PECULIARITIES OF REE PARTITIONING BETWEEN FLUORITE AND ORE FORMING FLUID

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Key words: fluorite, high temperature fluid, REE, abnormal Eu solubility, symmetry of Eu extremes, REE partitioning coefficients

Fluorite as a widespread mineral is used last decades for the revealing of both the chemical peculiarities and properties of ore forming fluids and REE fractionation in the processes of post magmatic ore formation. In particular, papers [1-3] are devoted to the peculiarities of REE pattern of fluorite in phenacite-bertrandite type of Be-deposits. A number of articles discuss the *factual* data on REE partitioning in the fluorite of rare metal deposits in respect to the possible physicochemical versions of its crystallization during ore forming processes [4, 5].

Our report is aimed to discuss the essence of REE-fluorite crystallization from hydrothermal chloride-fluoride solutions and to correlate the REE model pattern in fluorite with that in the residual fluid. The special attention has been given to Eu behavior. The method of thermodynamic modeling of REE behavior in the ore forming fluids of complicated composition over a wide range of T-P-X parameters has been described by the authors elsewhere [6, 7]. First of all it is based on HCh software package [8], the well known thermodynamic data base "SUPCRT98" and additional information presented by Kolonin et al. [9]. A model of ideal solid solution (REE)F₃ – CaF₂ obtained by application of the mentioned program package is radically new to be used for the description of REE-containing fluorite in terms of thermodynamics.

The chemical composition of the initial modal fluid was given by the conventional T - P - X path justified in [10] for the post magmatic rare metal deposits. Appropriate alumosilicate buffers were put into the system to check pH and concentrations of Ca and other petrogenic components (K, Na, Si, Al etc.) [7]. The essence of the numerical experiments was that first the composition of high temperature complicated fluid in equilibrium with the inputted buffer mineral association at 500°C and 2000 bar has been calculated (see Fig. 1 and its caption). Thereafter probable amounts of stable minerals, which can be precipitated from the fluid during its stepwise (in 100°C intervals) cooling from 500 to 100°C



Fig.1. The amount of solid phases precipitated from the cooling fluid (its initial composition is $1 \text{kg H}_2\text{O} + 0.05 \text{m}$ HF + 1.0m KCl + 0.5m NaOH) which has been reacted with the following mixture of solid phases at 500°C (mole per 1 kg H₂O): 3 Q(quartz) + 0.25 Ab + 0.25Mcl + 0.5 An + 0.1 phenacite + 0.001 each of five (REE)₂O₃.

followed by corresponding stepwise pressure decrease have been calculated. As an example of one such numerical experiment Fig. 1 shows the relationships of the amounts of basic solid phases precipitated from the alkaline-chloride solution including REE-containing fluorite (R-flu).

Fig. 2 demonstrates the most important results related to changes of Ca and REE concentration as a response of chemically closed system to the decrease of its P and T parameters. That is relationship between contents of REEfluoride components, which can be present in fluorite at tested temperatures and lanthanide concentrations in the solutions equilibrated with this fluorite. The eye primarily catches the fact that REE partitioning in fluorite is similar to that in the natural minerals and rocks. This kind of picture is sometimes called "bird wings". It is mainly related to the fact that Eu totally passes into the solution from the solid phase providing for the formation of deep and increasing minimum progressing with temperature. The concentration maximum in the solution corresponds to

this minimum. The other REE do not show any mirror asymmetry because of little difference between their concentrations in the solid phase and the solution (i.e. the coefficients of their partitioning are close to 1).

Based on the obtained data it is felt that widely known abnormal Eu behavior in geochemical processes is rather formally related to its dependence on red-ox conditions in the ore forming system. Its essentially higher solubility even in trivalent complex forms as compared to the similar forms of other lanthanides is of the utmost significance from our standpoint. This fact has been shown earlier by the example of fluorides in [6, 11] and is discussed more closely in the new paper [12].

Accumulated experience on thermodynamic analysis of multi-component REE-containing systems in the space of 5-6 independent variables makes it possible to pose and solve to a first approximation the problem of systematic calculation of coefficients of REE partitioning between solid phase (REEfluorite) and chlorite-fluoride fluid, which evolves along the given T-P-X path from the initial point with high P-T parameters to the final values of pressure and temperature.



Fig.2. Relationship of REE fluorides in fluorite at different temperatures calculated in the framework of the model of ideal solid solution (at the top) and Ca + REE-constituent of the solutions in equilibrium with it (at the bottom).

Financial support by RFBR, grant № 04-05-64370

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Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(24) 2006 ISSN 1819 – 6586 Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2006 URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/hydroterm-7e.pdf

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