

Kolonin G.R., Shironosova G.P. Thermodynamic modeling of possible reasons of REE fractionation with participation of high temperature fluids of complicated composition.

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The data base of the stability constants of the complex forms of REE in the solutions of complicated composition at temperatures up to 500°C and pressures of up to 2 kbar [1] has been adapted on the basis of the parameters of HKF equation for simple and complex REE ions [2,3]. An extended thermodynamic modeling of possible behavior of REE elements during the evolution of the parameters of complex fluoride-chloride-carbonate fluids, saturated with REE-containing fluorite, has been conducted on the basis of this data base [4], using the software package "Hch" [5]. The peculiarities of complexing of trivalent and bivalent Eu, including the influence of acidity-alkalinity on the ratio of total concentrations of Eu(III) and Eu(II), have been also discussed [6].

Specifically, it has been shown that during the evolution of fluid compositions typical of rare-metal fluorite-containing deposits of hydrothermal genesis [7], two REE groups, which differ in the specificity of the complex forms predominant in the fluid, can be recognized. In regard to the LREE (La, Ce, Nd and Pr), the LnF^{++} and LnF_2^+ (for reduced temperatures) fluoride complexes would be expected to dominate, if positively charged or neutral hydroxocomplexes are insignificant. As for MREE (Sm, Eu, Tb) and HREE (Ho, Yb and Lu), the anion or neutral hydroxocomplexes with the subordinate concentrations of LnF^{++} and LnF_2^+ fluoride complexes are bound to dominate.

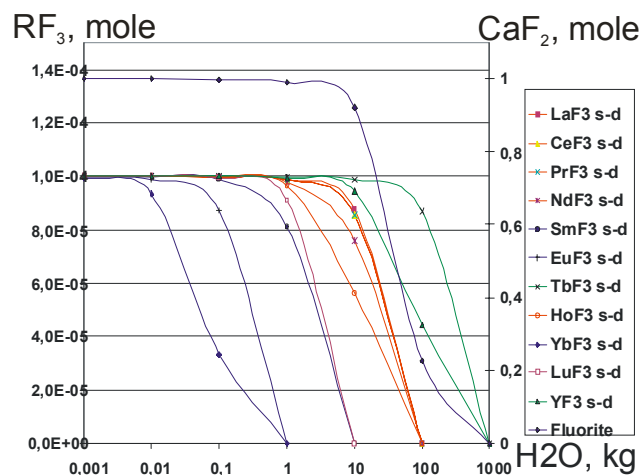


Fig. 1. The change of mole quantities in the fluoride solid phase of 1 g-mole $\text{CaF}_2 + n \cdot 10^{-4}$ g-mole RF_3 ($n=11$) composition in relation to the quantity of the reacted model solution of 4,0m NaCl + 1,5m H_2CO_3 + 0,001m HCl composition at 500°C and 2000 bar

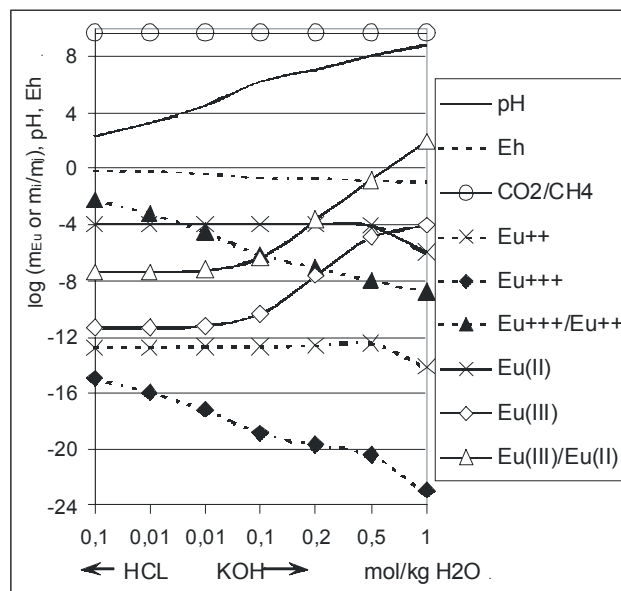


Fig. 2. The influence of acidity-alkalinity of a fluid on relationships between both concentrations of Eu^{2+} , Eu^{3+} and total concentrations of Eu(II), Eu(III) at $T=350^\circ\text{C}$, $P=1000$ bar and 1,0m NaCl, 0,1m HF, 0,5m H_2CO_3 .

Reasoning from the degree of solubility of 11 REE + Y model fluorides tested in the presence of fluorite, which provides high (about 10^{-2} m) total $\text{HF}^0 + \text{F}^-$ contents, the following three groups of REE are distinguished: 1) moderately soluble ($10^{-5} - 10^{-6}$ m) La, Nd, Pr, Ho and Lu; 2) highly soluble (more than 10^{-4} m) Sm, Eu and Yb; 3) the most low soluble (about 10^{-7} m) Tb and Y. Fig.1 demonstrates the expected differences in the solubility of fluorides, obtained on the basis of thermodynamic calculations. It shows an order of possible leaching or precipitation of REE together with fluorite in relation to the value of the fluid/solid phase. These results support the known evaluations of possible REE fractionation during the action of fluid on the minerals and rocks only in the case, when this ratio is higher than $10^{-2} - 10^{-3}$ [8].

The abnormal possibility of participation of a reduced Eu^{2+} forms in the processes of fractionation of the whole REE group is thought to be a reason, which causes Eu maxima and minima in the spectra of REE distribution in various minerals and rocks. The influence of temperature and pH solution as well as the presence of various complex-forming ligands (with sulfate sulfur as an example) on the conditions, which give rise to bivalent Eu has been thermodynamically analyzed in [9, 10]. Finally, [8] generally proves that the role of the complex formation of all REE and Eu, in particular, in the processes of their fractionation at the interactions of water/rock type needs to be studied.

Fig. 2 presents the influence of pH of the high temperature fluid under the effect of hematite-magnetite buffer both on $\text{Eu}^{3+}/\text{Eu}^{2+}$, $\text{Eu(III)}/\text{Eu(II)}$ and on more general red/ox characteristics: Eh and CO_2/CH_4 ratio. According to the commonly accepted expectations, practically complete reduction of aquaion of trivalent Eu to the bivalent one (see two low dashed lines), occurs at the elevated temperatures even in the presence of hematite. In this case their ratio decreases by more than 6 orders of magnitude as pH increases (according to the third dashed line, lower than 10^{-8}). Based on the complex formation three solid lines of total Eu(III) and Eu(II) concentrations

and their ratios really reflect the situation. These three lines begin to rise quickly at $\text{pH} > 6$, reaching positive values in the alkaline conditions. This fact can be explained by higher stability of Eu(III) hydroxocomplexes as compared to Eu(II) chlorocomplexes, which are dominant in the acid conditions.

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