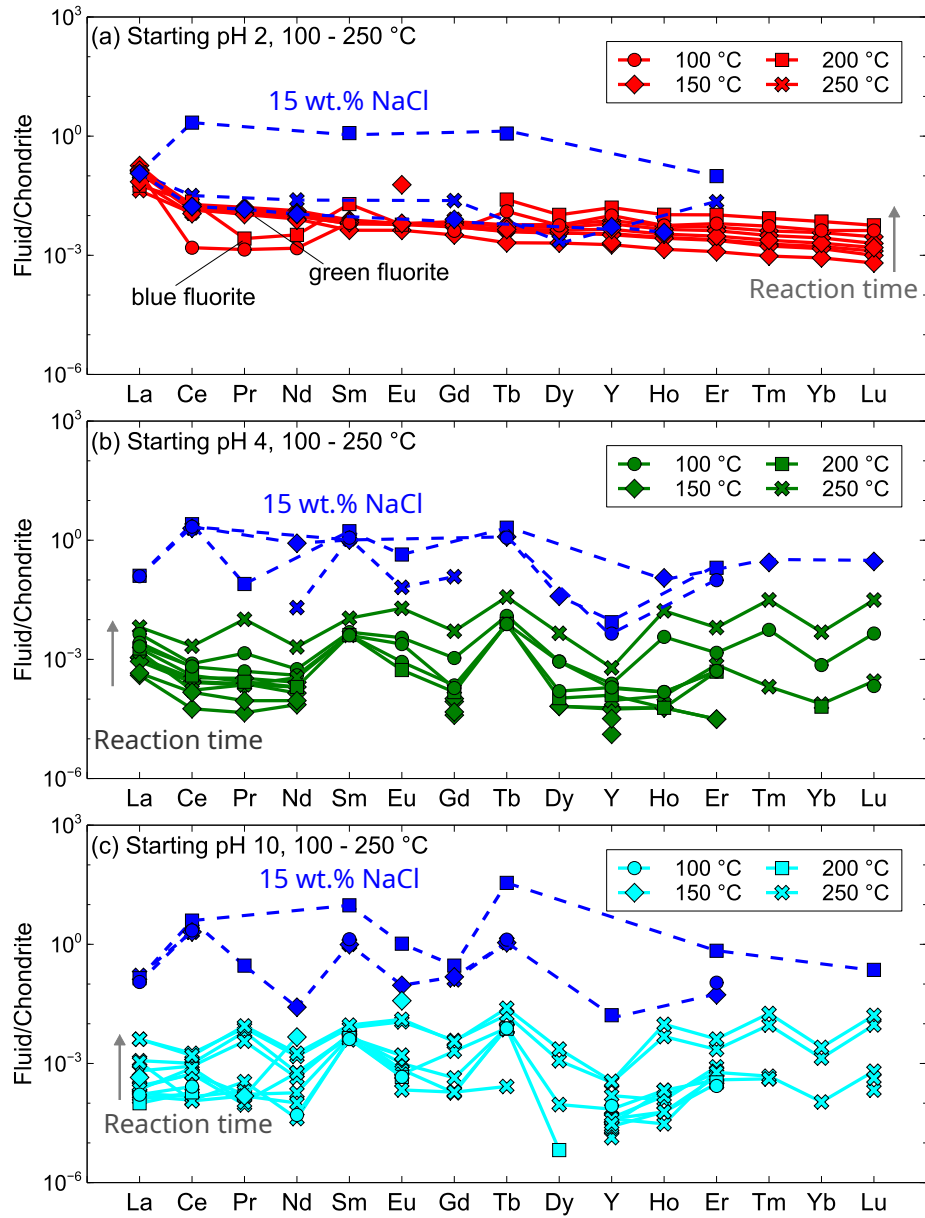


Figure 9: Chondrite-normalized REE concentrations measured in quenched solutions using ICP-MS. Rare earth elements distribution in (a) acidic solutions (pH 2), (b) mildly acidic solutions (pH 4), and (c) alkaline solutions (pH 10). Reaction time indicates experiments quenched after 1 to 14 days, and shows an increase in REE concentrations when reaching steady-state concentrations.

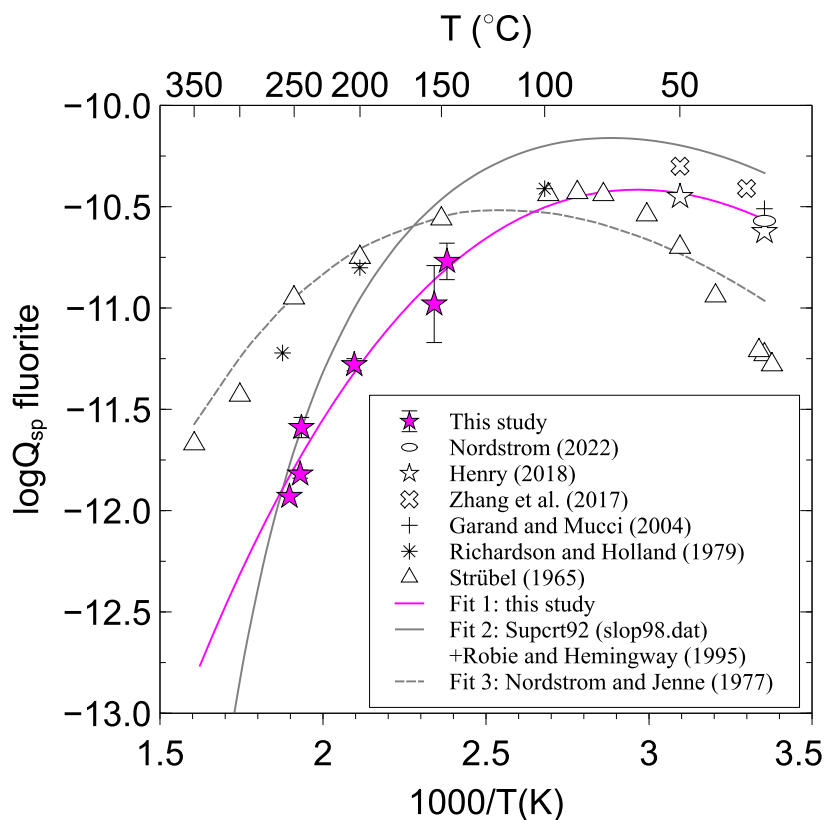


Figure 10: Fluorite solubility products ($\log Q_{sp}$) as a function of temperature showing a comparison of the experimental data from this study with other data sources (Supplementary Materials, Table A6). Fit 1 includes experimental solubility data between 150–250 $^{\circ}C$ from this study and data between 25–50 $^{\circ}C$ from Henry (2018) and Garand and Mucci (2004), and data at 100 $^{\circ}C$ from Richardson and Holland (1979); fitted parameters are listed in Table 5. Fit 2 was calculated using the properties of Ca^{2+} and F^{-} from Supcrt92, slop98.dat dataset (Sverjensky et al., 1997) and optimized by Miron et al. (2017), and fluorite properties from Robie and Hemingway (1995). Fit 3 was calculated from the parameters listed in Nordstrom and Jenne (1977).

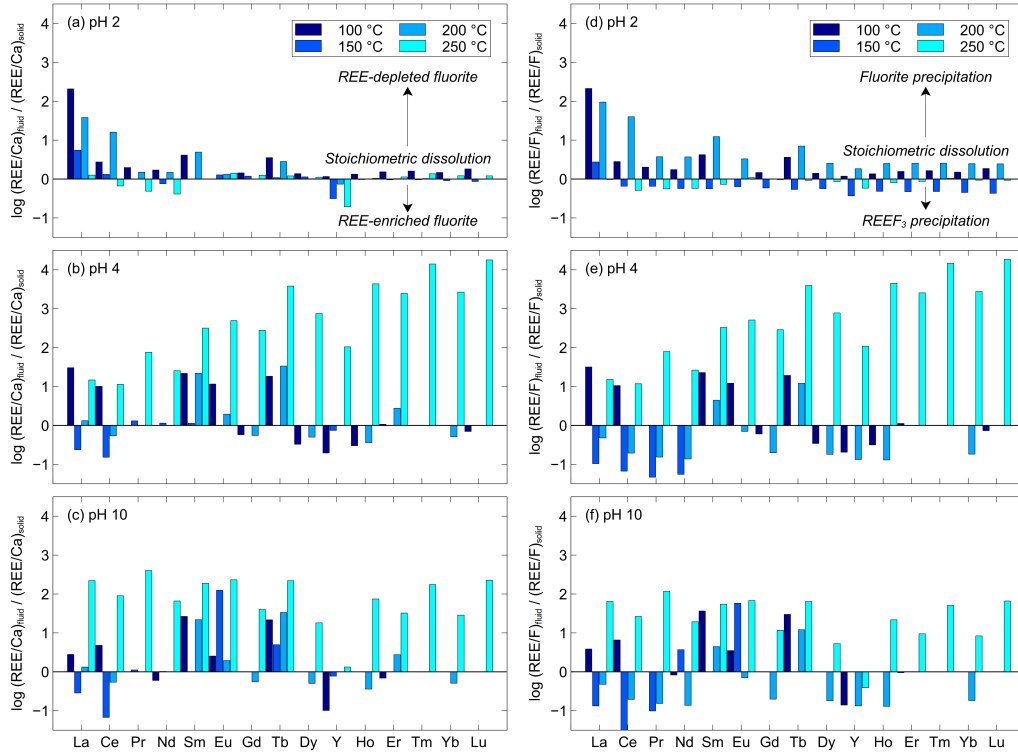


Figure 11: Mass balance calculations used to estimate the REE partitioning behavior between fluid and fluorite in experiments not doped with REE. Logarithm of (a-c) REE/Ca and (d-f) REE/F ratios were calculated from the REE concentrations measured in the fluorite and the quenched experimental solutions (Tables 1 and 3–4). Values above the stoichiometric dissolution line (i.e. ratios of 0) indicate an affinity for the precipitation of secondary REE-depleted fluorite. Values below the stoichiometric dissolution line indicate an affinity for the precipitation of either REE-enriched fluorite (a-c) or REE fluorides (d-f). The full dataset of calculated ratios can be found in the Supplementary Materials (Table A5).

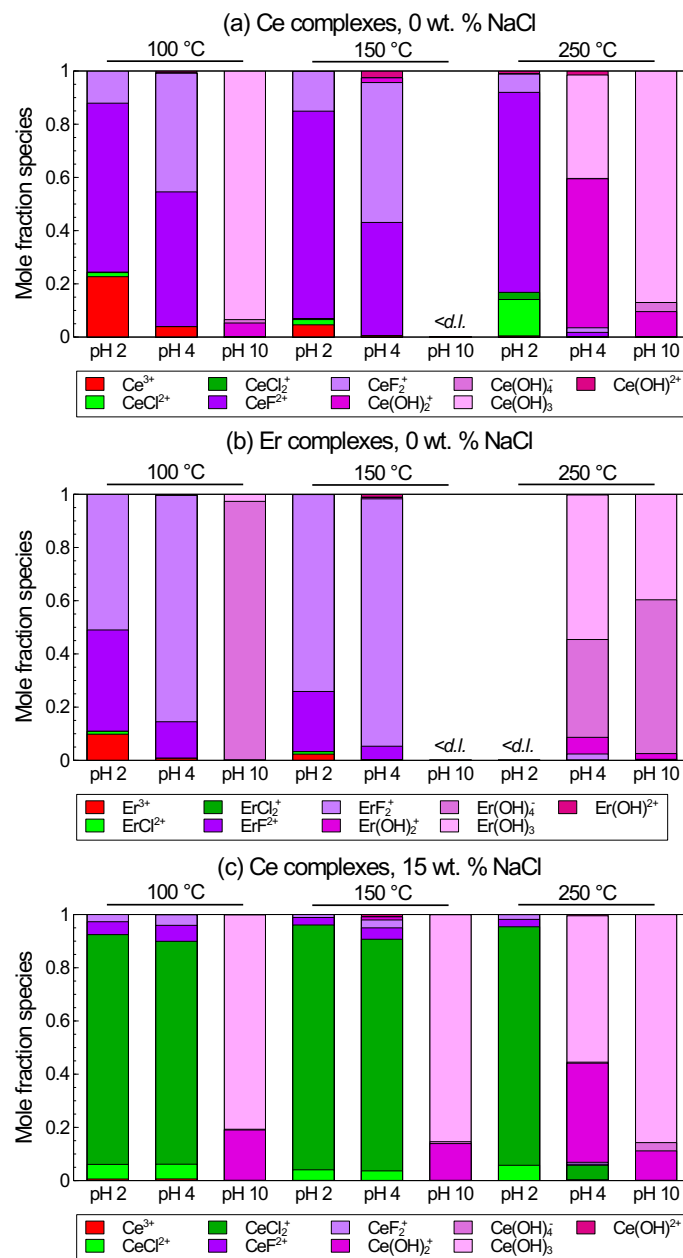


Figure 12: Cumulative mole fractions of stable Ce and Er aqueous species at the different experimental conditions. (a-b) Speciation calculated in the NaCl-free experiments. (c) Speciation calculated in the NaCl solutions. The full dataset of calculated REE species activities can be found in the Supplementary Materials (Table A4).

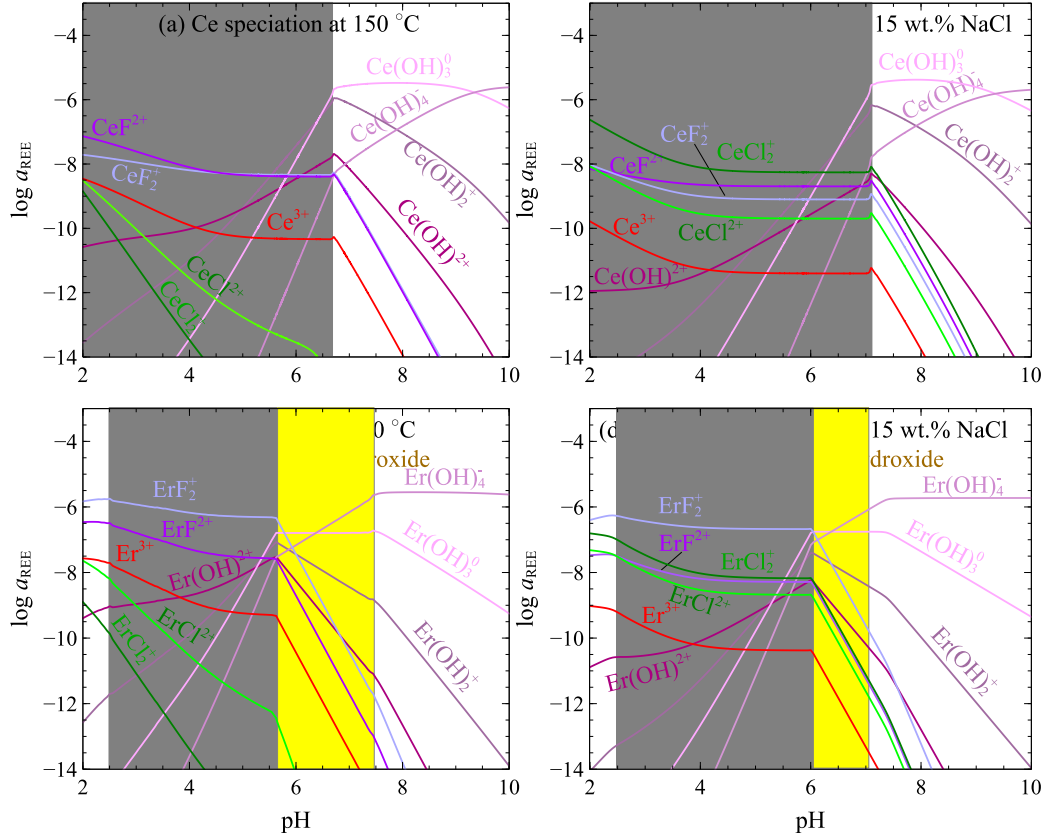


Figure 13: Modeled REE speciation diagrams at 150 °C showing the calculated logarithm activities of aqueous REE species in equilibrium with fluorite as a function of pH and starting salinity. The modeled fluid compositions (1000 g H₂O, 0–0.05 m HCl, 0–0.06 m NaOH, 0.5 ppm REE, 0 and 15 wt.% NaCl) were equilibrated with 5 g fluorite at pH values of 2 to 10 using the GEMS code package and an inverse titration model. Also shown are the stability fields for REE minerals (fluoride in grey shade and hydroxide in yellow shade).

Table 1: LA-ICP-MS data (in ppm) of unreacted fluorite crystals (green, blue, and purple) from the Cooke’s Peak mining district, New Mexico. Mean values and standard deviations (1σ) represent variation across fluorite crystal core to rim profiles. The full dataset can be found as Supplementary Materials, Table A1.

	Green		Blue		Purple		d.l.
	(n =104)	1σ	(n = 60)	1σ	(n = 10)	1σ	
Na (ppm)	8.5	3.8	19	14	8.4	1.1	0.6
Mg	7.8	6.2	13	8	5.7	0.8	0.03
Si	211	59	323	96	210	32	26
P	2.9	1.0	52	49	2.9	0.7	1.8
Sr	25	7.3	32	14	26	2	0.005
Y	43	32	114	75	1.0	0.5	0.003
La	27	10	1.2	1.2	12	2	0.003
Ce	36	14	2.9	2.3	13	2	0.002
Pr	4.9	1.9	0.6	0.4	1.4	0.3	0.001
Nd	20	9	3.4	2.0	4.2	1.1	0.005
Sm	4.0	2.2	2.0	1.0	0.6	0.2	0.007
Eu	1.3	0.7	0.8	0.4	0.3	0.1	0.005
Gd	4.4	3.0	4.8	2.4	0.4	0.2	0.01
Tb	0.8	0.5	1.1	0.6	d.l.	-	0.05
Dy	4.3	3.2	8.5	4.8	0.2	0.1	0.002
Ho	0.9	0.6	1.9	1.1	0.03	0.01	0.003
Er	2.4	1.8	5.5	3.4	0.05	0.02	0.002
Tm	0.3	0.2	0.7	0.5	d.l.	-	0.002
Yb	1.7	1.3	3.9	2.7	0.03	0.02	0.002
Lu	0.2	0.2	0.5	0.4	d.l.	-	0.006
Σ La-Lu	109	-	38	-	32	-	-

n = the number of spots measured; d.l. = detection limit

Table 2: Starting conditions of the fluorite solubility experiments. Starting pH values ($\text{pH}_{25^\circ\text{C}}$) were close to 2 (acidic), 4 (mildly acidic), and 10 (alkaline) at room temperature, with some solutions initially doped with ~ 15 wt. % NaCl and 0.5 ppm REE.

Type	Fluorite color	Exp	T ($^\circ\text{C}$)	Time (days)	$\text{pH}_{25^\circ\text{C}}$	$\log m\text{HCl}$ (mol/kg)	$\log m\text{NaOH}$ (mol/kg)	$\log m\text{NaCl}$ (mol/kg)	REE (ppm)
Acidic (pH 2)	blue	28	98	14	1.97	-1.97	-	-	-
NaCl	green	40	98	14	1.98	-1.98	-	0.36	-
	green	003A-F	154	1 to 14	1.98	-1.98	-	-	-
	green	5	154	14	1.97	-1.97	-	-	-
NaCl	green	7	154	14	1.98	-1.97	-	0.33	-
REE doped	green	15	154	14	1.99	-1.89	-2.58	-	0.5
	green	34	204	14	1.97	-1.97	-	-	-
NaCl	blue	37	204	14	1.98	-1.98	-	0.34	-
	green	10	244	14	1.97	-1.97	-	-	-
NaCl	green	12	244	14	1.98	-1.98	-	0.36	-
REE doped	green	20	245	14	1.99	-1.89	-2.58	-	0.5
Mildly acidic (pH 4)	green	42	98	14	3.94	-3.94	-	-	-
	blue	29	98	14	4.05	-4.05	-	-	-
	green ^a	33	98	14	4.05	-4.05	-	-	-
NaCl	blue	31	98	14	4.05	-4.05	-	0.34	-
	green	001A-F	147	1 to 14	4.05	-4.05	-	-	-
	green	19	154	6	4.05	-4.05	-	-	-
NaCl	green	17	154	14	4.05	-4.05	-	0.36	-
	green	35	204	14	3.94	-3.94	-	-	-
NaCl	blue	38	204	14	4.05	-4.05	-	-	-
REE doped	green	21	245	14	2.99	-1.93	-1.97	-	0.5

NaCl	green	22	245	14	4.05	-4.05	-	0.38	-
	green ^a	25	254	14	4.05	-4.05	-	-	-
	green	26	254	14	4.05	-4.05	-	-	-
Alkaline (pH 10)	blue	30	98	14	10.07	-	-3.93	-	-
NaCl	blue	32	98	14	10.07	-	-3.93	0.34	-
NaCl	green	41	98	14	10.07	-	-3.93	0.34	-
	green	6	154	14	10.07	-	-3.93	-	-
NaCl	green	18	154	14	10.07	-	-3.93	0.36	-
	green ^a	36	204	14	10.07	-	-3.93	-	-
NaCl	blue	39	204	14	10.07	-	-3.93	0.37	-
	green	043A-D	244	1 to 10	10.07	-	-3.93	-	-
	green	11	244	14	10.07	-	-3.93	-	-
	green	024A-F	245	1 to 14	10.07	-	-3.93	-	-
NaCl	green	23	245	14	10.07	-	-3.93	0.36	-
NaCl	green	27	254	14	10.07	-	-3.93	0.36	-

^a Green fluorite intergrown with minor purple fluorite; reacted solutions controlled by green fluorite composition.

Table 3: Major element compositions (logarithm molality) of the quenched experimental solutions and calculated pH (pH_T), solubility products (Q_{sp}), and aqueous species activities at the experimental temperature. Ca and Na concentrations were measured using ICP-OES; F concentrations were measured using IC. The full dataset can be found in the Supplementary Materials.

Exp	Time (days)	T (°C)	pH_T	$\log m_{\text{Ca}}$ (mol/kg)	$\log m_{\text{Na}}$ (mol/kg)	$\log m_{\text{F}}$ (mol/kg)	$\log m_{\text{Cl}}$ (mol/kg)	$\log Q_{\text{sp}}$	a_{HF}	a_{F^-}	$a_{\text{Ca}^{2+}}$	a_{CaCl^+}	$a_{\text{CaCl}_2^0}$	a_{CaF^+}	a_{CaOH^+}	a_{NaF^0}
Acidic (pH 2)																
28	14	98	2.17	-2.81	-	-2.56	-1.97	-11.56	-2.58	-4.23	-3.10	-4.20	-9.37	-6.18	-11.14	-13.13
40 ^{a,c}	14	98	2.48	-2.52	0.36	-2.22	0.36	-11.22	-2.28	-3.63	-3.95	-2.92	-5.95	-6.44	-11.71	-3.37
003A	1	154	2.36	-2.57	-	-2.31	-1.98	-11.58	-2.31	-4.33	-2.92	-3.77	-8.13	-5.56	-9.50	-13.02
003B	4	154	2.34	-2.58	-	-2.30	-1.98	-11.61	-2.30	-4.34	-2.93	-3.78	-8.14	-5.58	-9.53	-13.03
003C	5	154	2.40	-2.53	-	-2.29	-1.98	-11.44	-2.30	-4.28	-2.89	-3.74	-8.10	-5.47	-9.43	-12.97
003D	6	154	2.40	-2.53	-	-2.28	-1.98	-11.41	-2.29	-4.27	-2.88	-3.73	-8.09	-5.46	-9.42	-12.96
003E	7	154	2.37	-2.56	-	-2.28	-1.98	-11.49	-2.28	-4.29	-2.91	-3.76	-8.12	-5.51	-9.48	-12.99
003F	14	154	2.38	-2.55	-	-2.29	-1.98	-11.50	-2.30	-4.30	-2.90	-3.75	-8.11	-5.51	-9.47	-12.99
5	14	154	2.40	-2.52	-	-2.22	-1.97	-11.30	-2.23	-4.21	-2.88	-3.72	-8.07	-5.40	-9.42	-12.91
7 ^{a,c}	14	154	2.62	-2.50	0.33	-2.20	0.34	-12.12	-2.23	-3.99	-4.14	-2.94	-5.24	-6.44	-10.49	-3.62
15 ^b	14	154	2.16	-3.04	-2.58	-2.81	-1.89	-13.46	-2.82	-5.04	-3.37	-4.13	-8.39	-6.73	-10.15	-7.31
34 ^a	14	204	2.59	-2.42	-	-2.12	-1.97	-11.74	-2.12	-4.44	-2.86	-3.36	-7.01	-5.04	-8.39	-12.89
37 ^{a,c}	14	204	3.33	-2.27	0.34	-1.97	0.34	-11.42	-2.03	-3.60	-4.21	-2.74	-4.42	-5.55	-9.03	-3.07
10 ^a	14	244	2.59	-2.43	-	-2.13	-1.97	-12.79	-2.13	-4.90	-2.98	-3.11	-6.19	-5.09	-7.99	-13.10
12 ^{a,c}	14	244	3.36	-2.32	0.36	-2.02	0.36	-12.72	-2.05	-4.06	-4.61	-2.84	-4.01	-5.87	-8.87	-3.36
20 ^b	14	245	2.52	-2.50	-2.58	-2.22	-1.89	-13.20	-2.22	-5.07	-3.06	-3.09	-6.06	-5.32	-8.12	-6.83
Mildly acidic (pH 4)																
42	14	98	4.36	-3.77	-	-3.47	-3.94	-11.01	-4.12	-3.59	-3.83	-6.85	-13.93	-6.27	-9.69	-12.44
29	14	98	4.82	-3.75	-	-3.51	-4.05	-10.94	-4.55	-3.56	-3.81	-6.93	-14.12	-6.22	-9.20	-12.41

33	14	98	4.84	-3.82	-	-3.60	-4.05	-11.18	-4.66	-3.65	-3.87	-6.99	-14.18	-6.38	-9.25	-12.50
31 ^{a,c}	14	98	4.72	-3.45	0.34	-3.14	0.34	-12.25	-4.59	-3.69	-4.87	-3.85	-6.89	-7.41	-10.38	-3.44
001A	1	147	4.77	-3.85	-	-3.55	-4.05	-11.29	-4.16	-3.69	-3.91	-6.80	-13.26	-5.99	-8.21	-12.35
001B	4	147	4.79	-3.73	-	-3.41	-4.05	-10.90	-4.03	-3.55	-3.80	-6.70	-13.16	-5.74	-8.09	-12.21
001C	5	147	4.78	-3.75	-	-3.43	-4.05	-10.95	-4.04	-3.57	-3.82	-6.71	-13.17	-5.77	-8.11	-12.23
001D	6	147	4.89	-3.69	-	-3.38	-4.05	-10.76	-4.08	-3.50	-3.76	-6.66	-13.12	-5.64	-7.95	-12.16
001E	7	147	4.80	-3.71	-	-3.39	-4.05	-10.83	-4.02	-3.52	-3.78	-6.68	-13.14	-5.69	-8.05	-12.19
001F	14	147	4.86	-3.67	-	-3.36	-4.05	-10.71	-4.03	-3.48	-3.75	-6.64	-13.11	-5.61	-7.96	-12.14
19	6	154	5.13	-3.79	-	-3.54	-4.05	-11.12	-4.38	-3.63	-3.85	-6.70	-13.06	-5.80	-7.66	-12.26
17 ^{a,c}	14	154	5.08	-3.40	0.36	-3.10	0.36	-12.53	-4.44	-3.74	-5.05	-3.83	-6.11	-7.10	-8.95	-3.34
35	14	204	4.92	-3.80	-	-3.40	-3.94	-11.30	-3.72	-3.71	-3.89	-6.26	-11.78	-5.33	-7.08	-12.08
38 ^{a,c}	14	204	5.59	-3.06	0.38	-2.76	0.38	-12.09	-4.22	-3.53	-5.03	-3.52	-5.18	-6.30	-7.58	-2.97
21 ^b	14	245	3.34	-3.69	-1.97	-3.60	-1.93	-15.56	-3.64	-5.67	-4.22	-4.25	-7.23	-7.08	-8.46	-6.81
22 ^{a,c}	14	245	5.77	-3.03	0.38	-2.73	0.38	-12.62	-4.03	-3.64	-5.34	-3.55	-4.70	-6.17	-7.18	-2.92
25	14	254	5.73	-3.95	-	-3.70	-4.05	-11.93	-4.17	-3.93	-4.07	-6.04	-10.90	-5.06	-5.82	-11.95
26	14	254	5.36	-3.96	-	-3.54	-4.05	-11.93	-3.80	-3.93	-4.07	-6.04	-10.91	-5.05	-6.19	-11.94
Alkaline (pH 10)																
30	14	98	8.61	-3.83	-3.93	-3.70	-	-11.33	-8.50	-3.72	-3.89	-11.97	-	-6.46	-5.50	-7.49
32 ^{a,c}	14	98	8.02	-3.58	0.34	-3.28	0.34	-12.58	-7.98	-3.79	-5.00	-3.99	-7.04	-7.64	-7.22	-3.54
41 ^{a,c}	14	98	8.02	-3.41	0.34	-3.11	0.34	-12.08	-7.81	-3.62	-4.83	-3.81	-6.86	-7.31	-7.06	-3.37
6	14	154	7.64	-3.76	-3.93	-3.47	-	-10.84	-6.76	-3.49	-3.86	-11.66	-	-5.66	-5.15	-7.05
18 ^{a,c}	14	154	7.20	-3.24	0.36	-2.93	0.36	-12.00	-6.38	-3.56	-4.89	-3.66	-5.95	-6.75	-6.66	-3.16
36	14	204	6.63	-4.02	-3.93	-3.54	-	-11.26	-5.30	-3.57	-4.12	-11.54	-	-5.43	-5.60	-6.87
39 ^{a,c}	14	204	6.68	-3.03	0.37	-2.73	0.37	-11.95	-5.26	-3.48	-4.99	-3.50	-5.15	-6.21	-6.46	-2.93
043A	5	244	7.07	-3.97	-3.93	-3.63	-	-11.54	-5.38	-3.68	-4.19	-11.22	-	-5.07	-4.71	-6.71
043B	6	244	6.66	-4.16	-3.93	-3.64	-	-11.69	-4.99	-3.69	-4.31	-11.34	-	-5.20	-5.24	-6.72
043C	7	244	7.15	-3.94	-3.93	-3.65	-	-11.55	-5.48	-3.69	-4.17	-11.20	-	-5.06	-4.61	-6.72

043D	10	244	7.44	-3.79	-3.93	-3.73	-	-11.64	-5.85	-3.77	-4.10	-11.14	-	-5.08	-4.26	-6.80
11	14	244	6.53	-4.13	-3.93	-3.60	-	-11.59	-4.82	-3.66	-4.28	-11.31	-	-5.14	-5.34	-6.68
024A	1	245	7.20	-4.12	-3.93	-3.86	-	-12.14	-5.72	-3.89	-4.35	-11.37	-	-5.43	-4.72	-6.91
024B	4	245	7.09	-4.05	-3.93	-3.71	-	-11.76	-5.47	-3.75	-4.26	-11.28	-	-5.20	-4.75	-6.77
024C	5	245	7.07	-4.10	-3.93	-3.74	-	-11.85	-5.47	-3.78	-4.30	-11.32	-	-5.26	-4.81	-6.80
024D	6	245	7.11	-3.97	-3.93	-3.65	-	-11.59	-5.43	-3.70	-4.19	-11.22	-	-5.08	-4.66	-6.72
024E	7	245	7.04	-4.09	-3.93	-3.72	-	-11.81	-5.42	-3.76	-4.29	-11.31	-	-5.24	-4.83	-6.78
024F	14	245	5.74	-4.32	-3.93	-3.53	-	-11.84	-4.07	-3.70	-4.43	-11.46	-	-5.33	-6.27	-6.72
23 ^{a,c}	14	245	6.48	-3.10	0.36	-2.79	0.36	-12.75	-4.79	-3.68	-5.39	-3.61	-4.77	-6.26	-6.52	-2.97
27 ^{a,c}	14	254	6.51	-2.96	0.36	-2.66	0.36	-12.52	-4.61	-3.59	-5.35	-3.50	-4.54	-5.99	-6.35	-2.83

^a Experiments with ~15 wt. % NaCl. ^b Experiments with 0.5 ppm REE doped. ^c Analytical difficulty with F on ion IC

due to high sample chloride concentrations; F concentration calculated based on Ca concentrations ($mF=2\times mCa$).

Table 4: Rare earth element compositions (logarithm molality) of the quenched experimental solutions measured using solution ICP-MS.

Exp	Time	T	$\log m_{\text{La}}$	$\log m_{\text{Ce}}$	$\log m_{\text{Pr}}$	$\log m_{\text{Nd}}$	$\log m_{\text{Sm}}$	$\log m_{\text{Eu}}$	$\log m_{\text{Gd}}$	$\log m_{\text{Tb}}$	$\log m_{\text{Dy}}$	$\log m_{\text{Y}}$	$\log m_{\text{Ho}}$	$\log m_{\text{Er}}$	$\log m_{\text{Tm}}$	$\log m_{\text{Yb}}$	$\log m_{\text{Lu}}$
	(days)	(°C)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)	(mol/kg)
Acidic (pH 2)																	
28	14	98	-6.67	-8.17	-9.04	-8.32	-8.19	-	-8.28	-8.54	-8.07	-6.75	-8.73	-8.22	-9.10	-8.41	-9.23
40	14	98	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
003A	1	154	-6.51	-7.20	-8.15	-7.59	-8.38	-8.80	-8.39	-9.33	-8.51	-7.49	-9.33	-8.93	-9.85	-9.10	-10.05
003B	4	154	-6.64	-7.15	-8.03	-7.43	-8.15	-8.66	-8.08	-8.92	-8.12	-6.96	-8.83	-8.40	-9.34	-8.59	-9.55
003C	5	154	-6.62	-7.08	-7.97	-7.38	-8.12	-8.63	-8.05	-8.88	-8.05	-6.88	-8.74	-8.31	-9.22	-8.46	-9.39
003D	6	154	-6.70	-7.23	-8.12	-7.52	-8.21	-8.66	-8.18	-9.03	-8.25	-7.24	-9.05	-8.64	-9.60	-8.86	-9.85
003E	7	154	-6.65	-7.17	-8.08	-7.51	-8.22	-8.63	-8.18	-9.05	-8.26	-7.21	-9.03	-8.63	-9.55	-8.81	-9.74
003F	14	154	-6.62	-7.13	-8.00	-7.46	-8.18	-8.63	-8.14	-8.99	-8.18	-7.10	-8.95	-8.54	-9.46	-8.73	-9.66
5	14	154	-6.92	-7.31	-	-7.61	-	-7.66	-	-	-	-7.44	-	-	-	-	-
7	14	154	-6.70	-7.13	-8.02	-7.46	-	-	-7.99	-	-	-7.03	-8.90	-	-	-	-
15	14	154	-5.44	-5.48	-5.48	-5.48	-5.50	-5.50	-5.52	-5.52	-5.53	-5.26	-5.54	-5.54	-5.55	-5.56	-5.56
34	14	204	-7.02	-7.01	-8.76	-7.98	-7.72	-8.66	-	-8.24	-7.80	-6.55	-8.46	-8.00	-8.90	-8.18	-9.10
37	14	204	-6.67	-5.02	-	-	-5.93	-	-	-6.58	-	-	-	-7.03	-	-	-
10	14	244	-7.14	-7.30	-	-7.52	-	-	-7.99	-	-	-6.97	-	-	-	-	-
12	14	244	-6.71	-6.85	-	-7.11	-	-	-7.52	-	-8.45	-	-	-7.67	-	-8.30	-
20	14	245	-6.18	-6.19	-6.21	-6.24	-6.27	-6.28	-6.33	-6.28	-6.25	-6.12	-6.26	-6.23	-6.18	-6.11	-6.12
Mildly acidic (pH 4)																	
42	14	98	-8.35	-8.55	-9.48	-8.90	-8.39	-9.49	-9.55	-8.75	-8.88	-8.48	-10.30	-9.33	-	-	-
29	14	98	-8.44	-8.54	-	-	-8.40	-9.05	-9.62	-8.75	-9.62	-8.46	-10.30	-9.31	-	-	-10.52
33	14	98	-8.13	-8.46	-9.03	-8.74	-8.32	-8.89	-8.86	-8.55	-8.87	-8.37	-8.91	-8.85	-9.09	-9.17	-9.20
31	14	98	-6.67	-5.02	-	-	-5.94	-	-	-6.58	-	-7.10	-	-7.03	-	-	-

001A	1	147	-8.56	-8.72	-9.89	-9.19	-	-	-10.00	-	-10.05	-8.97	-11.00	-	-	-	-
001B	4	147	-8.82	-8.94	-9.82	-9.19	-	-	-10.22	-	-	-9.24	-	-	-	-	-
001C	5	147	-8.72	-8.82	-9.66	-9.08	-	-	-9.89	-	-10.00	-9.00	-10.70	-10.52	-	-	-
001D	6	147	-9.17	-9.60	-10.52	-9.64	-	-	-9.96	-	-10.00	-8.97	-10.70	-10.52	-	-	-
001E	7	147	-8.72	-8.92	-9.80	-9.35	-	-	-10.30	-	-	-9.64	-	-	-	-	-
001F	14	147	-9.11	-9.19	-10.22	-9.54	-	-	-	-	-	-	-	-	-	-	-
19	6	154	-7.96	-8.06	-8.36	-8.32	-8.51	-8.60	-8.54	-8.72	-8.73	-8.12	-8.80	-8.81	-8.89	-8.86	-8.88
17	14	154	-	-5.06	-	-5.57	-6.00	-	-	-6.56	-7.23	-	-7.43	-	-7.39	-	-7.38
35	14	204	-8.49	-8.76	-9.74	-9.19	-8.39	-9.70	-9.72	-8.75	-9.80	-8.65	-10.70	-9.33	-	-10.22	-
38	14	204	-6.66	-4.96	-7.28	-	-5.78	-6.79	-	-6.33	-	-6.82	-	-6.71	-	-	-
21	14	245	-4.97	-5.28	-5.64	-5.61	-5.44	-5.57	-5.60	-5.46	-5.56	-5.30	-5.56	-5.40	-5.55	-5.55	-5.56
22	14	245	-	-5.05	-	-7.20	-5.97	-7.62	-6.81	-	-	-	-	-	-	-	-
25	14	254	-7.96	-8.03	-8.17	-8.19	-7.97	-8.14	-8.19	-8.07	-8.16	-7.97	-8.26	-8.22	-8.34	-8.35	-8.36
26	14	254	-8.57	-9.14	-9.82	-8.96	-8.40	-	-9.64	-8.75	-	-8.79	-10.40	-9.15	-10.52	-10.15	-10.40
Alkaline (pH 10)																	
30	14	98	-9.55	-8.94	-	-9.80	-8.39	-9.77	-	-8.76	-	-8.82	-	-9.59	-	-	-
32	14	98	-6.72	-5.01	-	-	-5.88	-	-	-6.53	-	-	-	-6.99	-	-	-
41	14	98	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	14	154	-9.12	-	-10.00	-7.83	-	-7.85	-	-	-	-	-	-	-	-	-
18	14	154	-	-5.05	-	-7.08	-6.01	-7.46	-6.72	-6.60	-	-	-	-7.29	-	-	-
36	14	204	-9.77	-9.09	-	-	-8.37	-9.77	-	-8.77	-11.00	-	-	-9.49	-	-	-
39	14	204	-6.62	-4.76	-6.72	-	-5.02	-6.42	-6.43	-5.10	-	-6.54	-	-6.18	-	-	-7.50
043A	5	244	-9.34	-8.63	-10.22	-	-8.37	-9.70	-8.59	-8.75	-	-9.39	-	-9.42	-	-	-
043B	6	244	-9.59	-9.28	-9.64	-9.89	-8.38	-9.62	-	-8.76	-	-9.62	-	-9.39	-	-	-
043C	7	244	-8.95	-8.43	-8.62	-8.86	-8.27	-9.59	-9.64	-8.74	-9.85	-8.90	-10.15	-9.43	-10.22	-	-
043D	10	244	-8.70	-8.36	-8.39	-8.73	-8.31	-9.43	-9.26	-8.74	-	-8.56	-10.40	-9.10	-	-	-
11	14	244	-8.74	-9.30	-10.00	-9.49	-	-10.10	-9.62	-10.22	-	-9.27	-10.15	-	-10.22	-	-10.22

024A	1	245	-9.66	-9.11	-	-	-8.41	-	-	-8.78	-	-9.15	-10.70	-9.52	-	-	-10.52
024B	4	245	-9.42	-8.47	-10.15	-8.73	-8.35	-9.22	-	-8.79	-	-9.12	-10.30	-9.24	-10.15	-10.00	-10.05
024C	5	245	-9.52	-9.19	-9.89	-	-8.39	-9.23	-	-8.75	-	-9.15	-11.00	-9.21	-	-	-
024D	6	245	-9.37	-8.62	-9.96	-9.24	-8.34	-	-9.60	-8.75	-	-9.34	-10.70	-9.35	-	-	-
024E	7	245	-8.16	-8.10	-8.29	-8.32	-8.11	-8.38	-8.32	-8.42	-8.75	-8.23	-8.80	-8.67	-8.87	-8.90	-8.88
024F	14	245	-8.16	-8.16	-8.24	-8.24	-8.04	-8.32	-8.34	-8.25	-8.45	-8.20	-8.49	-8.40	-8.58	-8.63	-8.64
23	14	245	-	-5.05	-	-	-5.99	-	-6.79	-6.60	-	-	-	-	-	-	-
27	14	254	-6.55	-5.05	-	-	-6.01	-	-	-6.59	-	-	-	-	-	-	-

Table 5: Experimental solubility data ($\log Q_{sp}$) selected between 25–254 °C for deriving the fluorite solubility constants ($\log K_{sp}$, Eq. 1) as a function of temperature with regressed coefficients (A-D; with T in Kelvin) and derived standard Gibbs energy ($\Delta G^\circ_{298.15K}$), enthalpy ($\Delta H^\circ_{298.15K}$) and entropy $\Delta S^\circ_{298.15K}$ at 298.15 K and 1 bar. Subscripts indicate properties of formation from the elements ($_f$) and of reaction ($_r$).

	T (°C)	T (K)	1000/T (K ⁻¹)	$\log Q_{sp}$	1σ	Refs
Experimental data	25	298	3.35	-10.62	0.02	[2]
	50	323	3.09	-10.45	0.03	[2]
	25	298	3.35	-10.51	0.01	[3]
	100	373	2.68	-10.41	0.04	[4]
	147	420	2.38	-10.77	0.09	[1]
	154	427	2.34	-10.98	0.19	[1]
	204	477	2.10	-11.28	0.03	[1]
	244	517	1.93	-11.59	0.05	[1]
	245	518	1.93	-11.82	0.02	[1]
	254	527	1.90	-11.93	0.01	[1]
Fit	25	298	3.35	-10.56		[1]
Equation	A		B	C	D	
$\log K_{sp} = A + BT + C/T + D \log(T)$	171.180		0.01477	-7794.10	-64.6634	[1]
Thermodynamic properties	Values		Units			
$\Delta_r G^\circ_{298.15K}$	60.29		(kJmol ⁻¹)			[1]
$\Delta_r H^\circ_{298.15K}$	14.05		(kJmol ⁻¹)			[1]
$\Delta_r S^\circ_{298.15K}$	-155.1		(Jmol ⁻¹ K ⁻¹)			[1]
$\Delta_f G^\circ_{\text{fluorite}}$	-1176.6		(kJmol ⁻¹)			[1]
	-1175.3		(kJmol ⁻¹)			[5]
$\Delta_f H^\circ_{\text{fluorite}}$	-1227.9		(kJmol ⁻¹)			[1]
	-1228.0		(kJmol ⁻¹)			[5]
$S^\circ_{\text{fluorite}}$	72.3		(Jmol ⁻¹ K ⁻¹)			[1]
	68.9		(Jmol ⁻¹ K ⁻¹)			[5]
$\Delta_f G^\circ_{\text{Ca}^{2+}}$	-552.82		(kJmol ⁻¹)			[6]
$\Delta_f H^\circ_{\text{Ca}^{2+}}$	-543.10		(kJmol ⁻¹)			[6]
$S^\circ_{\text{Ca}^{2+}}$	-56.5		(Jmol ⁻¹ K ⁻¹)			[7]
$\Delta_f G^\circ_{\text{F}^-}$	-281.75		(kJmol ⁻¹)			[7]
$\Delta_f H^\circ_{\text{F}^-}$	-335.39		(kJmol ⁻¹)			[7]
$S^\circ_{\text{F}^-}$	-13.2		(Jmol ⁻¹ K ⁻¹)			[7]

[1] This study; [2] Henry (2018); [3] Garand and Mucci (2004); [4] Richardson and Holland (1979); [5]

Robie and Hemingway (1995); [6] Sucprt92 (slop98.dat) optimized by Miron et al. (2017); [7] Sucprt92

(slop98.dat), Sverjensky et al. (1997)