REE distribution coefficients in monazite–apatite–fluorite association depending on HF and *T–P–X* parameters of fluids (thermodynamic modeling)

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The dependence of the composition of equilibrium mineral association was shown in the range of 500-100°C. The Ln and Y distribution coefficients between the ideal solid solutions of REE-fluorapatite, REE-fluorite and monazite were received.

Key words: rare earth elements, monazite, apatite, fluorite, thermodynamic modeling, fractionation of lanthanides, fluid

Geochemical peculiarities of apatite and monazite composition are actively discussed in literature because they occur widely as accessory minerals. A close association of apatite and monazite is observed. In this case either monazite inclusions are observed in fluorapatite, or fluorapatite crowns sometimes with xenotime and allanite are the result of monazite substitution [*Harlov et al., 2002; Broska et al., 2005; Sindern et al., 2012; Gasser et al., 2012*]. The work [*Harlov et al., 2002*] clearly demonstrates how primarily REE enriched light apatite is converted into the REE depleted dark apatite with monazite inclusions under the action of metamorphosing solutions. The calculation of the ratio between Ce_2O_3 (wt.%) content in these monazite inclusions and Ce_2O_3 content in syngenetic dark apatite shows values of $(0.5–2.0) \cdot 10^3$. This work demonstrates the results of thermodynamic modeling of REE distribution between monazite fluorite and apatite in the temperature interval 500–100°C (the calculation conditions see in Table 1) with the help of HCh computer code [*Shvarov, 1999*]. The influence of the near neutral chloride–carbonate–fluoride solutions on monazite in the presence of calcite has been examined. The detailed description of physical-chemical model and the sources of the initial thermodynamic data are published in our previous paper [*Kolonin, Shironosova, 2011*].

Table 1. *P-T-X* conditions of thermodynamic calculations.

T°C	500	400	300	200	100
P, бар	2000	1000	500	250	125
[NaCl], m	4	3.5	3	2.5	2
[H_2CO_3], m	1.5	1.25	1	0.75	0.5
[HF], m	0.1–0.005	0.1–0.005	0.1–0.002	0.1–0.002	0.1–0.002
pH$_{equilibrium}$	5.9–6.3	5.6–6.0	5.5–5.7	5.8	6.5
pH$_{neutral}$	5.115	5.385	5.43	5.58	6.1

REE-containing minerals are treated in the calculations as ideal solid solutions: monazite ($LnPO_4$), REE-fluorite (CaF_2–(Ln, Y)F_3) and REE-fluorapatite ($Ca_5(PO_4)_3F$–(Ln, Y)$_3(PO_4)_3$), where Ln – La, Ce, Pr, Nd, Sm, Eu, Gd. It should be noted that this association has been obtained in a wide range of the initial HF concentration in the near neutral solutions at 500–300°C, and at 200°C only in the case of solution acidification. The interval of the initial HF concentration at which apatite is stable significantly narrows (0.06–0.002m) in the near neutral conditions at 200°C. Fig. 1 demonstrates as an example the diagrams of quantitative relationships of minerals in the equilibrium association at 500, 300 and 100°C. It is clearly seen that at 100°C the apatite stability field becomes narrower and xenotime (YPO4) appears instead of apatite.
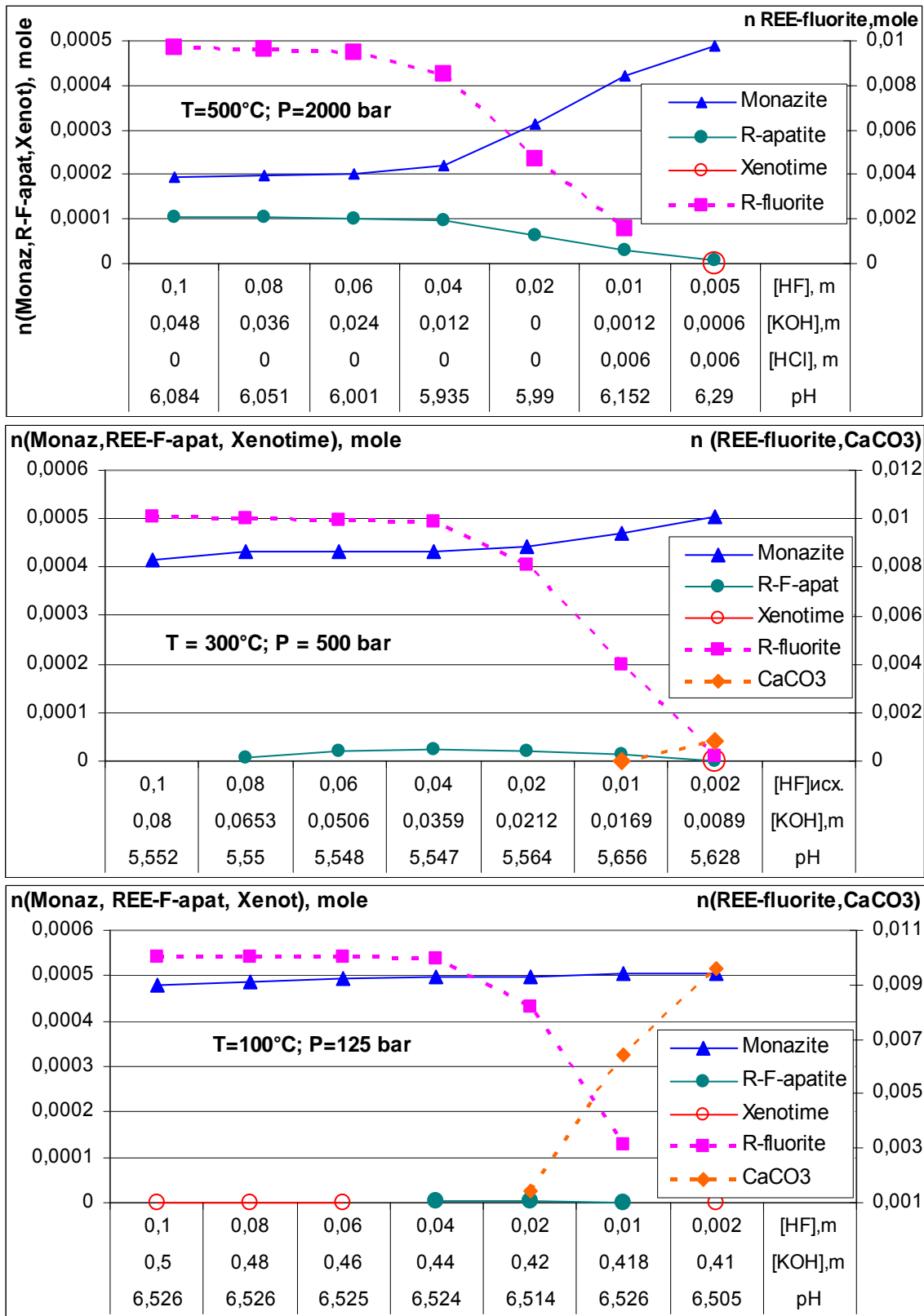
Fig. 1. The influence of the initial HF concentration on the phase composition in REE-fluorite–REE-fluorapatite–monazite equilibrium association during cooling of the system in the temperature interval 500–100°C
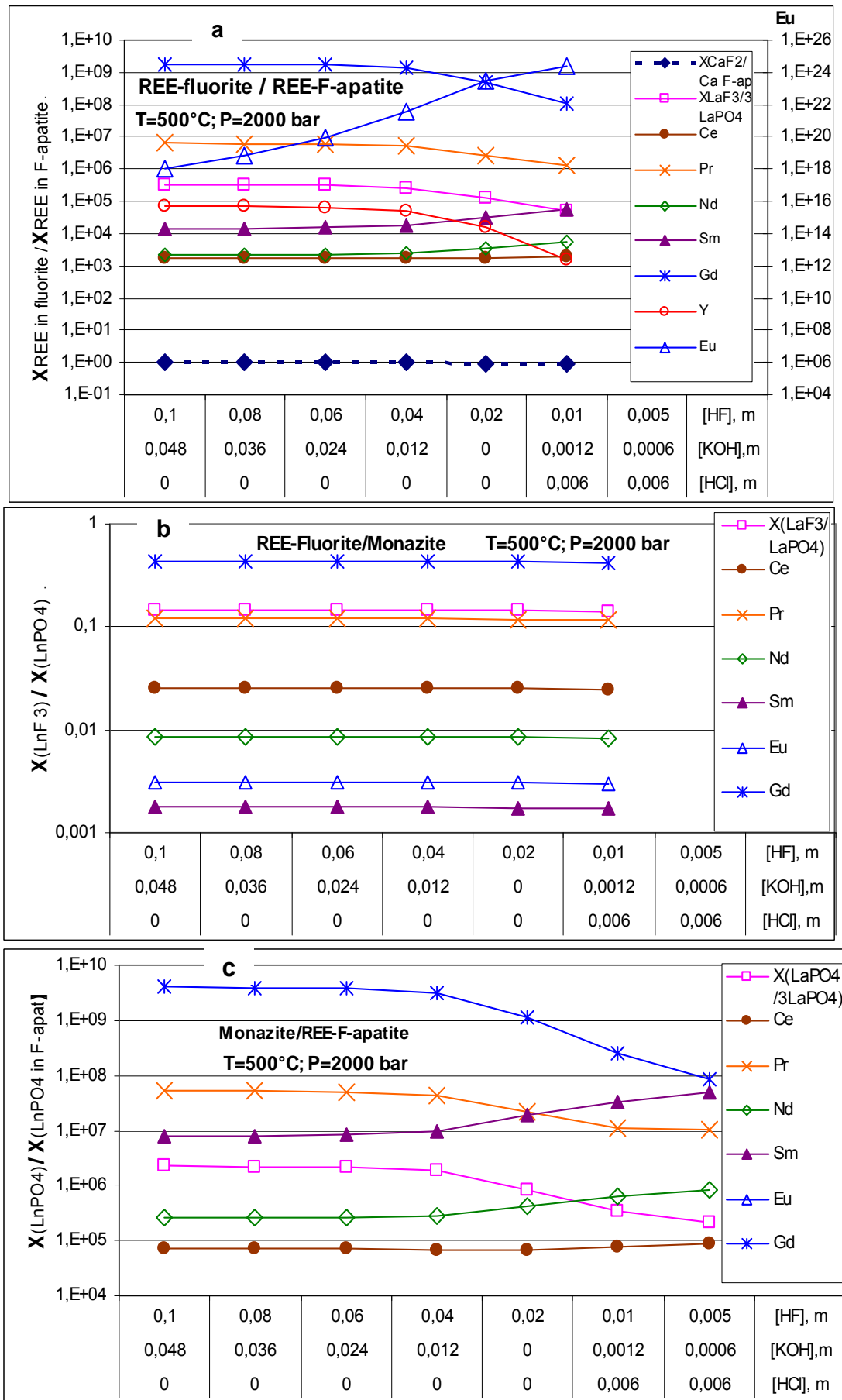
Fig. 2. The influence of the initial HF concentration on REE distribution coefficients in REE-fluorite–REE-fluorapatite–monazite equilibrium association at 500°C and 2000 bar; X – mole fraction of the corresponding component

When considering the REE distribution in the equilibrium association apatite-fluorite-monazite depending on HF at the constant temperature (diagrams only for 500°C are given as an example – Fig. 2) the stability of the coefficient of distribution between fluorite and apatite is observed only for Ce (diagram **a**). They are about 1800, 50 and 1 at 500, 400 and 300°C, correspondingly. The distribution coefficients of the rest REE under discussion appear to be stable only at high fluorine concentrations in the system (0.1–0.04m). Beginning from 0.04m HF they monotonously fall as it decreases and only for Nd, Sm (especially at 500°C) and Eu (in the whole temperature interval) the increase of the distribution coefficients in the fluorite/apatite pair is observed. It should be also noted that the dependence curves of distribution coefficients/HF concentration become much more flat as temperature decreases. In this case the distribution coefficients of all lanthanides have value greater than 1, i.e. they prefer to concentrate in fluorite but not in apatite. The distribution coefficients of yttrium are different. They significantly decrease as the initial HF concentration decreases as compared to La, Pr and Gd, but at 300°C become smaller that 1 in the whole interval of HF concentration, this means that yttrium prefers to concentrate in apatite.

The constancy of the distribution coefficients of all REE (from Ce to Gd) between fluorite and monazite within the whole range of HF concentrations is striking (Fig. 2, diagram b). Their values are similar both in the slightly alkaline and weakly acidic medium. The values of coefficients are lower than 1 in all conditions and the decreasing sequence is retained: Gd > La > Pr > Ce > Nd > Eu > Sm. A distinct temperature dependence of REE distribution coefficients between fluorite and monazite is traced (see Table 2.)

Table 2. The values of REE distribution coefficients in fluorite-monazite pair

T°C	La	Ce	Pr	Nd	Sm	Eu	Gd
500	0.15	0.025	0.12	0.008	0.002	0.003	0.43
400	0.06	0.008	0.05	0.002	$3 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	0.22
300	0.03	0.003	0.02	$5 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	0.12
200$_{acid}$	0.008	0.0004	0.005	$8 \cdot 10^{-5}$	$5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	0.06

REE distribution coefficients in monazite/apatite pair (Fig. 2, diagram c) are significantly higher than 1 and behave similar to the coefficients in fluorite-apatite pair, i.e. they are temperature dependent only at high HF concentrations. The curves of their HF dependencies in the areas of low HF concentrations also flatten as temperature decreases. In this case the distribution coefficients of Sm, Nd and Eu increase as HF concentrations decrease like in the fluorite/apatite pair but unlike La, Pr, and Gd. Ce distribution coefficient is nearly stable and temperature dependent only.
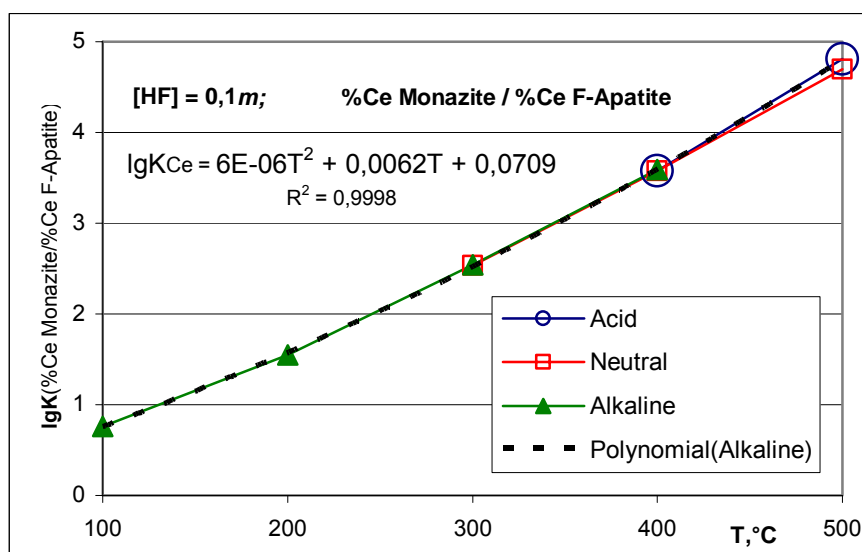

Fig. 3. Temperature dependence of weight Ce distribution coefficient between monazite and REE-fluorapatite for acid, near neutral and alkaline solutions

Fig. 3. demonstrates the temperature dependence of weight Ce distribution coefficient between monazite and REE-fluorapatite for three types of solutions: acid with pH 4.7, near neutral – 7.1 and alkaline – 8.2. The second-degree equation describes well the data for acid and alkaline solutions and slight deviation is observed only for near neutral solution at 500°C. Thus, cerium distribution between the minerals of apatite-fluorite-monazite equilibrium association can be an indicator temperature of its formation.

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