THERMODYNAMIC EVALUATION OF POSSIBLE REE CONCENTRATIONS IN THE FLUORIDE SOLUTION OF COMPLEX COMPOSITION DURING ITS GEOCHEMICAL EVOLUTION

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The given report is the first attempt of revealing the possible REE and Y concentrations in the model chloride-carbonate- fluoride fluid after its interaction with the mixture of quantitatively prevailing fluorite with REE and Y solid fluorides. The thermodynamic description of hydrothermal reactions with REE participation theoretically proves the possibility of their use as markers of both geochemical and technological processes. The stability constants of the main types of REE inorganic complexes in the wide range of temperatures and pressures have been recently calculated [1] using HKF equation [2]. At the same time Y, closely related to lanthanoides, remained outside systematic study. We have made this work using the same equation. The initial values of the constants for YF+2, YF2+, YF30 and YCl+2 at 25°C are taken from [3, 4] and for YCO3+ and YHCO3+2 from [5]. Subsequent to the last-named and other authors, it is expected that Y constants bear close similarity to the middle (mean-numbered) REE due to their greatest similarity to the ion radii and other Y properties. At the same time the change of stability constants of halogenide and carbonate Y complexes is acceptable at 25-500°C within the range of variations of the constants for the whole group of REE. This is related to the fact that on the one hand Y is an electronic analogy of La, but on the other one it is close to Lu, the finite member of REE row, which has a complete electronic f-subshell. Besides, the similar change of Y position in the lanthanoide series, depending on the temperature, is revealed for its hydroxide complexes in accordance with their HKF parameters given in [6].

The thermodynamic modeling of the scales and peculiarities of the solubility of REE and Y fluorides in the ore-forming fluid of the complex composition has been carried out with the help of the "HCh" software package [7]. At the first stage, the influence on the final results of deviations in the initial constants of the solid REE fluorides (presented both in [8] and [9]) has been evaluated. It is found out, that the total REE concentrations for Nd and Eu differ no more than by 0.1-0.2 log. units, and for La and Y they are about 0.3-0.4 log. units. Because the deviation reaches 1.5 order of magnitude for Ce, this requires additional thermodynamic analysis of the possible reasons and the choice of the most justified values of the initial constants.

The second stage of modeling reveals the influence of the change of natural fluid on solubility of the mixture of fluorite and eleven selected fluorides of REE and Y, including those which are usually analytically determined in geochemical objects, using the method of neutron activation [10]. In this case the initial constants for solid phases are taken from [8], where the complete set of needed information for all REE-Y fluorides is presented. The composition and P-T parameters of the evolving model fluid are selected on the basis of the generalized results of the study of gas-fluid inclusions in vein quartz of different stages of formation of Iultin, Khingan (Far East, Russia), Akchatau (Kazakhstan) and other REE deposits [11]. These data are presented as mutually coordinated five-scale abscissa in fig. 1.

The following main conclusions can be made basing on this Figure: 1) the closeness of total fluorine concentration, obtained as a result of dissolution of the model fluoride mixture (the upper curve), to both the results of investigations of fluid inclusions in quartz [11] and to the evaluations, presented in [12]; 2) the drawing together of CaF2 solubility with the solubility of REE-Y fluorides during temperature decrease and chemical evolution of ore-forming fluid; 3) the most high and close to CaF_2 level of solubility for fluorides of Eu, Yb, Sm, which can present in natural fluid in both three- and two-valence forms [13]; 4) the minimum solubility of Y and Tb fluorides, which is at 4-5 orders of magnitude lower than CaF_2 solubility; 5) the sparing and sufficiently close (within one order of magnitude) solubility of fluorides of the mixed REE group (light La, Pr and Nd, intermediate Ho, heavy Lu); 6) the conditional position of solubility curve for CeF3, related to mentioned above divergence of literature data about its thermodynamic constants. On the whole, the obtained results should be very useful for further development of physico-chemical principles of the use of REE-Y as the markers of their fractionation in the processes of hydrothermal formation.

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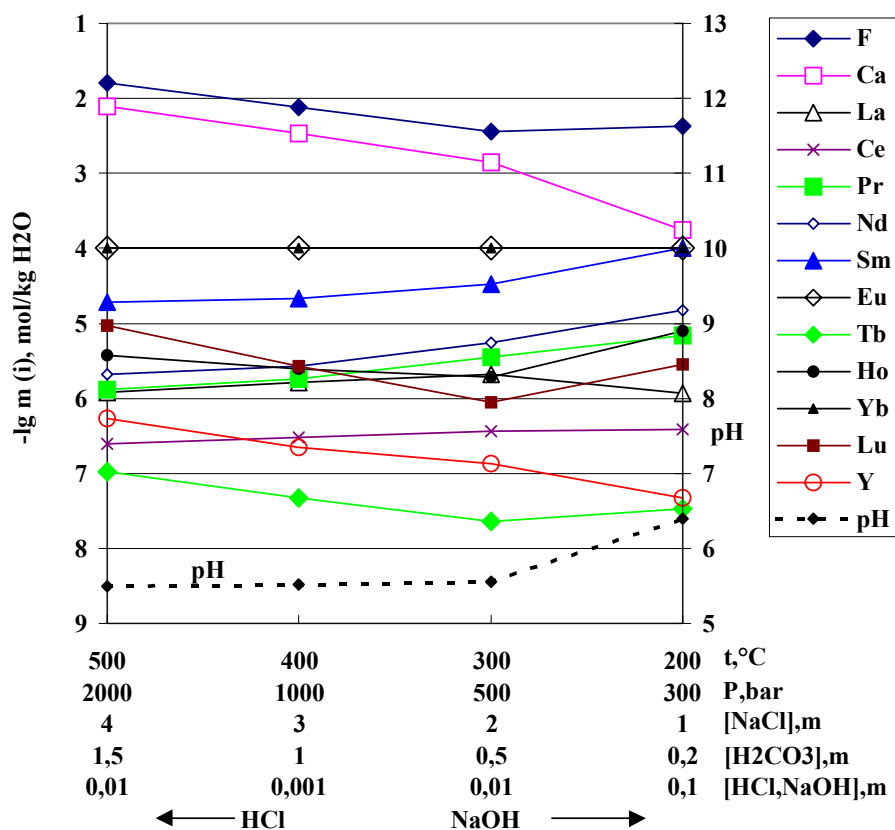13. Wood S.A. Chem. Geol. 1990, v.88, p.99-125.

Fig. 1. The dependency of solubility of Ca, Y and REE fluorides on the composition and P-T parameters of the developing fluid.