ISSN 1028-334X, Doklady Earth Sciences, 2006, Vol. 408, No. 4, pp. 649–651. © Pleiades Publishing, Inc., 2006.
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GEOCHEMISTRY

Physicochemical Properties of Europium as a Possible Marker of Mineral Formation Conditions

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Presented by Academician N.V. Sobolev August 12, 2005

Received September 2, 2005

DOI: 10.1134/S1028334X06040313

The anomalous position of Eu in chondrite-normalized REE patterns of minerals has attracted the attention of geochemists for several decades. The works by J.A. Philpotts (1966–1973) on behavior of Eu and other REEs in igneous rocks commonly serve as theoretical principles for interpretation of this phenomenon. Based on similar radii of Eu^{2+} and Sr^{2+} ions, Philpotts suggested that an excess of Eu relative to the neighboring REEs is caused by reducing conditions in the mineral-forming system. The aim of this work is to expand substantially the physicochemical basis that allows interpretation of complicated geochemical relationships of Eu with other REEs in natural systems, especially with participation of high-temperature fluids.

First, it should be emphasized that there are strong arguments against the traditional grouping of Eu with trivalent REEs. Cotton and Wilkinson highlighted the key points somewhat differently: “monazite and other minerals carrying lanthanides in the +3 oxidation state are unusually poor in europium which, because of its relatively strong tendency to give the +2 state, is often more concentrated in the calcium group minerals” [1, p. 501]. Moreover, precisely Eu and, to a lesser extent, Yb and Sm reveal distinct positive deviations from the generally horizontal graphs of the dependence of free energy of the formation of fluorides, phosphates, carbonates, and oxides on ordinal numbers of lanthanides [2, 3]. In the course of thermodynamic modeling, these relationships led to anomalously high concentrations of the aforementioned REEs in high-temperature fluids. By the way, the overview of data in [4] showed that these three elements are distinguished from other elements by a relatively weak affinity to oxygen and chlorine, fugacities, and other specific physicochemical properties.

Returning again to the comprehensive review [1], let us note that already at that time the lanthanides under discussion were regarded as top-priority candidates for valence +2. This is in good agreement with the configuration of their outer electron shells, first of all, Eu ($4f^7$, i.e., just one-half of 14 f-electrons). This is also consistent with experimentally determined standard potentials of such pairs as Eu^{3+}/Eu^{2+}: 0.43 for Eu, 1.15 for Yb, and 1.55 for Sm. These values are related to common (near-room) temperatures. As has been shown in the subsequent publication [5], the field of aqua-ion Eu^{2+} stability expands with increase in temperature. This relationship has been shown in [6] for all three elements considered above. Finally, Bau [7] set forth some general principles of possible application of Eu to the solution of petrogenetic physicochemical problems.

Some years ago, together with G.P. Shirnosova we performed the detailed thermodynamic calculations of hydrothermal equilibria with participation of Eu (III) and Eu (II) within the temperature range from 200 to 500°C [8, 9]. The use of constants from [10–12] as a thermodynamic basis allowed us to take into account a possible influence of complexing of speciation of Eu in high-temperature fluids. Thus, we accomplished a principle transition from the traditional consideration of redox equilibrium between aqua-ions $Eu^{3+} \cdot aq/Eu^{2+} \cdot aq$ to the equilibrium $\Sigma Eu(III)/\Sigma Eu(II)$ that takes into consideration the formation of chloride, hydroxide, fluoride, and carbonate complexes of Eu.

In particular, Fig. 1 shows that the chloride complexes of Eu (II) are absolutely predominant in the modeling Eu-bearing chloride–fluoride–carbonate fluid even in equilibrium with hematite (i.e., in an extremely oxidizing environment) at the following conditions: T = 200°C, NaCl concentration 1.0 mole/kg H_2O or more, and pH = 2.3–8.1. It has also been established that anionic chloride complexes of Eu (II) designated by open and filled boxes in Fig. 1 are the main species of europium occurrence in the fluid. Relatively high Eu (III) concentrations may be expected either in low-temperature acid fluids (as cationic fluorocomplexes shown

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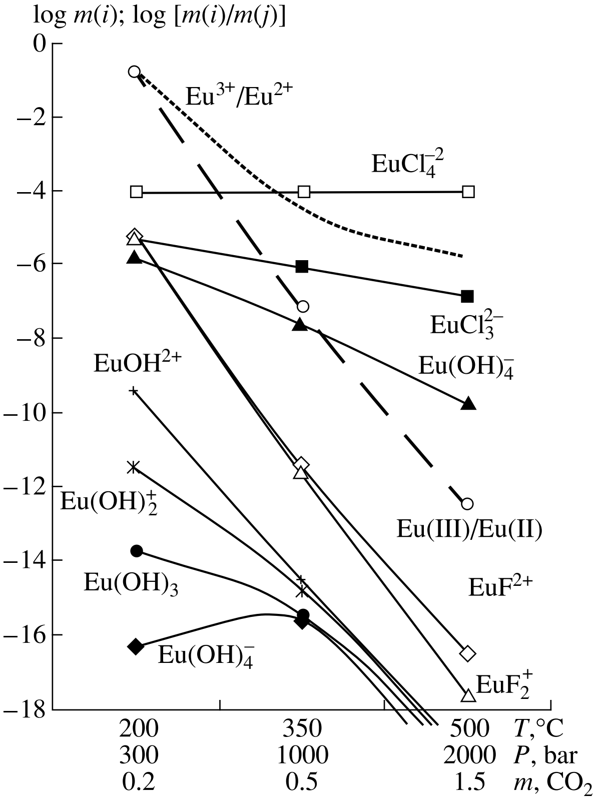

Fig. 1. Logarithms of total concentrations of Eu (III) and Eu (II) and their major complexes versus temperature and other parameters of model fluid composition 1.0*m* NaCl + 0.1*m* HF + (1.5–0.2)*m* CO_2 fluid calculated on the basis of initial data in [9]. The dotted line shows equal $Eu^{3+} \cdot$ aq and $Eu^{2+} \cdot$ aq concentrations. The dashed line shows equal total Eu(III) and Eu (II) concentrations.

by open diamonds and triangles in Fig. 1) or in low-temperature alkaline fluids (as anionic hydroxide complex $Eu(OH)_4^-$ shown by filled triangles in Fig. 1). The table also shows typical dependence of the thermodynamically calculated total molal concentrations of Eu (II) and Eu (III) and their ratios at 350°C on pH.

The estimation of degree of oxidation (valence state) of Eu in crystalline matrices of REE-bearing minerals is quite a different problem. From the theoretical point of view, it is worthy to remind, for example, that more than 40 years ago R.M. Garrels demonstrated the following fact: abundant Fe^{3+}-bearing oxides, such as magnetite and even hematite, turn out to be thermodynamically stable down to the lower electrochemical boundary of water stability, i.e., under conditions of their possible equilibrium with native iron. This relationship seemingly contradicts the normal redox potential of Fe^{3+}/Fe^{2+} (+0.77 V) in solution. A similar absence of correlation between the degree of oxidation in minerals and solutions is also known for some other elements of variable valence (e.g., for Cu in chalcopyrite, Sn in cassiterite or stannite, As and Sb in enargite and famatinite, and so on). The question concerning the valence state of Eu in REE-bearing minerals also remains open so far.

To our knowledge, the first experimental determination of this kind was reported in [13]. It was established that the Eu^{2+}/Eu^{3+} ratio in REE-bearing apatite from the Llallagua deposit (Bolivia) ranges from 0.12 to 0.22 at total Eu content of 700 ppm. These results were obtained on the basis of x-ray absorption near-edge spectroscopy (XANES) with synchrotron radiation. Recently, we have reported the results of the determination of oxidation state of Eu in apatite from the Malyshevo beryllium deposit in the central Urals [14]. These results show that Eu^{3+} accounts for approximately one-half of total europium (0.4–0.6 in one sample and 0.5–0.7 in another sample). Thus, the available data confirm our suggestion on possible coexistence of Eu in different states of oxidation in REE-bearing minerals. This situation repeats, to a certain extent, the coexistence of Eu (II) and Eu (III) in mineral-forming fluids.

In conclusion, let us dwell on one more aspect of the issue of interpretation of anomalous behavior of Eu in the chondrite-normalized patterns of natural REE-bearing minerals. It is well known that the thermodynamic prerequisites, at least with respect to natural processes, bear a character of recommendation because of the problems related to achievement of equilibrium. In particular, it is worthy to recall that the influence of fluid-

Indicators of the Eu state in chloride–fluoride–carbonate fluid at 350°C as a function of pH (in inverse logarithms of molal concentrations)

	pH						
	2.3	3.3	4.5	6.2	7.1	8.0	8.9
$-\log[Eu^{2+}]$	12.7	12.7	12.7	12.7	12.6	12.5	14.1
−log[Eu(II)]	**4**	**4**	**4**	**4**	**4**	**4.1**	**6.0**
$-\log[Eu^{3+}]$	15.0	15.9	17.2	18.8	19.7	20.4	22.9
−log[Eu(III)]	**11.3**	**11.4**	**11.2**	**10.4**	**7.6**	**4.9**	**4.0**
$-\log[Eu^{2+}]/[Eu^{3+}]$	2.3	3.2	4.5	6.1	7.1	7.9	8.8
−log[Eu(II)]/[Eu(III]	**7.3**	**7.4**	**7.2**	**6.4**	**3.6**	**0.8**	**−2**

Note: Bold font designates total concentrations of bi- and trivalent Eu and their ratios as characteristics of REE-bearing natural fluids.

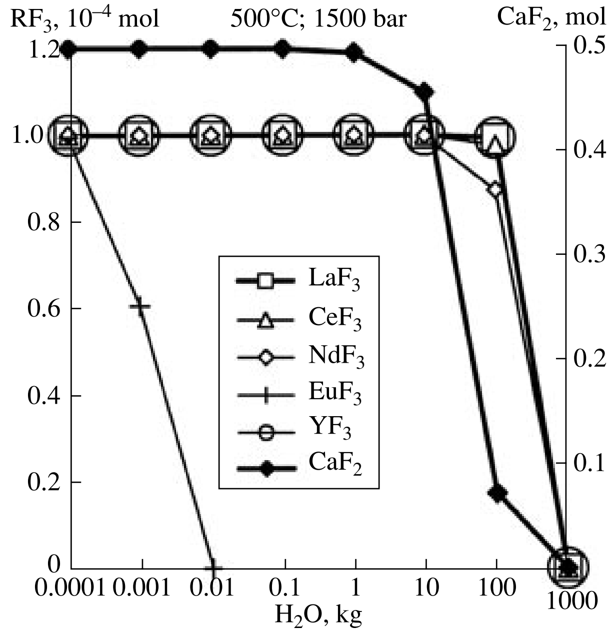

Fig. 2. Stepwise decrease in solid fluoride concentrations (mol/kg) for (REE + Y) and CaF_2 phases (left and right scales, respectively) as a function of the amount of carbon dioxide–chloride fluid that reacted with a charge at 500°C and 200 MPa in accordance with data [3]).

and rock-dominant regimes on mineral equilibria was a topical issue for hot discussion a few decades ago. Moreover, since the solubility of REE-components in minerals is expected to be very low, the transition of lanthanides into a relatively mobile state is possible only at the absolute excess of fluid, e.g., at the fluid/rock ratio of no less than 10^3 [8].

The diagram fragment reproduced in Fig. 2 from [2] clearly demonstrates the strong dependence of the dynamics of dissolution of fluorite (matrix mineral), fluorides of ordinary REEs (La, Ce, Nd, and Y), and europium fluoride on their thermodynamic solubilities. For the sake of clarity, the values on the *x*-axis indicate the amount of modeling solution (recalculated to the pure solvent, i.e., H_2O) required for reaction with the initial charge to dissolve the amount of solid components indicated on the *y*-axis. The calculation results have shown that owing to the irregularly higher solubility of EuF_3, it is appreciable leached already from the first portions of the solution. Theoretically, i.e., in the case of ideal mixing and achievement of equilibrium, the reaction may be completed by action of 0.010 kg H_2O (~0.012 kg of solution). However, the marked dissolution of initial CaF_2 must begin only after addition of a few kilograms of H_2O (solution). Finally, a notable dissolution of the quantitatively modest residue of REE-constituent of the charge requires hundreds of kilograms of solution.

This concluding statement is apparently the most important and principal result of our study. Taking into consideration facts mentioned above, our results clearly demonstrate a possible physicochemical mechanism of selective leaching (in comparison with other REEs) of anomalously soluble Eu components (EuF_3 in our case). At the same time, precisely such mineral products of intense leaching of Eu, which probably appear in the course of transition of the system from the rock- to fluid-dominant regime, may reveal minimums on the chondrite-normalized REE patterns. In this case, one can expect that the excess Eu should be recorded in positive anomalies both in the REE-bearing solutions and in late mineral generations forming at the subsequent stages of geochemical processes.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 04-05-64370.

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