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Mineral equilibria in systems of K₂O(Li₂O)–Al₂O₃–SiO₂–HF–H₂O with topaz: experimental data, T=400°C P=100 MPa

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Greisen formation, one of the most widespread, is of primary practical importance among metasomatic formations of the stage of acid leaching related to granitoid magmatism because it is in association with stannum, tungsten, beryllium, molybdenum, niobium, and tantalum ores. [*Beus and Dikov*, 1967], [*Runqvist*, 1971], [*Mutschler*, 1981]. Greisens form under the action of fluorine-bearing solutions which is reflected in stability of fluoride minerals in formation parageneses and makes them quite different from other high temperature metasomatic formations. In the presented work the experimental study of mineral equilibria with topaz (one of the main indicator of F-bearing minerals) in system K₂O(Li₂O)–Al₂O₃–SiO₂–HF–H₂O was carried out at temperature of 400°C and pressure of 100 MPa for the purpose of obtaining of a quantitative estimation of solution composition (in particular of lithium contains) for the decision of questions of genesis of greisen deposits.

Study of mineral equilibria in specified system at the specified minerals forming parameters was not examined experimentally earlier except for the works devoted to study of phase equilibria in systems a granite-H₂O-HF and a granite-H₂O-KF in high-temperature area [*Gluk and Anfilogov*, 1973], [*Kovalenko*, 1977]. The topology of potassium systems in connection with paragenesis of greisen deposits were considered by D.Burt [*Burt*, 1981]. He plotted schematic diagrammes of phase equilibria in co-ordinates of chemical potentials of HF and KF which has been use for experimentally studied of mineral equilibria in model system of K₂O-Al₂O₃-SiO₂-HF-H₂O in the temperatures range of 300–600°C, at pressure of 100 MPa [*Shapovalov*, 1988]. There are enough of works devoted to theoretical and experimental study of systems Na₂O-Al₂O₃-SiO₂-HF-H₂O and CaO-Al₂O₃-SiO₂-HF-H₂O [*Dolejs and Baker*, 2004], [*Dolejs and Baker*, 2007] at present, however considerable interest represents of experimental modelling of lithium and potassium containing systems as in them mineral associations of a topaz with field spars and micas (lepidolite or muscovite) are formed.

Experiments were carried out by ampoule technique. Ampoules in volume of 2 sm³ in quantity of 8 thing, made of heat-resistant Cr–Ni alloy and lined by gold, were loaded by the sample of a topaz monocrystal and powder mixture of different components of reactions (AlF₃, Ms, And, Ksp, Qtz, Lpd et al.), filled in with certain volume doubly distilled water, providing necessary pressure, with the additive of corresponding quantities of KF, LiF and HF. Hermetically closed ampoules were placed in a heat-resistant autoclave in volume of 280 ml which was filled in with water distillate with the same filling coefficient, as the ampoules placed in it. Duration of runs was 14 days. After end of runs, the autoclave was quenched in cold water and then was opened. Weight change of topaz crystal and new formed phases showed the direction of shift of reactions. Products of experiences were examined with the help of X-Ray and microprobe analyses.

As a result influence of lithium on shift of topaz stability field on the diagram $\lg_{(mHF)} - \lg_{(mKF)}$ established earlier [*Shapovalov*, 1988] for modeling system K₂O–Al₂O₃–SiO₂–HF–H₂O has been estimated (Fig. 1). At low concentration of LiF and high concentration of HF in the solution the line limiting the topaz field for monovariant equilibrium topaz–AlF₃ moves downwards to the axis $\lg_{(mHF)}$. Muscovite and K_nAlF₃ stability fields are replaced by lepidolite (Fig. 2II) and (K, Li) _nAlF_{3+n} (Fig. 2III) fields accordingly at relatively high concentration of LiF and low concentration HF in the solution. Absence of potassium in the solution leads to formation of the lithium-bearing alumina-fluoride phase (Fig. 2IV).



Fig. 1. The generalised diagramme showing displacement of topaz stability field established earlier [*Shapovalov*, 1988] for model system $K_2O-Al_2O_3-SiO_2-HF-H_2O$ (red line) depending on LiF content in the solution (blue lines and points) at T =400 ° C and P = 100 MPa, quartz in excess. *Symbols:* Tz – topaz, And – andalusite, Ms – muscovite, Ksp –K-feldspar, Lpd –lepidolite



Fig. 2. Results of experiments: I – the outgrowth on topaz grain (topaz stability field), II – dissolution of topaz grain (lepidolite stability field), III – formation of alumina–fluoride phases: (K, Li) $_{n}AlF_{3+n}$, IV – lithium-bearing alumina-fluoride phase

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