THERMODYNAMIC MODELING OF PHYSICAL-CHEMICAL BEHAVIOR OF REE IN HYDROTHERMAL FLUORIDE-PHOSPHATE SYSTEMS

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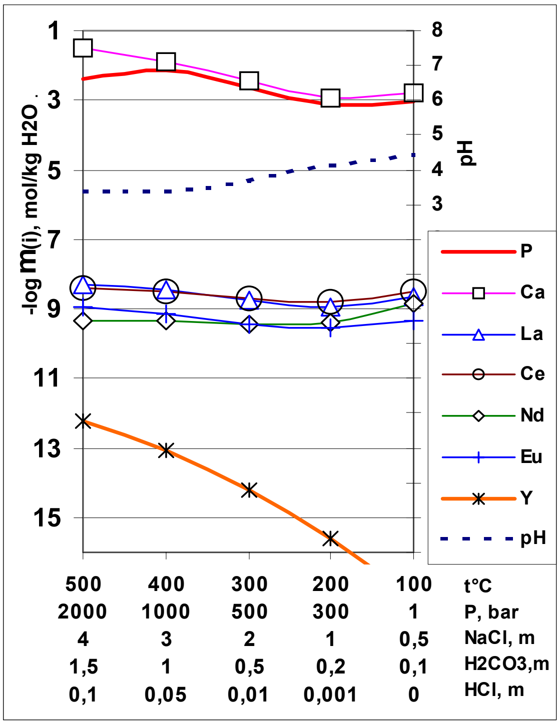
Introduction

Rare earth fluorides and phosphates represent an important part of the minerals of the deposits of the REE hydrothermal genesis [1] and they are better characterized by thermodynamic constants. The thermodynamic modeling of the formation conditions of the REE fluorite during geochemical evolution of hydrothermal fluid of complicated composition [2-5] demonstrated a possibility to reveal both the main reasons of lanthanides precipitation and their fractionation that is related to a specific nature of complex formation of different REE. The present report offers the first results of evaluation of the influence of temperature, acidity-alkalinity and fluoride concentration in the model fluid on the conditions when an earlier phosphate REE mineralization gives way to more late fluoride mineralization. The calculations have been carried out with the aid of the HCh [6] program-code using both the thermodynamic constants of OH- and F-apatites and the REE phosphates from [7].

Results

Fig.1 represents lines of suggested concentrations of phosphorus, Ca, four main light REE and Y, which appear at the interaction with mineral association hydroxyl-apatite + ”model monazite” (quantitatively equivalent mixture of $CePO_4$, $LaPO_4$, $NdPO_4$, $EuPO_4$) and YPO_4 (xenotime) of the model evolving fluid. Its composition and properties are chosen from the Table 1 from [8] and other literature data. As the temperature decreases, pH of this fluid continuously increases within the interval of 3,4 – 4,4 through the additional HCl concentrations, which are shown in the lower line at the five-parametric x-coordinate. The main peculiarity of the discussed system is very low solubility of all “monazite” components not only relative to apatite but also as compared to fluorides of the same



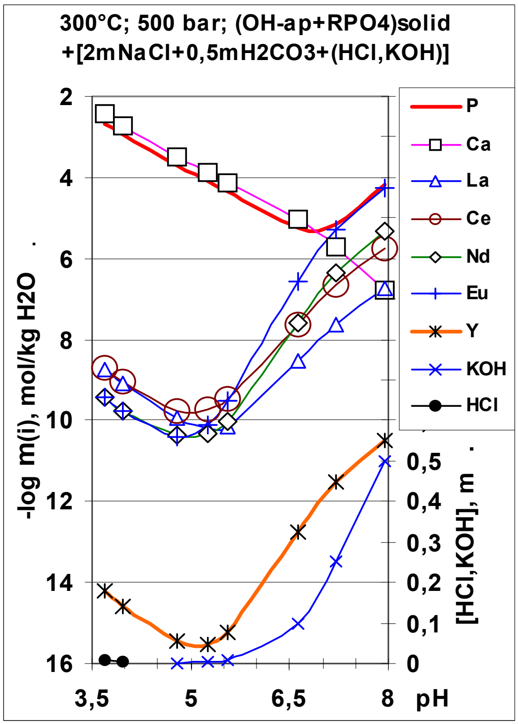


Fig. 1 (left). The curves of conjugated solubility of quantitatively prevailing OH-apatite (0,1 g-mol) and La, Ce, Nd Eu and Y phosphates (0,01 g-mol of each) in the evolving fluid of the given composition.

Fig. 2 (right). The V-shaped curves of dependence of solubility of phosphates of light REE and Y on pH (the development along pH axis of the section of Fig. 2 for T=300°C and P=500bar).

REE [3]. The solubility of YPO_4 turns to be minor from the point of view of geochemistry (lower than 10^{-12} mol/kg H_2O).

Fig. 2 graphically demonstrates a great dependence of the solubility of phosphates of light REE on pH fluid especially under alkaline conditions, when at pH=8 they reach the solubility of OH-apatite and even exceed it. Let us pay attention to the fact that La and Ce phosphates are most soluble at the acid branch of V-shaped curves where REE chloride complexes prevail according to the calculations. These two phosphates are the least soluble at the alkaline branch caused by hydroxocomplex formation. It should be noted that the alkaline branch of the given diagram related to 300°C and 500 bar can be considered as a peculiar development (involute) of the corresponding section (Fig. 1). The development seems to be perpendicular to its plane because the concentration of KOH as an additional variable occurs. Rather detail modeling of the temperature influence on the starting HF concentrations in the considered model fluid has been carried out. These concentrations are necessary to substitute the earlier apatite - REE-phosphate mineralization for fluorite-fluoride mineralization. This modeling has demonstrated the following results:

1) Fluorine appearance in the system leads to the processes of substitution of OH-apatite for F-apatite which increase in the direction from 400 to 200°C;
2) CaF_2 is formed instead of F-apatite, accompanied by lowering of Ca-concentration in the fluid as compared to phosphorus concentration;
3) Substitution of phosphates for REE fluorides is noted with cooling of evolving ore forming fluid beginning from 400°C, especially at a drop of up to 300-200°C;
4) Starting fluorine concentration, which is necessary for generation of model “monazite”, reduces from 0,25 (at 400°C) to 0,1 mol/kg H_2O (at 200°C);
5) Ce, La and Nd concentrations in solution sharply increase (2-3 orders of magnitude) when passing from phosphate to fluoride associations, they slightly vary with temperature and remain within the interval of $10^{-7} – 10^{-6}$ mol/kg H_2O.

Conclusion

The thermodynamic modeling gives a chance to reveal possible physical-chemical conditions of a change of early high-temperature apatite-monazite REE mineralization to fluorite-fluoride mineralization. It is shown that both the presence of moderate HF concentrations (about – 0,1 mol/kg H_2O) in the model fluid and its cooling to 400°C and lower is needed and sufficient for replacement of REE phosphates by fluorides in non-carbonate weakly acid environments (pH=4).

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