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Complex Formation of Trace Elements in Geochemical Systems: Stability Constants of Fluoro Complexes of the Lanthanides in a Fluorite Bearing Model System up to 200 °C and 1000 bar*

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The fractionation of chemically similar trace elements in minerals is used as an indicator of the geochemical conditions of the mineral formation. Ca minerals, e.g., fluorites, contain traces of the lanthanides, the proportions of which (normalized to that in meteorites such as chondrites), differ in almost the same manner; the light members of the series are more abundant than the heavy. The fractionation between Tb and La, however, is more distinct than that between Tb and Lu [1–10]. The extent of the fractionation is too high to be explained by kinetic effects (e.g., diffusion). Equilibria effects, such as complexation of the lanthanides in the mineral bearing solution as well as their distribution between this solution and the crystallizing mineral, are more likely to lead to the observed fractionation.

Consequently, an investigation programme has been initiated in our laboratory to study the complex formation and distribution equilibria of trace elements in geochemical systems under hydrothermal pressure and temperature conditions. The goal of this research is to reveal the mineral genesis; *i.e.*, to find out under which conditions of pressure p, temperature T and chemical composition X, it was formed. To approach this aim, the theoretical fractionation of the trace elements in the minerals considered has to be calculated as a function of their complex formation constants and their distribution coefficients, which must be determined at different p, T and X values of the mineral bearing system. Diagrams can then be constructed giving the theoretical fractionation as a function of p, T and X. A comparison of the analytically found fractionation with these diagrams yields the mineral formation conditions.

Within the scope of this programme, the complexation of the lanthanides with fluoride in a fluorite (CaF_2) bearing hydrothermal model system has been studied up to 200 °C and 1000 bar.

Experimental

The formation of the fluoro complexes of Ce, Nd, Tb, Er and Lu has been studied by the measurement of the fluoride activity by means of a fluoride ion sensitive electrode and an Ag/AgCl reference electrode. Both electrodes were constructed in a special way for operation under high pressure and high temperature conditions. The electrochemical cell used was as in Scheme 1. The salinity of the most hydrothermal solution bearing minerals is determined by NaCl in the concentration of about 1 M. The ionic strength was therefore held constant at 1 M using NaCl. The measurements were carried out at an initial pH of 3.4 to prevent precipitation of the lanthanides at high temperature due to hydrolysis. The pH has been followed up to 200 °C by measuring $[H^+]$ by means of a Pt/H_2 electrode in a high pressure–high temperature cell developed by Becker and Bilal [11]. The concentration of NaF was increased up to 1.75×10^{-4} M. Higher concentration led to precipitation of the lanthanides at high temperature. Figure 1 shows the change of $[H^+]$ of the sample with increasing temperature.

Results and Discussion

The average ligand number $\bar{n}$ of the fluoro complexes of the lanthanides was calculated according to:

$$\bar{n} = \frac{C_F - [F] - \delta_1[H][F] - \delta_2[H][F]^2}{C_{Ln}} \qquad (1)$$

where C_F = total fluoride concentration; $\delta_{1,2}$ = formation constant of HF, HF_2; C_{Ln} = total concentration of the lanthanide ion considered.

Reference electrode:			Sample:		Fluoride membrane electrode:		
Ag/AgCl	|	NaCl (1 M)	‖	NaCl (0.996 – x M) HCl (0.0004 M) NaF (x M)	|	NaCl (0.1 M) NaF (0.1 M)	| Ag/AgCl
			↑ diaphragm		LaF_3		

Scheme 1.

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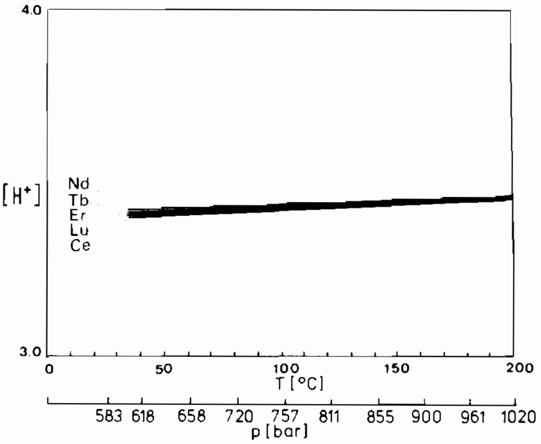

Fig. 1. pH dependence of T and p in the presence of lanthanides.

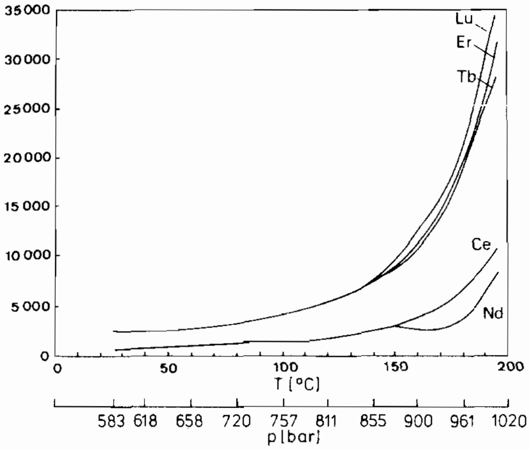

Fig. 2. Stability constants as a function of T and p.

δ_1 has been determined previously by Becker and Bilal [12] up to 250 °C and 1000 bar. No indication of the formation of HF_2 was found in their work, which was carried out under conditions similar to those of our study. Therefore $\delta_2[\mathrm{H}][\mathrm{F}]^2$ did not need to be considered in the calculation of n. The stability constants β_i were determined by means of a fit of the function (2) considering only the formation of fluoro complexes

$$\bar{n} = \sum_{i=1}^{i=N} i\beta_i[\mathrm{F}]^i \Big/ 1 + \sum_{i=1}^{i=N} \beta_i[\mathrm{F}]^i \qquad (2)$$

which is rearranged to:

$$\sum_{i=0}^{i=N} (\bar{n} - i)[\mathrm{F}]^i\beta_i = 0 \qquad (2a)$$

where N = maximum ligand number.

No reasonable values of β_2 were obtained from the fit, since relatively low concentrations of NaF were used. Figure 2 shows the stability constants of the monofluoro complexes of the five lanthanides in the range between 25 °C, 583 bar and 200 °C, 1020 bar. A drastic increase is observed with rising temperature. $(\beta_1)_{\mathrm{Tb}}$, for instance, increases from *ca.* 2000 M^{-1} to *ca.* 30000 M^{-1}.

β_1 changes in quite a different manner within the lanthanide series. It increases from Ce to Tb by a factor of *ca.* 5, while a very slight increase between Tb and Lu is observed. This tendency reflects roughly the fractionation of the lanthanides in hydrothermally formed fluorites. Assuming that only the 'free' uncomplexed lanthanide ions $[\mathrm{Ln}^{3+}]$ are involved in the distribution equilibrium between the crystallizing fluorite and the fluorite bearing solution, a higher complexation degree of Tb than that of La leads to a higher concentration of $[\mathrm{La}^{3+}]$ than that of $[\mathrm{Tb}^{3+}]$. Therefore, $[\mathrm{La}^{3+}]$ is preferably coprecipitated with the crystallizing fluorite.

However, a modification of the found complexation tendency of the lanthanides was found by the authors [13] at higher pH values, due to hydrolysis and the formation of fluorohydroxo mixed ligand complexes.

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