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Fluocerite as a precursor to rare earth element fractionation in ore-1 forming systems 2 3 Andrew Strzelecki^{1*}; Artas Migdisov¹; Hakim Boukhalfa¹; Kirsten Sauer¹; Kathryn McIntosh²; 4 Robert P. Currier²; Anthony E. Williams-Jones³ 5 6 7 ¹ Los Alamos National Laboratory, Earth and Environmental Sciences Division, P.O. Box 1663, 8 M.S. J966, Los Alamos, NM 87545, USA ² Los Alamos National Laboratory, Chemistry Division, P.O. Box 1663, M.S. G740, J567, Los 9 Alamos, NM 87545, USA 10 11 ³ Department of Earth and Planetary Sciences, McGill University, 3450 University Street, 12 Montreal H3A 0E8, Canada

Emerging renewable energy technologies (e.g., wind and solar power generation) and 14 low-carbon transportation rely heavily on the unique optical and magnetic properties of the rare 15 earth elements (REE). The medium to heavy REEs (M/HREEs), neodymium to lutetium, are the 16 most sought by industry, but are the least abundant in nature, and only a very minor proportion 17 of known REE deposits is enriched in M/HREE. Thus, there is an urgent need to discover new 18 19 sources of M/HREE, which requires an in-depth understanding of the mechanisms responsible for the formation of such highly fractionated deposits (such understanding guides exploration). 20 21 Here, we report the first experimental demonstration of a mechanism that could be responsible 22 for the enrichment of *M*/*HREE* in ore-forming systems. We show that fluocerite (*LnF*₃) can serve as an intermediate phase, which triggers REE fractionation, but is subsequently converted to 23 more thermodynamically stable REE minerals, such as REE-phosphates or fluoro-carbonates. 24 The data reported in this contribution suggest that exploration aimed at the discovery of 25 M/HREE-enriched deposits should focus on geological settings in which fluocerite is observed or 26 27 expected.

28

The REEs consist of the thirteen naturally occurring lanthanides, yttrium, and scandium.¹ 29 These elements have bulk crustal abundances equal to those of copper, zinc, and molybdenum^{2,3}, 30 although they are rarely concentrated to economic levels. The less valuable light REEs (Ce, La) 31 typically comprise 60–90% of REE ores, whereas the M/HREEs (Nd, Eu, Tb, and Dy⁴), which 32 are in most demand from industry, are rarely concentrated to economic levels. Nevertheless, 33 there are a few deposits, notably Lofdal (Namibia) and Browns Range (Australia), in which the 34 M/HREE can make up >80% of the total REE budget^{5,6}. A rapid demand for M/HREE due to 35 expanding green technologies, combined with politically insecure supply chains (90 % of REE 36

on the market is supplied by China)⁷, makes discovery of new deposits of this type a societal 37 issue that requires urgent resolution. Such discovery, however, will not be possible without an 38 in-depth understanding of the controls of REE fractionation (M/HREE enrichment) in natural 39 systems, and the development of genetic models that will help provide the new tools needed to 40 ensure exploration success. Understanding of these processes is unfortunately in its infancy, and 41 does not go much further than a few hypotheses based on thermodynamic modelling^{8,9}. These 42 hypotheses are mostly underpinned by the assumption that the fractionation of REE is the result 43 of hydrothermal processes. Indeed, there is now incontrovertible evidence that hydrothermal 44 45 fluids mobilize the REE and in some cases concentrate them to potentially economic levels. The most compelling evidence of this is the occurrence of REE deposits of hydrothermal origin, such 46 as the giant Bayan Obo REE deposit in China^{10,11}. Hydrothermal mobilization and concentration 47 of REE have also been documented for a number of other, smaller, but still potentially economic 48 deposits^{e.g.,12,13}. The hypotheses proposed for explaining the concentration of the REE by 49 50 hydrothermal processes and the preferential enrichment of the M/HREE are based on two chemico-physical mechanisms, which can operate together, but generally apply to chemically 51 different systems. The first mechanism utilizes the differential (at elevated temperature) aqueous 52 53 mobility of REE-chloride complexes and the interaction of the fluid with phosphate-bearing rocks (containing minerals such as apatite) to trigger precipitation and consequent separation of 54 the LREE phosphates from the HREE phosphates.^{8,9} The other mechanism is based on the 55 56 differing solubility of REE-fluoride, fluocerite, solid phases and uses fluid interaction with 57 fluorite (CaF₂; a common gangue mineral associated with REE deposits) to precipitate fluocerite^{9,10,12,14}. Neither mechanism has been demonstrated experimentally leaving a number of 58 59 issues unresolved. For example, the extremely low solubility of REE-phosphates, and thus their

resistance to hydrothermal alteration, suggests that meaningful fractionation of LREE from
HREE will entail large amounts of fluid and time. This raises the question of whether the large
hydrothermal convection cells needed to form strongly fractionated deposit can continue to
operate on the required timescales.

In the fluorite-induced depositional model, the REE fluoride mineral, fluocerite (LnF₃), is 64 65 formed. Despite the fact that fluocerite is more soluble than the REE phosphates (and most of the common REE ore minerals), and, thus, its REE content can be re-distributed hydrothermally, the 66 possibility that it could play a major role in REE fractionation has not received attention. The 67 main reason for this is that there are no fluocerite ore deposits¹⁵. Although there are examples of 68 silicate (eudialyte, allanite, cerite, and gadolinite) and oxide (aeschynite) REE ore minerals¹⁶, the 69 two principal groups of economic REE ore minerals are phosphates and fluocarbonates (both of 70 which are extremely resistant to hydrothermal alteration⁹). In contrast, fluocerite remains a rare 71 accessory mineral¹⁷. It should be noted, however, that although details of the mechanisms 72 73 controlling the formation of REE fluocarbonates are still unclear, for a few locations in Sweden, 74 Finland, and South Africa, there is some evidence that REE-fluorocarbonate formation may involve carbonation of a fluocerite precursor $^{18-20}$. 75

The goal of this study was to experimentally probe the mechanisms that have been proposed for REE fractionation in ore-forming hydrothermal systems and to identify conditions under which this can occur. Natural hydrothermal ore forming systems were simulated at the bench-top scale using columns packed with apatite, or fluorite, or a 1:1 mixture of these minerals. These columns were heated to 250 °C and REE-bearing solutions pumped through them. As the objective of the experiments was to identify the mechanisms of hydrothermal REE deposition and fractionation, the system was highly simplified to ensure clear results unaffected

by additional factors, such as, for example, the nature of the host rock, or the complexity of a 83 natural hydrothermal fluid. Thus, the REE-bearing solution employed in the experiments 84 85 contained equal proportions (500 mg/kg) of La, Nd, and Er (L/M/HREE), 2 wt% NaCl at a pH adjusted to 2 using HCl; the only solids introduced in the experiments were apatite and fluorite. 86 The inlet and outlet solution composition was analyzed using inductively coupled plasma-mass 87 88 spectrometry and inductively coupled plasma-optical emission spectrometry and the solids that formed during the experiments were characterized using X-ray fluorescence spectrometry, 89 mirco-X-ray fluorescence spectrometry, powder X-ray diffraction, optical microscopy, and 90 scanning electron microscopy. A detailed description of the experimental conditions and 91 procedures and the sample characterization is provided in the electronic supplement. 92

93 The experimental data confirm the basic features of the depositional mechanisms referred 94 to above. Interaction of the REE-bearing hydrothermal solution with the three column types 95 triggered deposition of REE fluorides or phosphates resulting in a nearly complete loss of the 96 aqueous REE load. The initial total REE content of 1500 mg/kg decreased to <100 µg/kg in the 97 effluent at all conditions tested.

Although deposition of the REE on fresh apatite grains was very efficient initially,
extraction of the REE from the aqueous solution was subsequently inhibited, as shown by a sharp
decrease in the concentration of calcium eluted coincident with a sharp increase in the
concentrations of REEs eluted (Figure 1). The rate of REE mineral deposition appears to have
been reduced sharply by the formation of a dense impermeable layer of REE phosphate, which
coated the grain surfaces and blocked access of the solution to the only source of phosphorus for
REE phosphate deposition. This process can be generalized as:

105
$$Ca_5(PO_4)_3OH(apatite) + 3REE^{3+} + H^+ = 3REEPO_4(monazite) + 5Ca^{2+} + H_2O$$
 (1)

106 or through the formation of monetite as an intermediate phase;

- 108 Thus, on losing contact with apatite, the aqueous solution would have become depleted in Ca,
- 109 which is consistent with the observation that a sharp drop in the Ca concentrations in the effluent
- solutions coincided with a sharp increase in the REE content of these solutions (Figure 1B).



Figure 1. (A.) Relative concentrations of La, Nd, and Er (concentration in the solution before interaction with apatite $[C^{\circ}]$ versus the concentration after exit from the column [C]) in the solution after interaction with the apatite column at 250 °C as a function of the total volume of solution pumped through the column. (B.) A comparison of the relative concentrations of total dissolved REE and Ca in the solutions. A sharp increase in the concentration of the REEs was not observed in the effluent from the fluorite-packed column (the uptake of the REE solution load was >99.96 %).



short-lived $(100 - 10,000 \text{ years})^{23-26}$, barriers of this type could be important in inhibiting REE



119 deposition and hydrothermal fractionation.

Figure 2: Artificial color SEM images of post-experimental grains of apatite (A) and fluorite (B). Figure 2A shows an impermeable layer of REE phosphates coating a grain of apatite. Figure 2B illustrates brecciation of the fluorite grain and growth of fluocerite through veinlets penetrating into the fluorite core.

| 121 | In contrast to the apatite-initiated deposition of REE, no rate inhibition was detected for |
|-----|--|
| 122 | the fluorite-filled columns. The reason for this is the inability of fluocerite to form an insoluble |
| 123 | veneer coating, evidence of which can be seen in Figure 2B: formation of fluocerite was |
| 124 | accompanied by intense brecciation of fluorite crystals and occurred through the penetration of |
| 125 | micro-veinlets into the grain cores. Although the experiments reported in this contribution did |
| 126 | not reach a stage where there was complete replacement of fluorite, it is likely that this process |
| 127 | can occur indefinitely until complete exhaustion of the available fluorite. Thus, whereas REE |
| 128 | deposition of monazite through replacement of apatite is limited to a veneer that prevents further |
| 129 | access of the REE to phosphate, deposition of fluocerite through the replacement of fluorite is |
| 130 | limited only by the availability of fluorite. |

We speculate that the reason for the large difference in the apatite-monazite and fluorite-131 fluocerite replacement processes lies in the fact that dissolution of apatite is incongruent, 132 whereas that of fluorite is congruent. Apatite dissolves by first releasing OH⁻ and then Ca²⁺ to the 133 fluid, leaving behind phosphate, which reacts with the REE and, in the process, is coated by 134 monazite. As the OH^{-} ion is released before the Ca^{2+} ion, it is also possible that formation of 135 monazite does not occur directly but through a thin films of monetite. In contrast to apatite, the 136 dissolution of fluorite proceeds through the simultaneous release of F⁻ and Ca²⁺, which will occur 137 preferentially along dislocations that have propagated from within a crystal to its surface. As a 138 result, the REE penetrate into the interiors of crystals, where they react with F⁻ to precipitate 139 fluocerite. The key to why this process is so efficient (replacement of fluorite was accompanied 140 by brecciation and the formation of microveinlets of fluocerite) lies in the large difference in the 141 unit cell volumes of the two minerals. The unit cell volume of fluocerite is nearly twice that of 142 fluorite (319.61 versus 163.04 A³) and as a result, precipitation of fluocerite in cracks within the 143 fluorite inevitably increases the widths of the cracks and ultimately leads to complete brecciation 144 of the fluorite crystals. 145

In addition to the above difference in the apatite- and fluorite-mediated mechanisms of 146 147 REE mineral deposition, there are also large differences in the associated REE fractionation . As can be seen in Figure 3, interaction of the fluid with fluorite not only led to the nearly complete 148 replacement of fluorite by fluocerite near the beginning of the column (first 5-15 cm, >90% of 149 REEF₃; Figure 3A), but also resulted in very pronounced fractionation of the HREE (Er) from 150 the L/MREE (La, Nd; Figure 3B). This was predicted by thermodynamic models^{9,15}, which 151 showed that the solubility of the LREE fluorides is several orders of magnitude lower than that 152 of HREE fluorides, which makes the HREE more mobile in hydrothermal (phosphate-free) 153

- systems. Because of this, the LREE fluorides are deposited immediately after a REE-bearing
- solution encounters fluoride (or is able to interact with this source due to the effect of pH; see
- ^{9,15}), whereas the HREE are able to travel further and are deposited in the more distal parts of
- 157 hydrothermal systems. In the case of our



Figure 3: Solid phase characterization of post-experimental columns (XRF). (A.) Accumulation of REEs (wt%) in the fluorite-packed column, assuming pure end member fluocerite, as a function of distance along the column. (B.) Mole fractions of individual REEs with respect to the total REE deposited in the fluorite-packed column. (C.) Accumulation of REEs (wt%) in the apatite-packed column, assuming pure end member REE phosphates, as a function of distance along the column. (D.) Mole fractions of individual REEs with respect to total REE apatite column. (D.)

- simulations, this corresponds to more distal parts of the column. In contrast to the fluorite-
- 160 mediated deposition of REE, the apatite-mediated deposition did not involve more than 30%
- 161 replacement of the apatite available in the system (for most of the column, the replacement was

significantly lower than this value; Figure 3C), and was not accompanied by significant 162 fractionation of the REE (Figure 3D) for the most of the column length; in the first few 163 centimeters, Nd phosphates were deposited preferentially. We attribute this effect to the coating 164 of the apatite grains by REE phosphates discussed above, which leads to considerable retardation 165 of the reaction of the solid with the fluid interaction, and to the extremely low solubility of REE 166 phosphates⁹. Consequently, the results of the experiments reported here did not reproduce 167 thermodynamic predictions of REE fractionation^{8,9}. On the other hand, the evidence of REE 168 fractionation accompanying replacement of apatite by REE phosphates in the most altered part of 169 170 the column (0-10 cm; Figure 3C), suggests that REE fractionation may occur in natural systems. This fractionation, however, will be kinetically retarded and require a very high water/rock ratio 171 to be significant. 172

As noted above, fluorite is the common gangue mineral in REE ore deposits, including 173 those, for which the apatite-mediated depositional mechanism has been proposed ^{e.g.,10,11}. It is 174 therefore of interest to investigate the effect of a combination of fluorite-mediated and apatite-175 mediated depositional mechanisms, and to evaluate their contribution to the fractionation of REE 176 in hydrothermal processes. This pairing is especially intriguing considering that, at the conditions 177 178 of saturation with both fluoride and apatite, REE fluorides (fluocerites) are thermodynamically unstable, and REE phosphates (monazites/xenotimes) are relatively insoluble and prone to 179 precipitation (for more detail see the electronic supplement). In principle, the kinetic retardation 180 of apatite-mediated REE phosphate deposition discovered in this study should favor deposition 181 182 of fluocerite and associated fractionation of REE over the formation of REE phosphates. It is therefore interesting to compare this prediction with what was observed in experiments 183 involving a packed column containing a 1:1 mixture of fluorite and apatite. In Figure 4, we show 184

- the results of MicroXRF mapping of the mixed column after being flushed with a relatively
- small amount of REE solution (200 pore volumes of pumped solution corresponding to 50% of
- 187 the duration of



Figure 4: Micro-beam X-ray fluorescence (mXRF; wt %) maps of the apatite/fluorite, column for La, Nd and Er. From these maps, it is evident that Nd and La were deposited proximal to the inlet, whereas erbium was deposited furthest from it. These results indicate that the REE were deposited mainly as fluocerite as the results replicate those shown in Figure 3a and 3b.

| 189 | the experiments with a single mineral). The REE-bearing phases deposited in this column |
|-----|--|
| 190 | comprised both REE phosphates and REE fluorides. From Figure 4, however, it can be seen that |
| 191 | even a short exposure of this column to the REE fluid led to the fractionation of REE, and |
| 192 | moreover, that the signature of this fractionation corresponds to that expected of fluocerite- |
| 193 | dominated REE-mineral deposition (separation of the L/MREE from the HREE and preferential |
| 194 | deposition of HREE/Er fluorides at the end of the column). We believe that this observation |
| 195 | provides strong evidence that, at an early stage in the evolution of REE ore forming |
| 196 | hydrothermal systems, deposition of fluocerite control the fractionation of the REE load. After |
| 197 | this stage, the solids will be represented by monazite/xenotime-coated apatite and highly |
| 198 | fractionated fluocerite, which will host the major part of the total mass of accumulated REE. It |

will be recalled, however, that the assemblage monazite/xenotime coated apatite and fluocerite is
thermodynamically unstable. Thus, although monazite/xenotime may coexist with fluocerite for
some period of time, over the life time of an ore-forming hydrothermal system^{23–26}, fluocerite is
likely to be converted into fluorite and monazite or xenotime, depending on which of these
phosphate phases is thermodynamically more stable at the conditions of the system. This may
explain the rarity of fluocerite in nature.

The conversion of fluocerite into thermodynamically more stable phases also has been the 205 206 subject of other publications. In this case, however, the phases were bastnäsite and parasite and the process involved carbonate-rich fluids.^{18,20,27}. We do not think it likely, however, that the 207 mechanism described above is likely to apply to the deposition of REEs from such fluids. This is 208 because bastnäsite, which is much less soluble than fluocerite, is likely to precipitate in its place⁹. 209 The thermodynamic properties of bastnäsite are poorly understood and it is unknown if the 210 fractionation seen with fluocerite will occur with this mineral. As the solubility of bastnäsite is 211 212 comparable to that of monazite, however, fractionation involving will require similarly large fluxes of fluid for fractionation to occur and it is therefore unlikely that the mechanism proposed 213 here would be applicable to bastnäsite-depositing systems. Considering that REE ore forming 214 215 hydrothermal systems commonly have high carbonate concentrations, this may also help explain 216 the rarity of strongly fractionated bastnäsite ores. For the mechanism proposed above to operate 217 in natural systems, the hydrothermal fluids need to be F-rich and CO₂-depleted. Nevertheless, formation of bastnäsite may still occur during secondary events as pseudomorphs of 218 fluocerite.18,20,27 219

Although fractionation of the REE is commonly involved in nature, a mechanism for thisfractionation mediated by metastable fluocerite has not been proposed, due perhaps to the fact

- that this rare mineral attracted little attention. The results of this study show that, if the REE
- 223 mineralization is the product of fluorine-rich, carbonate-poor hydrothermal systems, and if this
- 224 mineralization was accompanied by fractionation of the REE, enrichment of LREEs would have
- occurred in the more evolved part of the system (higher water to rock ratio) and HREE
- enrichment close to the alteration front.

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1. Benchtop experiments

360 a. Experimental technique



The experiments involved investigating hydrothermal aqueous deposition and 361 fractionation of light, medium, and heavy rare earth elements (L/M/HREEs) in contact with 362 363 varying ratios of solid phosphates (apatite) and fluoride (fluorite) minerals at temperatures of 100°C and 250°C, and a pressure of 100 bar. A sketch of the experimental set up is shown in 364 Figure S.1. and an image of the experimental set up is shown in Figure S.2. These experiments 365 were performed in a dynamic flow-through cell (8-11 cm³ internal volume) manufactured from 366 either: stainless steel, titanium, or Monel 400 alloy, illustrated in Figure S1. B. Experiments 367 which were analyzed using micro-X-ray fluorescence (mXRF) mapping were conducted with a 368 flow through cell lined with Teflon allowing for the solid packing material to be extruded and 369 370 analyzed in a pseudo in situ setting.

Experimental solutions were prepared with de-ionized water and solid REE-chlorides of La, Nd, and Er (Alfa AesarTM 99.9%) and have a La, Nd and Er concentration of 500 mg/L. The solution $pH_{25^{\circ}C}$ was approximately 2 and was obtained by adding an appropriate amount of HCl (Fisher Scientific, Optima grade). All solutions were prepared with NaCl (Fisher Scientific,

| 376 | differential mobility of the REE-chlorides as function of increasing atomic number ⁹ and 2) as the |
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| 377 | most reliable and experimentally proven activity model at a high temperature was developed |
| 378 | with NaCl dominated solutions $^{28-30}$. |

379 Flow through cells were packed with apatite and fluorite in the ratios 1:0, 0:1, and 1:1; grain size was 0.15 - 1.0 mm. The mineral grains occupied, on average 69% of the internal 380 381 volume of the flow-through cell, providing for a fluid rock ratio of roughly 1:3. The experimental solution was then pumped through the cell at a rate of 0.05 - 0.1 mL/min using a 382 383 Teledyne SSI LD-Class 12 dual piston pump (Figure S1A); the flow-through cell pressure was monitored through pumps built into the pressure monitoring system and controlled through a 384 back pressure regulator. Outflowing solutions were collected fractionally with a Teledyne ISCO 385 Foxy Jr. Fraction Collector, with a collection every 1-2 hours depending on the flow rate. The 386 samples, which were analysed for their REE and major ion content, had a volume of ~ 6 ml. 387 The concentrations of La, Nd, and Er in the inlet and outlet aqueous solutions were 388 measured using inductively coupled plasma – mass spectrometry (ICP-MS) techniques with a 389 PerkinElmer NexIon Mass Spectrometer. The concentrations of major cations, such as Ca, Sr, 390 391 and Fe, being eluted from the column were measured using inductively coupled plasma – optical

emission spectrometry (ICP-OES) techniques, with a PerkinElmer Optima 2100 DV OpticalEmission Spectrometer.

Prior to the experiments, unaltered apatite and fluorite were analyzed using powdered Xray diffraction (XRD) techniques in order to determine if there was any hydrothermal alteration during experiments. After experiments were finished, the resulting solids were extruded and analyzed again using XRD. The XRD analyses were done with the use of a Siemens D500 X-ray diffraction spectrometer. XRD spectra were collected from 5° to 70° 2-Theta, with a dwell time

| 399 | of 6 seconds and a step size of 0.02. All XRD peak analysis and phase identification was done |
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| 400 | using the analytical software JADE, Materials Data Incorporated. |

The bulk chemical composition of the solid phase was analyzed, both prior to and after an experiment using X-ray fluorescence (XRF) spectrometry. Fused glass discs of the solid materials were made from sample and lithium tetraborate in the ratio 1:36 and fused at a temperature of 1100°C. The fused discs were analyzed on a Rigaku ZSX Primus II X-ray diffractometer.

In addition to XRD and XRF, scanning electron microscopy (SEM) and micro-XRF
(mXRF) were used to characterize the solids. Further detail on these two techniques is provided
below.

409 **b. Results**

The results of the benchtop simulation of hydrothermal ore forming systems illustrates that when hydrothermal REE bearing, chloride dominated, fluids come in contact with either fluorite or apatite, this causes the immediate deposition of the REEs from solution. This is evident in the composition of the reacted solution, which was analyzed via ICP-MS and shown in Figure 1A for the apatite column and Figure S2 below.

This interaction of the hydrothermal fluid and the minerals led to the metasomatic reaction of fluorite to fluocerite and apatite to REE-phosphate. This is evident from inspection of the powdered X-Ray diffraction data shown in Figure S2 and Figure S3. In Figure S3, it can be observed that in the post-experiment segmented column, the 3-4 inch segment peak at 28.3° changes from a singlet to a doublet. In addition, the peak at 47.0° disappears completely from the diffractograms. Both indicate

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Figure S2: ICP-MS results of analyses of the composition the solution exiting from the fluorite column. The graph shows individual REE concentrations in the fraction (C) divided by the initial concentration of the stock solution (C_{\circ}) versus the pore volume of the column.





Figure S3: Powder X-ray diffractograms of fluorite from the bench top experiment in which the data are plotted as a waterfall and each of the diffractograms corresponds to a one-inch segment down the column. The peaks characteristic peaks of fluorite are at 24.9, 47.1, 55.9 degrees 2-theta. The peaks characteristic of fluocerite are at 28.3 and 47.0 degrees 2-theta. The peaks at 38.4 and 40.1 correspond to titanium and are purely a relic of the mount on which the analysis was done.

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Figure S4: Powder X-ray diffractograms of apatite from the bench top experiment in which the data are plotted as a waterfall and each of the diffractograms corresponds to a two-inch segment down the column.

424 that fluorite underwent a complete phase change from fluorite to fluocerite. This interpretation is supported by the fused disc XRF data, shown in Figure 3A, for which the highest level of 425 426 accumulation of REE was from this segment. In Figure S4, it can be observed that there was a 427 subtle peak shift. The peak analysis showed that the apatite peaks never fully disappeared and that apatite was partially replaced by rhabdophane, a hydrated REE-phosphate. This is further 428 supported by the XRF data which show that REE accumulation in the column never exceeded 429 430 33%, which explains why the XRD data show that after reaction, apatite was present through the entire column. 431

- 432 2. Characterization of Solid
- 433
- 434a. Scanning Electron microscopy

| 435 | Several grains were extracted from 1 cm intervals of both the apatite and fluorite |
|-----|---|
| 436 | columns, mounted in epoxy, and polished to expose the center of each grain. The grain mounts |
| 437 | were imaged using a FEITM Inspect F scanning electron microscope (SEM) at Los Alamos |
| 438 | National Laboratory. Samples were Au-coated prior to SEM analysis. Imaging with the SEM |
| 439 | was performed using a 15 kV accelerating voltage and a 3.0 spot size. Energy dispersive X-ray |
| 440 | spectroscopic (EDS) measurements were made in both point analysis and mapping mode at 20 |
| 441 | kV with a 5.0 spot size using an EDAX Octane Elite silicon drift detector and EDAX TEAM |
| 442 | software for data processing. |
| 443 | Point and mapping analyses illustrated the nature of the REE-alteration products. Cores |
| 444 | of apatite grains were observed to be unaltered. Rims of REE-rich and Ca-depleted phosphates |
| 445 | formed around the edges of the apatite grains and alteration was not observed to extend into the |
| 446 | center of the grains. In comparison, fluorite grains are extensively fractured and REE-rich |
| 447 | fluoride minerals (i.e., fluocerite) deposited in cracks within the mineral. |
| 448 | b. MXRF |
| 449 | Elemental mapping was done using a Bruker M4 Tornado MXRF instrument. A focusing |
| 450 | polycapillary optic on the Rh anode X-ray tube produced an excitation spot size nominally of 20 |
| 451 | μ m. Sample analysis was conducted under ambient atmosphere using two silicon drift detectors |
| 452 | (SDD) with 30 mm2 active area. Measurements were conducted at 50 kV and 600 $\mu A.$ |
| 453 | Sample preparation for MXRF required removing the upper portion of the Teflon lining |
| 454 | around the column to expose the packed material. The samples were interrogated directly while |
| 455 | placed in a 3D-printed holder which eased handling and ensured a fixed distance from X-ray |
| 456 | source and detectors. Maps were collected over an area of 154 mm by 13 mm with a 40 μm step |

size and 10 ms per pixel dwell time. Full spectral data were collected for each pixel and signalintensities for La, Nd, and Er were plotted to evaluate the elemental distribution.

459 3. Thermodynamic calculations

Relative stability diagrams for end-member REE fluorides and phosphates were plotted 460 in log $a(F) - \log a(PO_4^{3-})$ co-ordinates for 250 °C and saturated pressure of water vapor. In order 461 to evaluate the conditions of saturation of the fluid with respect to apatite and fluorite (assuming 462 co-existence of these phases and the aqueous solution), the activity of F⁻ and PO₄³⁻ were modeled 463 in solutions of variable pH for the system Apatite-Fluorite-H2O-HCl – NaCl containing 0.5 464 mol/kg of NaCl. Stability fields were calculated for La, Nd, and Er phosphate end-members 465 $(LnPO_4)^9$ and La, Nd, and Er fluoride end-members $(LnF_3)^9$. The activity of PO₄³⁻ and F⁻ in 466 solutions equilibrated with apatite and fluorite was calculated for the following aqueous solution 467 model: H⁺, OH⁻, O₂°, H₂°, Na⁺, NaOH°, NaCl°, HCl°, Cl⁻, Ca²⁺, CaOH⁺, CaCl⁺, CaCl²°, H₂PO₂⁻, 468 H₃PO₂°, HPO₃²⁻, H₂PO₃⁻, H₃PO₃°, PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, H₃PO₄°, P₂O₇⁴⁻, HP₂O₇³⁻, H₂P₂O₇²⁻, 469 $H_3P_2O_7$, $H_4P_2O_7$ °, HF° , F-, HF_2 , NaF° , and CaF^{+31-35} . The system modeled considered the 470 following solid phases: Fluorite (CaF₂)³⁶, Apatite-F (Ca₅(PO₄) F)³⁶, Apatite-OH (Ca₅(PO₄)₃OH) 471 ³⁶, Whitlockite (Ca₃(PO₄)₂) ³⁶, Monetite (CaHPO₄)³⁷, and Brushite (CaHPO₄(H₂O)₂)³⁷. The 472 properties of water were modelled using the Haar-Gallagher-Kell model³⁸ and the model derived 473 by Marshall and Franck³⁹. Individual ion activity coefficients were calculated using the extended 474 Debye-Heckle equation recommended for NaCl-dominated solutions up to 600 °C, 1000 bar and 475 I(ionic strength) $< 6^{40-42}$. 476

The result of the above calculations is shown in Figure S5. As can be seen from this
Figure, the conditions of saturation with respect to Ca phosphates and fluorides (Apatite,
Monetite/Whistlockite, Fluorite) are restricted to the stability fields of REE phosphates, which

means that at these conditions REE fluorides are metastable and cannot form at equilibrium in 480 the above system system. The way to ensure formation of the latter phases is to decrease the 481 PO₄³⁻ activity, which likely occurs when apatite becomes coated by REE phosphate phases and 482 the solution loses contact with the Ca phosphates. It should be noted, that these calculations were 483 performed for REE fluoride and phosphate end-members, whereas in natural systems these 484 485 minerals occur as solid solutions, involving multiple REE. The effect of solid solution has not been accounted for in our calculations due mainly to the lack of thermodynamic data. Although 486 there are estimates of the solid solution properties of REE phosphates ^{e.g.,8}, there are no data on 487 REE fluoride solid solutions. However, considering that the difference in terms of the activity of 488 PO₄³⁻ between the saturation with Ca-bearing minerals and the stability field of REE fluorides 489 exceeds an order of magnitude (for La) or more (for other REE), we propose that the effects of 490 solid solution should not cause a major change in the observed trends 491



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