

Experimental study of joint solubility of pyrochlore and uraninite in fluoride solutions at 800°C, 2300 bars, and Co–CoO buffer

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The solubility of a synthetic U-Pyrochlore (approximate composition $(\text{Na}_{1.0}\text{Ca}_{0.7}\text{U}_{0.3})(\text{Nb}_{1.0}\text{Ta}_{1.0})\text{O}_6\text{F}_{0.7}$) and uraninite ($\text{UO}_{2.03}$) has been studied in the solutions of P-Q type containing from 5 to 35 wt. % of fluorides and up to 2 mol/kg H_2O of silica at $T=800^\circ\text{C}$ and $P=2300$ bars. The composition of the fluids were taken from experimental data analyses in the system Li-F-granite – fluoride-chloride fluid at specified T – P conditions. The compositions correspond to 3 phase fluid systems ($L_1+L_2+\text{Si-solution-melt}$). The init solutions also contained 0.667 mol/kg H_2O of chlorides (Na, K, Li) and 0.01M HCl. The acidity of the solutions in equilibrium with Li-F-granite melt was in range of 0.01–0.1M HCl. The data obtained indicate that total U and Nb solubility in the fluids was substantial (from 0.001 to 0.01 mol/kg H_2O) and it has a positive trend from total fluoride concentration in the solutions.

Key words: experiment, pyrochlore, uraninite, solubility, fluoride solutions, fluid immiscibility

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The oxide compositions of niobium (V), uranium (IV), and tantalum (V) have low solubility in diluted solutions of electrolytes. The most stable complexes of the concerned elements in aqueous solutions are fluorides. Essential values (>0.001 mol/kg H_2O) of these complexes may appeared only in high-salt solutions. At the same time, the compositions and properties of solutions depend from magma (fulfils a role of basic-acid buffer) composition, ore compounds content in it, temperature, pressure, red ox potential in the system melt – solution – volatile, and total salts concentrations in the solution. As a possible magmatic source of the ores can performed a water-saturated granitic magma situated in region (T – P -salt concentration) of fluid immiscibility, i.e. at T – P parameters higher than point Q and the salts concentration lies between L_1 and L_2 fluid phases. The solutions of P-Q type in T – P region of immiscibility are of interest as ore compounds solvent because they give rise to pair of fluid phases L_1 and L_2 of different salts content and the solubility of ores in them. The total salts concentration of P-Q type effects on the ratio L_1 and L_2 phases but do not affect on accumulation of anion compound in co-existent Al-Si-melt. The main compound of solution equilibrated with model Li-F-granite melts is NaF [Redkin *et al.*, 2011]. The system NaF– H_2O is the system of second P-Q type with the critical point Q lies at about $T=760^\circ\text{C}$ and $P=2000$ bars [Kotel'nikova, Kotelnikov, 2010]. Thus, the conditions of the experiments $T=800^\circ\text{C}$, $P=2300$ bars were chosen wittingly from the region of immiscibility of the system NaF– H_2O . Red ox conditions set up with Co–CoO buffer to stabilize uraninite $\text{UO}_{2.0}$ as a stable uranium-oxide phase.

The aim of the studies are to find the conditions for mobilize uranium by magmatic origin hydrothermal solutions in concentrations sufficient to form gigantic hydrothermal ore deposits. This work demonstrate influence of total fluorides concentration on uraninite and pyrochlore solubility in the solutions of P-Q type which have the compositions close to the solutions in equilibrium with Li-F-granite melts at T – P parameters higher than point Q.

Experiments performed in the system granite melt – F-Cl-solution – ores (columbite and uraninite) at 800–950°C, 2300 bars indicated that the composition of granite glass changes during interaction with solution. Smallest changes were determined in the solutions where fluorides compounds ratio was as 0.705Na₃AlF₆/0.211K₂SiF₆/0.07LiF/0.013CaF₂. As a solvent, we used a next chloride solution (Cl-1):

0.373mNaCl+0.107mKCl+0.117mLiCl+0.0187mAlCl₃+0.0067mCaCl₂+0.01mHCl.

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The results of microprobe analyses of granite glasses after runs (75U-78U) and the compositions of the solutions in equilibrium with them at the condition of the runs are presented on the triangle diagrams in Figs. 1-a, 1-b. The solution compositions in the run were calculated by mass balance method based on the average composition of the glasses, the total system taking in account that the melts (glasses) capture 8 wt. % of H₂O. In Fig. 2, the dependences of main rock-bearing compounds in the solutions in equilibrium with granite melts are plotted against the total F⁻ in solutions. In spite of presence of high Si (as K₂SiF₆) in initial solution, a removal of silica from granite melt occurs (Fig. 1-a). The quartz solubility in water at 800°C, 2300 bars according different sources consists from 0.27 [Shibue, 1996] to 0.32 [Manning, 1994]. The total Si (mainly as silica) in heterogeneous solution is about 2 mol/kg H₂O (Fig. 2) and it does not depend from the total fluorides concentration. It is obvious that fluid system is presented at least by three phases: L₁, L₂, and Si-solution-melt. The L₁ and L₂ phases is found in granite melt in view of ball inclusions of different density. Silicate fluid-melt phase is not observed in electron microscope visual inspection, but it can participate as a surface-active substance between granite melt, L₁ and L₂ fluoride fluid phases. In spite of high fluoride contents in the fluid-magmatic system, the granite-melt phase did not accumulate fluorine. To the contrary, according electron microprobe analyses it has been found fluorine withdraw from the model granite melt (Fig. 1-b). The solutions compositions after runs including ore elements (Fig. 3) had substantial difference from the total init compositions owing to capture of major part of L₁, L₂, and Si-phases as fluid inclusions in the granite melts. Thus, the granite melt was removed in these experiments and as the models (initial) were used the solutions shown in Fig. 2. As in most early carried out experiments, the solution of 0.667 *m* of chloride, Cl-1 was used as the solvent and fluorides were added in the form of powder (milled fluoride glass F5) in amount from 5 to 35 wt. %, plus calculated amount of amorphous SiO₂, so that the total SiO₂ contents in the solutions were 2 mol/kg H₂O. The powder F5 was composed from

0.374 NaF, 0.13 AlF₃, 0.019 K₂SiF₆, and 0.121 LiF.

The synthetic uraninite (UO_{2.03}) and maximum saturated pyrochlore of pyrochlore-microlyte series (of composition (Na_{1.0}Ca_{0.7}U_{0.3})(Nb_{1.0}Ta_{1.0})O₆F_{0.7})) were used as the ore minerals. The experiments were carried out in Pt capsules on hydrothermal equipment at 800°C, 2300 bars, Co-CoO buffer. Runs lasted 8 days. The run products were washed out from the capsules by 50-fold volume of 0.01 *M* HCl and then were analyzed by ICP methods. The filled symbols and their linear approximation (solid lines) in Fig. 3 represent the results of the analyses. For comparison, the results ICP analyses of the experiments carried out in similar solutions but in the presence of model Li-F-granite melt (hollow symbols and dotted lines) are shown in the Fig. 3. As might be expected, the concentrations uranium, niobium, and tantalum in the system ore minerals – solution were 1-2 order greater than in the system ore minerals – granite melt – solution. Data obtained indicate that 90-99 % U, Nb and Ta remain in fluid inclusions in granite glass after quenching. The saturated concentrations of Nb and U in high-concentrated fluoride solutions interacting only uraninite and U-pyrochlore are substantial (>0.001 mol/kg H₂O) and these solutions may be as a media to produce large uranium ore deposits. As the predominant species of uranium at that conditions could be sodium-fluoride or fluoride uranium complexes which were mainly in L₂ and silica fluid-melted phase and precipitated from them during quenching in form of low-soluble fluorides of sodium and uranium, Na_{1+x}UF_{6±y} of pale blue colour. The average composition of sodium-uranium fluoride phase was NaUF₆, what remain on presence of oxidized forms of uranium (mainly U(V)) in the system despite the reduction conditions (Co-CoO buffer) of the runs.

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References

- Redkin, A. F. et al. (2011). The features of interaction of high concentrated fluoride solutions with granite melts at *T* 800–950 °C and *P* 2300 bars. *The proceeding of a Conference «Granites and Ore forming processes»*. IGOD, pp. 105-106.
- Kotel'nikova, Z. A., A. R. Kotel'nikov (2010). Experimental study of heterogeneous fluid equilibria in silicate–salt–water systems. *Geology of Ore Deposits*, v. 52 (2), pp. 154–166.
- Shibue, Y. (1996). Empirical expressions of quartz solubility in H₂O, H₂O+ CO₂, and H₂O+NaCl fluids. *Geochemical Journal*, v. 30, pp. 339–354.
- Manning, C. E. (1994). The solubility of quartz in H₂O in the lower crust and upper mantle. *Geochim. Cosmochim. Acta*, v. 58, pp. 4831-4839.

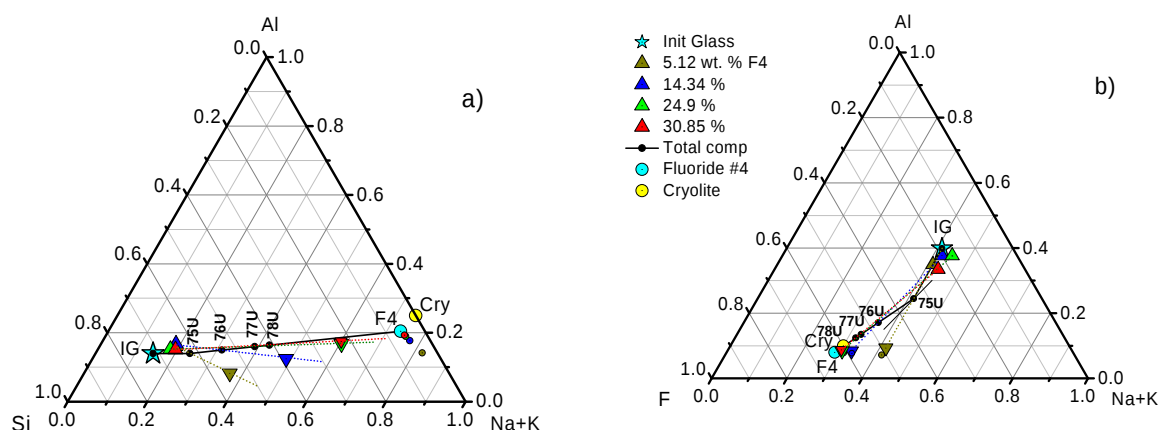


Fig. 1-a, -b. System model granite melt (Δ) – fluoride fluid (▽) at 800°C, 2300 bars, Co-CoO buffer. Symbols: star (IG) – init composition of granite melt, triangles – glasses after runs in solutions of 5.12 wt. % of fluorides (dirty green), 14.34 % (blue), 24.9 (light green), 30.85 % (red); F4 (blue circle) – fluoride glass; Cry (yellow circle) – cryolite; small colored circles – init solutions; small black circles numbered 75U-78U – the total composition in the runs; reverse colored triangles – calculated compositions of the solutions in equilibrium at different fluoride fluid compositions from 5.12 to 30.85 wt. %.

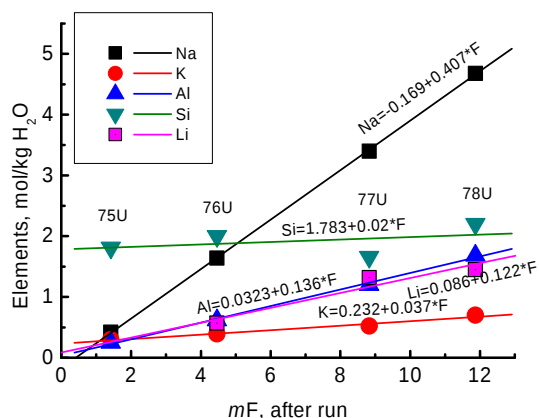


Fig. 2. Dependence of the fluoride solutions compositions in equilibrium with granite melts from the total fluoride in the solutions in the runs # 75U-78U (calculated data)

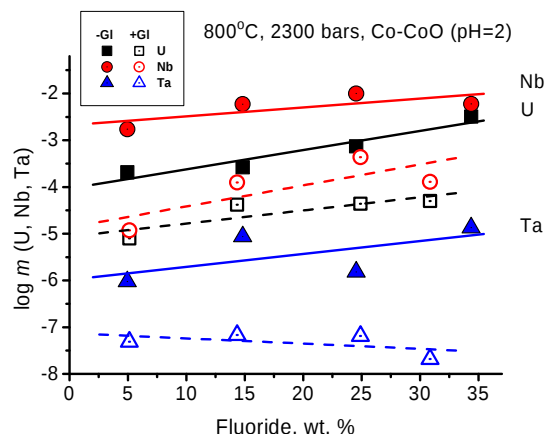


Fig. 3. Apparent solubility of uraninite and U-pyrochlore in 3-phase fluid system based on fluoride glass F4 (experiments with granite melt) and F5 (only solution) (pH=2)