Experimental study of quartz influence on the pyrochlore solubility in fluoride solutions

Експериментално изследване на влиянието на кварца върху разтворимостта на пирохлора в флуорсъдържащи разтвори

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To estimate the influence of quartz (the most widespread mineral of ore rare-earth metal granitoid complexes) on pyrochlore solubility \((\text{Ca, Na})_2(\text{Nb, Ta})_2\text{O}_6\) \((\text{O, OH, F})\) special runs (with quartz and without it) have been done. The runs lasted 7–15 days at 550, 650 and 850 °C and pressure 1 kbar in the solutions LiF (0.08 M), NaF (1M), KF (0.5 and 1M) on hydrothermal devices with the external heating and cold valve and in “gas bombs”. The accuracy of temperature regulation was ±5 °C; pressure ±50 bar. As initial materials quartz (Perekatnoye deposit, Aldan) and natural pyrochlore of the following composition (recalculation by 4 cations taking charge balance into account) have been used:

\[
(\text{Na}_{0.92}\text{Ca}_{0.95}\text{Sr}_{0.06})(\text{Ti}_{0.04}\text{Nb}_{2.02})_2\text{O}_6 \quad [\text{F}_{1.02}\text{(OH)}_{0.18}]_{1.20}.
\]

To estimate phase fluid state we used a method of synthetic fluid inclusions in quartz. Quenching solution after the run was analyzed by ICP/MS and ICP/AES (mass-spectral and atomic-emission) method for the elements (Nb, Ta, Na, Ca, Mn, Fe, Ti, etc.). Solid charge was analyzed on the electronic microprobe CamScan MV2300 (VGA TS 5130MM) and by the x-ray phase method.

Fluid phase state

The runs with LiF solution (concentration 0.08 M). At pressure 1 kbar and temperatures 550 and 650 °C a fluid was in a heterogeneous state: two-phase gas-liquid \((G+L)\) and three-phase gas-liquid-crystal \((G+L+C)\) inclusions occurred in the samples. Two-phase inclusions are homogenized into liquid. In three-phase inclusions one more liquid phase is formed at heating. It accumulates itself round a gas bubble, what testifies to the fact that its density is lower than that of the remained liquid.

The runs with NaF solution (concentration 1M). In contrast to LiF solutions at pressures 0.5 and 1 kbar and temperature 550 °C a fluid was in a homogeneous state: only two-phase \(G+L\) inclusions were found. At temperature rise up to 650 °C the interaction of the fluid with solid phases resulted in precipitation of a small amount of solid phases. The process of homogenization of two-phase inclusions is closely critical what shows the approximation of the run parameters to the critical point of the system.

The runs with KF solution (concentration 0.5–1M). At 550 °C and 1 kbar in case of the initial concentration of the solution 2.9 mass % (0.5M) a fluid is homogeneous: only G+L inclusions occur. If at the same P-T conditions the concentration of the initial solution increases up to 1M (5.8 mass %) then a fluid is heterogenized what testifies to the formation of different type inclusions. Multi-phase inclusion is shown at different temperatures; homogenization at heating up to 500 °C is not attained, though all crystals (C) are dissolved and a gas bubble (G) has markedly got smaller. Together with \((G+L1+L2+C)\) inclusions, inclusions \((G+L)\) also occur what proves fluid inhomogeneity.

Pyrochlore solubility

It is experimentally determined that at T=550 °C quartz presence decreases essentially Nb content in KF solutions (more than by 3 orders). For temperatures 650 and 850 °C quartz presence in the system increases the equilibrium content of Nb in the solution by an order of magnitude: at 650 °C Nb content in 1mKF without quartz is \(2.91\times10^{-5}\) mol/kg \(H_2O\); but in quartz presence it is \(1.59\times10^{-4}\) mol/kg \(H_2O\); at 850 °C the number of Nb without quartz is \(2.38\times10^{-4}\), but with quartz (or with granite melt) is \(2.39\times10^{-3}\) mol/kg \(H_2O\). The measurement of pH solutions before and after the runs has shown that for 550 °C the initial solution 1m KF gets alkaline after the run, what decreases pyrochlore
solubility; for 650 °C pH shifts into the acidic region but only by half an order of magnitude; for 850 °C pH after the run shifts into the acidic region markedly (pH bef/exp.=7.32, but pH aft/exp.=1.901). It has been suggested that by means of fluid-magmatic interaction at T=850 °C HF concentration in fluid essentially increases.

The investigation of fluid inclusions in quartz has shown that under the conditions of the runs the reactions of high-temperature hydrolysis KF take place: KF+H₂O=KOH↓+HF↑; here the interaction with quartz takes place: SiO₂+2KOH=K₂SiO₃+H₂O, with the formation of silicate glass phase (aqueous solution-melt).

The phase of alkaline glass synthesized in the runs on pyrochlore solubility at 650 and 850 °C and pressure 1 kbar (in the solution 1M KF) is a concentrator of Nb (Nb₂O₅ up to 16 mass %). The distribution coefficient of Nb between glass and fluid is equal to 500 (in favor of glass). It is shown that the phase of the alkaline silicate solution–melt can serve as an effective concentrator of the ore component (Nb) at the last low-temperature stages of crystallization of rare-metal granites.

On the basis of the obtained results, the following scheme of the process of ore genesis of fluoric granites with Nb-Ta type of mineralization can be outlined: granite melt (rich in F, Li, K) with the fluid (in a sub-saturated state of the melt); rising of the melt upwards (at a simultaneous decrease of PT parameters); heterogenization of the melt is possible in this case. Ore elements are concentrated available in the phase of the silicate (granite) melt (T~900 °C; P ≤2–3 kbar) → melt (or two melts) under the conditions of fluid separation from the silicate melt (“retrograde boiling”), fluid heterogenization into liquid and vapor phases. Melt and fluid rise upwards. Hydrolysis reactions of a fluid with the formation of the alkaline silicate phase:

KF+H₂O→HF↑+KOH; 2KOH+SiO₂→K₂SiO₃+H₂O (“a heavy fluid”). Redistribution of ore elements in the system silicate melt–alkaline silicate melt in favor of the alkaline melt (“a heavy fluid”) (T <900 °C; P ~1 kbar) → subliquidus conditions, beginning of crystallization of feldspars, presence of liquid phase of alkaline silicate (quasi-granite) melt. Ore elements are concentrated in the phase of alkaline silicate melt (T~800 °C; P <1 kbar) → total crystallization of granite melt (including alkaline silicate phase), crystallization of ore minerals of tantalum-niobates. Ore elements are in the form of minerals of tantalum-niobates (T <650 °C; P <1 kbar).

Conclusions

1. A considerable influence of quartz presence on pyrochlore solubility in aqueous solutions of fluorides of alkaline metals under hydrothermal conditions is shown.
2. A phase composition of a fluid under the run parameters is studied by method of synthetic fluid inclusions in quartz.
3. It is shown that at temperature 650 °C and higher a phase of silicate melt is formed (due to fluoride potassium hydrolysis).
4. A phase of silicate alkaline melt concentrates niobium (up to 17 mass % Nb₂O₅) and can serve as a phase-concentrator of ore elements under the formation of tantalum-niobates deposits.

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