The dependence of monazite composition on HF concentration and T-P-X parameters of fluids (thermodynamic simulation)

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Thermodynamic modeling of the probable effect of fluoride on the lanthanide relationship in the REE component of the "conditional" monazite has been carried out by HCh computer code [*Shvarov*, 1999; *Shvarov, Bastrakov*, 1999]. The calculations were made at T-P-X parameters given in Table 1. Additional amounts of KOH and HCl were added to stabilize pH of the equilibrium solutions (see captions to x-axis). Modeling was the calculation of the equilibrium composition of solid phase associations and coexisting fluid, which formed since that solutions influenced on monazite in the presence of calcite. $5,07 \cdot 10^{-4}$ mole monazite with REE was introduced into the system in the ratio of (mole of the corresponding phosphates): La – $1,3 \cdot 10^{-4}$; Ce – $2,4 \cdot 10^{-4}$; Pr – $2,7 \cdot 10^{-5}$; Nd – $8,3 \cdot 10^{-5}$; Sm – $1,17 \cdot 10^{-5}$; Eu – $4,7 \cdot 10^{-7}$; Gd – $9 \cdot 10^{-6}$; Y – $9 \cdot 10^{-7}$ and 0,01 mole $CaCO_3$. Monazite association with REE-fluorite and REE-fluorapatite has been obtained in these near neutral slightly alkaline carbonate-chloride solutions.

Table 1. Fluid parameters, which acted upon the monazite*) and calcite mixture.

T°C	500	400	300	200
P, bar	2000	1000	500	250
[NaCl], *m*	4	3,5	3	2,5
[H$_2$CO$_3$], *m*	1,5	1,25	1	0,75
[HF]$_{starting}$, *m*	0,1 – 0,005	0,1 – 0,005	0,1 – 0,002	0,1 – 0,002
pH$_{in\ equilibrium}$	5,9 – 6,3	5,6 – 6,0	5,5 – 5,7	5,8
pH$_{neutrality}$	5,115	5,385	5,43	5,58

*) REE composition corresponds to the sample N 67199 from the Fersman Mineralogical Museum (Yakutia, Timptonsky region, Treugol'naya mountain, Mitinga site), it was determined by ICP-MS in the IGM SB RAS.

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. We are forced to choose this set of lanthanides because temperature dependence of heat capacity is known only for their phosphates. Thermodynamic characteristics of individual REE phosphates are taken from [*Popa, Konings*, 2006], for individual REE trifluorides – [*Greis, Haschke*, 1982] and for fluorite, OH- and F-apatite, calcite – [*Robie, Hemingway*, 1995]. Data on the stability of the first fluoro- and first and second lanthanide chlorocomplexes are taken from [*Migdisov et al.*, 2009] and for the rest lanthanide complexes – from [*Haas et al.*, 1995]. Thermodynamic data for ions and complex particles of fluid macro components are taken from SUPCRT database, version 98 [*Shock et al.*, 1997; *Sverjensky et al.*, 1997]. The composition of equilibrium monazite in relation to T-P-X parameters of the system is discussed below.

It is found that cerium phosphate prevails in the composition of equilibrium monazite in all conditions similar to the initial monazite, but its content is 2-3 times higher than the content of lanthanum and neodymium phosphates. The following regularity is observed in La and Nd ratio: at 500 and 400°C in the range of initial HF concentrations 0,1-0,02 m Nd > La, so monazite composition is unusual – cerium>neodymium>lanthanum, and the inversion in the monazite composition occurs as HF concentration decreases, it tends to be standard – cerium > lanthanum > neodymium. In this case

the highest neodymium content as compared to lanthanum is observed at 500°C, neodymium content is three times higher than the content of lanthanum in the range of initial HF concentrations 0,1 – 0,04 m (Fig. 1). Neodymium content is approximately twice as much as the content of lanthanum at 400°C in the same range of initial HF concentrations (Fig. 2).

At 300°C in the range of initial HF concentration 0,1-0,04 m the neodymium and lanthanum concentrations occur to be the same with negligible neodymium predominance if initial HF concentration is 0,1 m, at initial HF concentration of 0,02 m and lower lanthanum concentration in the monazite composition increases (Fig. 3).
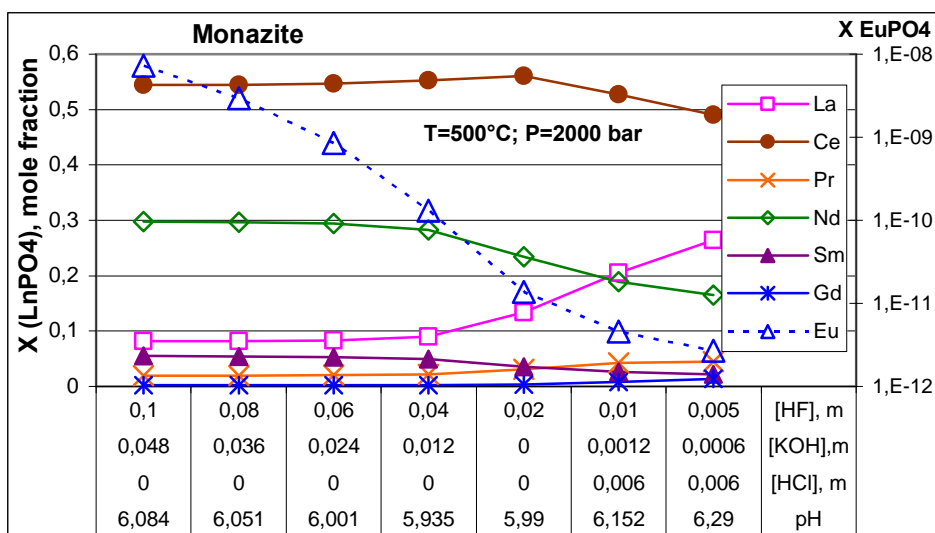

Fig. 1. Monazite composition (mole fraction – X of lanthanide phosphates) versus the initial HF concentration at 500°C, 2000 bar.
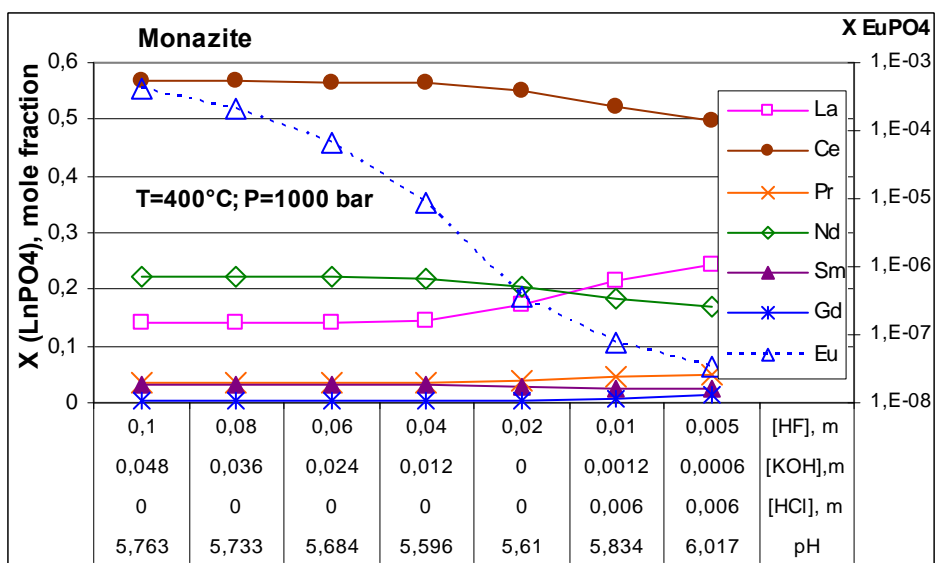

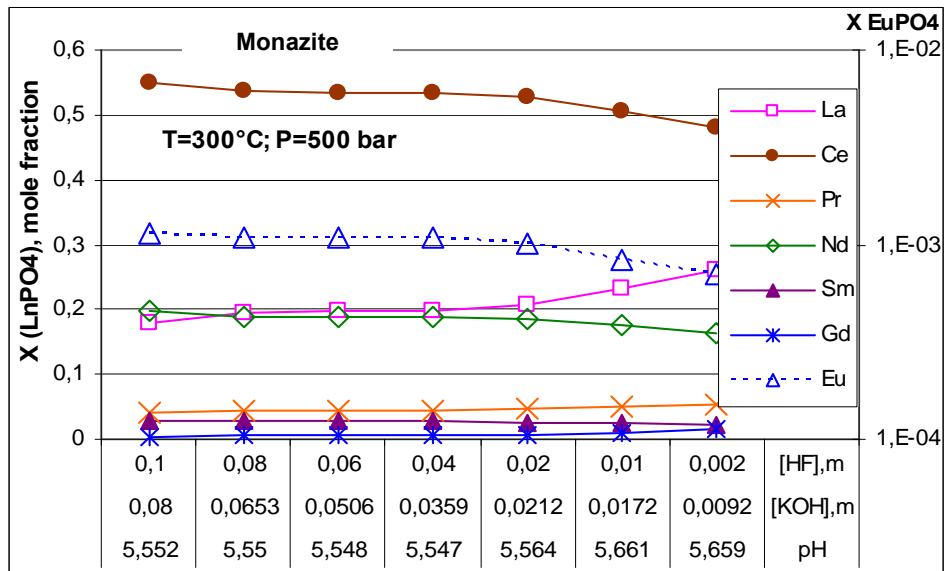**Fig. 2**. The same at 400°C, 1000 bar.
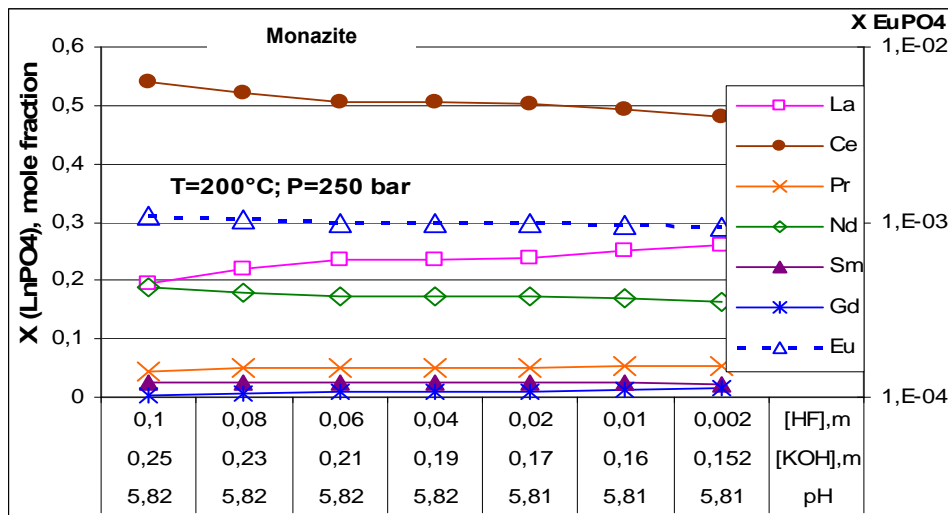
Fig. 3. The same at 300°C, 500 bar.

Fig. 4. Monazite composition (mole fraction - X of lanthanide phosphates) versus the initial HF concentration at 200°C, 250 bar.

At 200°C (Fig. 4) similar La and Nd content is observed only at high initial HF concentration of 0,1m and further La becomes dominant in monazite composition as initial HF concentrations decrease.

Lanthanum and samarium relationships are rather interesting. If samarium content approximates the content of lanthanum in the range of starting HF concentrations of 0,1-0,04m at 500°C ($SmPO_4$ mole fraction is about 0,06 and $LaPO_4$ – ~0,08), so at 400°C the difference between their contents drastically increases ($SmPO_4$ – 0,033 and $LaPO_4$ – ~0,14). This difference tends to widen ($SmPO_4$ mole fraction – 0,028 and $LaPO_4$ – ~0,2) at 300°C. Ratio between Sm and Pr is the most interesting at 500°C (Fig.1) as in the range of elevated HF concentrations Sm > Pr and then they change places. Pr > Sm at all other temperatures.

The unusual relationships of the main lanthanides in the monazite composition have been obtained in our studies of dark monazites – kularites [10]. Broken lanthanide ratio is observed in the central parts of kularite grains: Ce > Nd > La > Sm > Pr, whereas monazite composition becomes ordinary in the rims: Ce > La > Nd > Pr > Sm. It is believed that kularite core have nucleated and formed in combination of elevated fluorine content with sufficiently high temperatures. Probably the main factor, which produces the lanthanide fractionation, is ratio of their complexes stability in the equilibrium fluids.

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