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GEOCHEMISTRY

REE Distribution between Fluorite and Ore-Forming Fluid Based on Results of Thermodynamic Modeling

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Being rather abundant, fluorite is widely used for the study of its REE patterns depending on the conditions of postmagmatic ore formation. It is very indicative that the turn of the century was marked by several publications in Russia and abroad devoted to discussion of the REE distribution in fluorites of rare-metal deposits from the viewpoint of possible physicochemical scenarios of its crystallization in the course of hydrothermal process [1–4]. Despite the apparent diversity of chondrite-normalized patterns of REEs depending on their ordinal number, they are commonly distinguished by two main parameters: (1) the relative LREE and HREE concentrations and (2) the measured Eu content normalized to the half-sum of its nearest neighbors (Sm

Total contents of elements, mol/kg H_2O in equilibrium fluids of the 18-component model system* versus temperature and pressure

Component	500°C, 2000 bar	400°C, 1000 bar	300°C, 500 bar	200°C, 250 bar	100°C, 125 bar
Si	$6.37 \cdot 10^{-2}$	$2.52 \cdot 10^{-2}$	$1.04 \cdot 10^{-2}$	$3.67 \cdot 10^{-3}$	$1.16 \cdot 10^{-3}$
Al	$2.10 \cdot 10^{-5}$	$7.11 \cdot 10^{-6}$	$1.45 \cdot 10^{-6}$	$1.27 \cdot 10^{-7}$	$2.77 \cdot 10^{-9}$
Be	$1.52 \cdot 10^{-3}$	$8.23 \cdot 10^{-4}$	$4.82 \cdot 10^{-5}$	$2.67 \cdot 10^{-6}$	$1.53 \cdot 10^{-6}$
F	$4.02 \cdot 10^{-3}$	$2.29 \cdot 10^{-3}$	$9.70 \cdot 10^{-4}$	$5.17 \cdot 10^{-4}$	$3.31 \cdot 10^{-4}$
Ca	$6.72 \cdot 10^{-2}$	$6.67 \cdot 10^{-2}$	$6.61 \cdot 10^{-2}$	$6.59 \cdot 10^{-2}$	$6.58 \cdot 10^{-2}$
La	$5.03 \cdot 10^{-6}$	$2.95 \cdot 10^{-7}$	$4.12 \cdot 10^{-8}$	$2.54 \cdot 10^{-8}$	$2.40 \cdot 10^{-8}$
Nd	$3.57 \cdot 10^{-5}$	$8.72 \cdot 10^{-6}$	$3.14 \cdot 10^{-6}$	$2.91 \cdot 10^{-6}$	$2.89 \cdot 10^{-6}$
Eu	$2.00 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$	$2.00 \cdot 10^{-3}$
Gd	$6.47 \cdot 10^{-6}$	$1.92 \cdot 10^{-7}$	$1.91 \cdot 10^{-9}$	$9.28 \cdot 10^{-11}$	$7.78 \cdot 10^{-12}$
Ho	$6.89 \cdot 10^{-5}$	$1.98 \cdot 10^{-5}$	$3.01 \cdot 10^{-6}$	$2.02 \cdot 10^{-6}$	$1.90 \cdot 10^{-6}$
Yb	$1.85 \cdot 10^{-3}$	$1.84 \cdot 10^{-3}$	$1.84 \cdot 10^{-3}$	$1.84 \cdot 10^{-3}$	$1.84 \cdot 10^{-3}$
Lu	$1.81 \cdot 10^{-4}$	$6.25 \cdot 10^{-5}$	$5.30 \cdot 10^{-6}$	$1.79 \cdot 10^{-6}$	$1.24 \cdot 10^{-6}$
Y	$3.05 \cdot 10^{-6}$	$2.71 \cdot 10^{-8}$	$1.85 \cdot 10^{-10}$	$4.97 \cdot 10^{-12}$	$3.35 \cdot 10^{-13}$
Na	3.70	3.40	3.10	2.80	2.50
Cl	4	3.7	3.4	3.1	2.8
K	0.165	0.165	0.165	0.165	0.165
pH	5.548	5.592	5.472	5.955	7.115

* Compositions of initial fluid and solid phase at 500°C and 2000 bar: $\{1\ \mathrm{kg}\ H_2O + 0.5\ \mathrm{M}\ HF + 4.0\ \mathrm{M}\ NaCl + 0.1\ \mathrm{M}\ NaOH\}_{\mathrm{solution}}$ + (in mole), {3 quartz + 0.25 albite + 0.25 microcline + 0.5 anorthite + 0.1 phenakite + 10^{-3} R_2O_3 (for each REE) + 1 (Ni + NiO) for stabilization of redox conditions$\}_{\mathrm{solid}}$.

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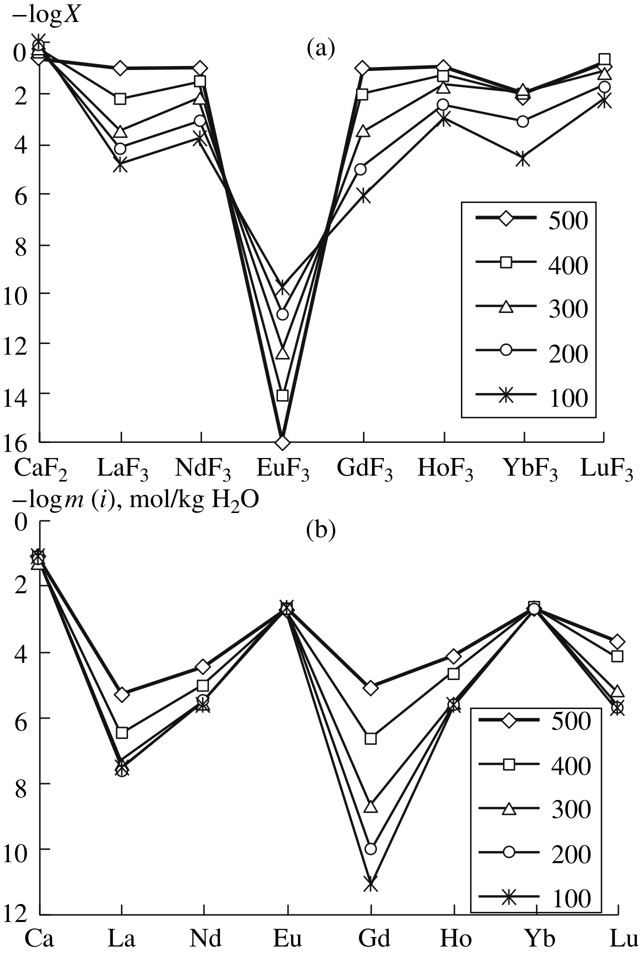

Fig. 1. (a) Concentrations of REE-fluorides in fluorite as an ideal solid solution and (b) REE component of solutions in equilibrium with the fluorite.

and Gd) designated as Eu/Eu*. The latter ratio is used as a formal estimate of the sign and rate of the anomalous behavior of Eu, because the denominator plays the role of the virtual (undistorted) Eu content. It should also be noted that symmetric chondrite-normalized LREE and HREE patterns with a prominent negative Eu anomaly are recently defined as “bird wings”. Such patterns are especially characteristic of Li–F granites or rhyolites and genetically related rare-metal deposits [1, 3–5].

The aim of this study is to consider the results of our thermodynamic modeling of the precipitation of REE-fluorite from high-temperature chloride–fluoride–carbonate fluid. These results characterize equilibrium distribution of absolute (unnormalized) contents of REE present in the model ore-forming system briefly described in [6]. The model was realized using the HCh software package [7] and the well-known SUPCRT98 thermodynamic database. The database contains not only thermodynamic constants of the major components of the model fluid but also characteristics of the main types of complex REE aqueous species in a wide *TP* range [8, 9]. It should be noted that we used in our model the ability of the HCh software package to consider REE-fluorite as an ideal solid solution of macrocomponent CaF_2 and seven microcomponents selectively represented by trifluorides of La, Nd, Eu, Gd, Ho, Yb, and Lu. Their thermodynamic constants were taken from [10, 11] and previously discussed in [12].

While performing numerical experiments, we first calculated the composition of high-temperature REE-fluorite in equilibrium with the initial fluid at 500°C and 2000 bar (pH of the fluid was buffered by the chosen quartz–feldspar mineral assemblage). Afterward, the compositions of the newly formed REE-fluorite and equilibrium fluid were computed at decreasing temperatures and respective pressures with a step of 100°C. Let us emphasize that we made allowance for possible stepwise formation of all types of REE complexes characterized in terms of thermodynamics [8], including the most important fluoride- and hydroxocomplexes [6]. The table presents equilibrium compositions of model fluids that evolved in the course of decrease in *TP* parameters toward gradual depletion in major components (Na, K, Ca, Si, Al, Be) and REE. It should be emphasized that the *final* fluid composition at the given *TP* conditions represents the *initial* composition for the next step of the model (i.e., for $T = -100°C$ and two times lower pressure).

Figure 1 shows the stepwise (after each 100°C) variation of REE contents in the model REE-fluorite and the equilibrium fluid. As can be seen from the upper panel (Fig. 1a), the decrease in temperature and pressure in the matrix of the predominant CaF_2 is accompanied by regular depletion in concentrations of six REE fluorides expressed in mole fractions. The only exception is Eu, the concentration of which in REE-fluorite is negligible at 500°C ($X_{Eu} = 10^{-16}$) and increases by six orders of magnitude in the course of cooling down to 100°C. Nevertheless, its concentration remains minimal in comparison with other REEs. The lower panel (Fig. 1b) demonstrates that the Eu concentration in fluids is retained practically unchanged and remains equal to the initial value of $2 \cdot 10^{-3}$ M within the entire temperature range.

As was mentioned in [6, 13], Yb turns out to be the closest analogue of Eu in the model high-temperature fluid. The Yb concentration in fluid also remains virtually constant and close to the initial value ($1.84 \cdot 10^{-3}$ M) in the course of cooling. At the same time, the behavior of Yb in the model fluorite is close to that of other REEs; i.e., its contents fall from high to lower temperature, however, only by two orders of magnitude (approximately as in the case of neighboring Ho and Lu). For comparison, the decrease is approximately four orders of magnitude for La and Nd and approximately five orders of magnitude for Gd. As follows from Fig. 1a, the contents of trifluorides of La, Nd, Ho, and Lu in fluorite at a high temperature are almost equal

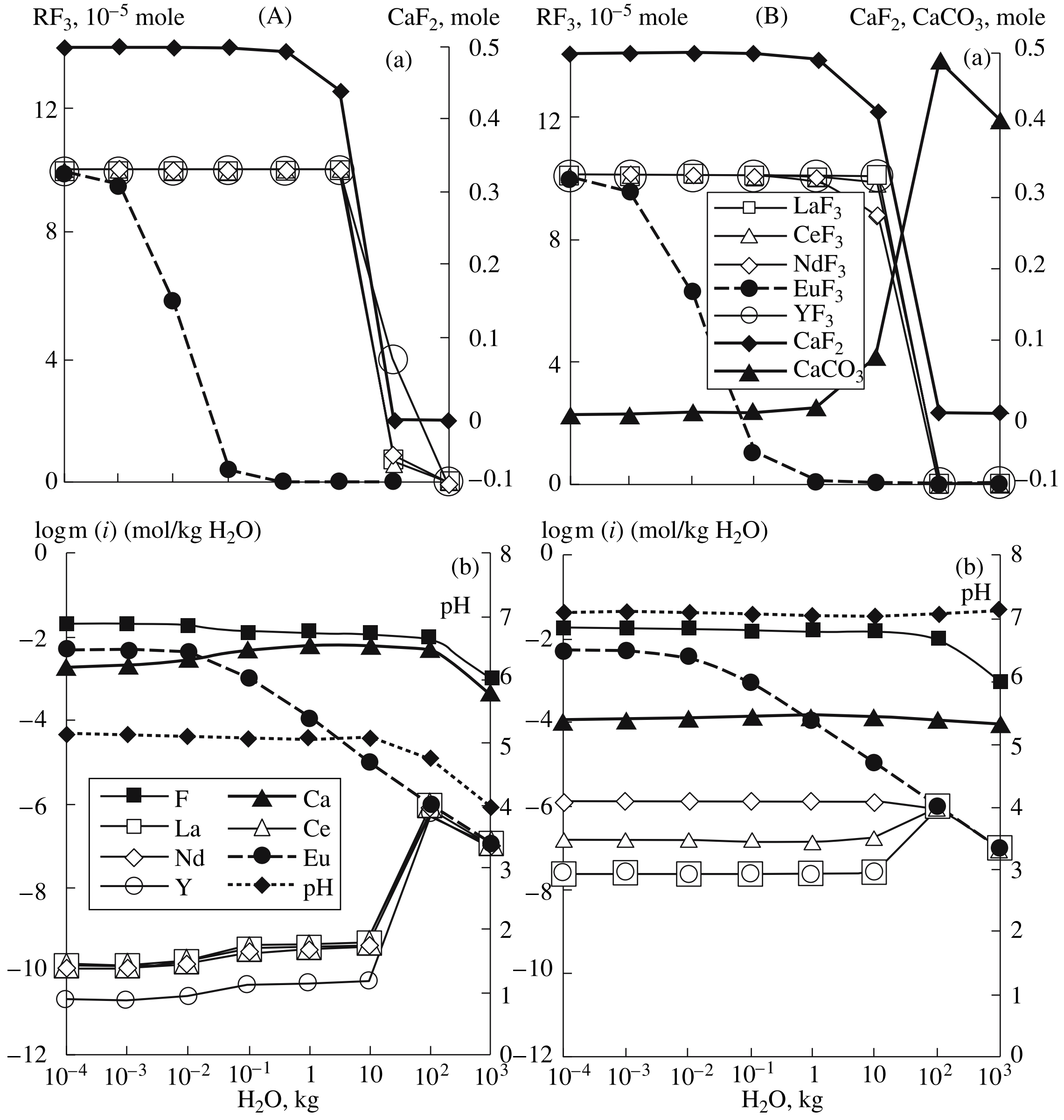

Fig. 2. Thermodynamic model of stepwise variation of (a) REE-fluorite and (b) REE in equilibrium fluid at 400°C and 1 kbar vs. the amount of reacted fluid of the initial composition corresponding to (A) 3M NaCl + 1.0 MH_2CO_3 + 0.01M HCl or (B) 0.1M KOH. The solid phase is REE-fluorite as an ideal solid solution based on the CaF_2 matrix (0.5 mole) with the addition of five REE and Y fluorides indicated in the legend (10^{-4} mole each).

(within an order of magnitude), but the symmetry of the distribution of these elements (especially La) becomes appreciably distorted at lower temperatures.

In the fluid (Fig. 1b), the trend is opposite in many respects. In the interval 100–300°C, the La, Nd, Ho, and Lu concentrations practically do not depend on temperature and are very close to one another except for La. However, its content in fluid at 500°C approaches those of other REEs. Thus, ignoring some details, one can say that in terms of the idealized REE-fluorite–fluid model, the behavior of Eu and, to a lesser extent, Yb is anomalous with respect to other REEs.

The suggested chemical (intrinsic) mechanism of the formation of the Eu minimum in natural minerals and rocks is also supported by the results of additional numerical experiments presented in Fig. 2. These results develop and supplement the above reasoning. They clearly demonstrate the physicochemical dynamics of the advanced leaching of Eu from the model REE-fluorite by both acid (Fig. 2A) and alkaline (Fig. 2B) solutions in the course of gradual increase in the ratio of the reacted solution to the initial amount of mineral. In general, transfer of the whole amount of EuF_3 (~20 mg) from solid phase into solution requires only 0.1 kg H_2O (recalculated to the pure solvent) in the case of an equi-

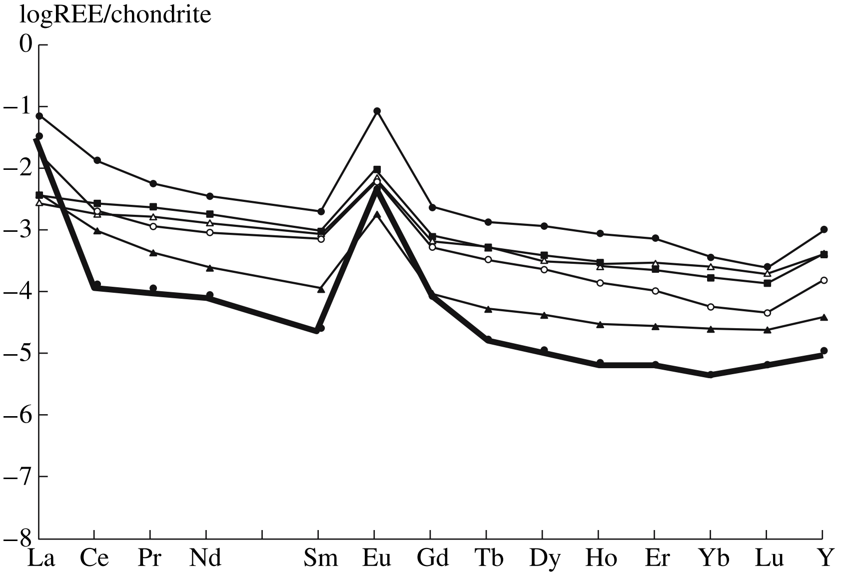

Fig. 3. Experimental data [14] on REE leaching from peridotite by chloride solutions at 400°C and 500 bar (heavy line) in comparison with the chondrite-normalized REE patterns of hydrothermal vents in the Mid-Atlantic Ridge (the upper thin line corresponds to the Rainbow system; the middle line with circles, to the Snake Pit system; and the lower thin line, to the Lucky Strike system) and in the East Pacific Rise, EPR 13N (the second thin line with filled boxes).

librium process. The leaching of other REE fluorides is theoretically completed only after interaction of fluorite with 100 and 1000 kg H_2O for alkaline and acid solutions, respectively.

Based on the modeling results, it may be supposed that the well-known anomalous behavior of Eu in geochemical processes is related not only to its ability to pass easily from the tri- to bivalent state depending on redox conditions in the ore-forming system. The high reactivity of Eu owing to the elevated free energy of EuF_3 formation relative to other REE fluorides is also of great importance. Hence, both the anomalous Eu contents and the respective Eu/Eu* values in the chondrite-normalized REE patterns of minerals and rocks can hardly be explained only by redox conditions without allowance for their possible dependence on the fluid/rock ratio achieved by the rock-forming system.

The recently published experimental data on the advanced dynamics of hydrothermal leaching of Eu from serpentinized harzburgite (sample USGS Rock Standard PCC-1) [14] serve as an important confirmation of the proposed model of anomalous Eu behavior in the course of water–rock interaction. The principal character of the problem under discussion compels us to reproduce the final illustration from [14] (Fig. 3). The heavy curve shown in this figure is a summary result of autoclave experiments with a run period of two months at 400°C and 500 bar with the use of NaCl + $MgCl_2$ solutions. After the run, the solution shows a distinct Eu maximum that appreciably exceeds the measured concentrations of other REEs. The authors of [14] specially emphasize the complete analogy of experimental REE patterns with distribution of REEs in solutions from some bottom hydrothermal vents in both the Mid-Atlantic Ridge (including the seepage from ultramafic rocks in the Rainbow hydrothermal system at 36° N) and the East Pacific Rise. According to [14], the fluid/rock ratio must be taken into account for the quantitative assessment of REE leaching.

Systematic data on the regularity of Eu distribution in fluorites from rare-metal deposits in the Erzgebirge [2, 4], Siberia, Far East, Central Asia [3], and other regions may be regarded as obvious geochemical corroboration of our interpretation of Eu anomalies. The authors of [2–4 and others] emphasize directly or indirectly the advanced loss of Eu recorded as its minimums in the chondrite-normalized patterns of altered rocks and newly formed minerals, including fluorite. For example, the authors of [4] convincingly demonstrate that the depth of Eu minimum in REE patterns of host rocks at the Zinnwald cassiterite deposit increases from slightly to severely altered rhyolites and further to the albitized granites. The minimum is most prominent in topaz and mica greisens.

Finally, our model suggests that the excess Eu can be accumulated in natural fluids similarly to that in Fig. 3 under certain conditions in the form of Eu maximums in the REE patterns of late minerals. Such maximums have been established in the late fluorite generations in the Russian Far East (Khingan, Arsen'ev, Pravourmiisk, and Tigriny cassiterite deposits) [3] and, particularly, in the Erzgebirge (Ehrenfriedersdorf tin deposit) [2].

Indeed, the authors of [2] have shown that the Eu minimum can be replaced by a maximum (!) while passing from violet fluorite at the outer contact of greisen bodies to the pale pink fluorite in tourmaline veinlets at the outer contact of these bodies. They also noted that the height of the Eu maximum in fluorite from cassiterite–quartz veins in the outer contact zone gradually rises in the process of overgrowth of variously colored fluorite zones: the peak is poorly developed in green fluorite (Eu/Eu* = 1.3), medium in the milky green fluorite (Eu/Eu* = 3.1), and highest in the white-violet fluorite (Eu/Eu* = 3.5).

Thus, our thermodynamic model of crystallization of REE-fluorite shows that the characteristic Eu anomalies may be controlled not only (and not so much) by the redox conditions of its crystallization. It is also important to keep in mind the low thermodynamic stability of trifluoride and other important compounds of Eu [15] expressed as significant positive deviations of the free energy of their formation relative to other REEs. Therefore, we must emphasize once again that Eu can serve as a peculiar fluidometer that reflects the effective fluid/rock ratio achieved by the mineral-forming system in a specific place and at a specific time of its evolution.

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