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Experimental modeling of greisenization in voznesenka granites

A. M. Aksyuk, V. S. Korzhinskaya
Institute of Experimental Mineralogy RAS, Chernogolovka
Anatoly.Aksyuk@iem.ac.ru; vkor@iem.ac.ru, fax: 8 (496) 524 6205, phone: 8 (496) 522 5861

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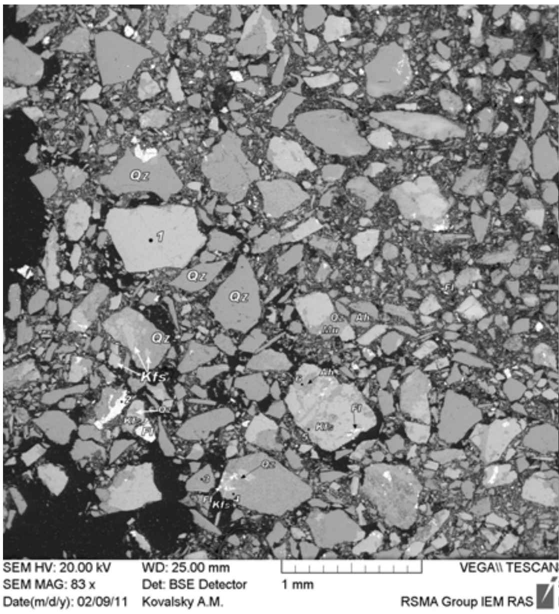
At the Voznesenka ore area (Primorsky Krai, Russia) there are different known (Ta-Nb, W, Sn etc.) deposits which formation is connected with greisenization modeling of granites of the voznesenka complex. Two phases carry to this complex: biotite and lithium-fluoric granites. Lithium-fluoric granite composes small (to 1–2 km) stocks representing or independent magmatic bodies, or transformed ledges of greisenized granites from underlying the more massive (with a diameter greater than 10 km) massif of biotite granites (type as yaroslavka or pervomyka massifs). The source of ore-bearing fluids was the deep magma chamber. Deposits Ta-Nb, W, Sn, fluorite of the Voznesenka ore area in Primorsky Krai are connected with greisenized granites of the voznesenka complex. Therefore, on geological cross-section of the Voznesenka and Pogranichnoe deposits the Li-F granite stocks were intensely greisenized. In the apical endocontact part of granites, K-feldspar and albite zones are formed and turned into fluorite ores in exocontact zone carbonate rocks [*Lugovskoy,* 1968]. From the physical and chemical point of view the gresenization of granite is mainly a reaction of hydrolysis of field spars and replacement by their association quartz-mica-topaz (Fig. 1).

Fluorine played a big role in formation of greisens and greisen deposits of the Voznesenky area. By our estimation obtained with the mineral geofluorimetrs, concentrations of fluorine were nearby 0.1-1 m_{HF} in a granite fluid of this area [*Aksyuk,* 2002].

We conducted experiments on modeling greisen formation in endocontact of voznesenka biotite and Li-F granites at temperatures 400^o, 500^o, 600^{o}C and pressure 100 MPa. They were carried out in autoclaves by two different techniques: 1) using double ampoules (for 600^o; 2) using sealed container, lined with platinum (for 400 and 500^o). The internal volume of the case was made about 20 cm^3, where an open platinum capsules was placed, stuffed with mashed powder granite weighing about 0,3–0,4 g. The container was filled with a water solution of preset concentration HF. The parity rock-fluid was about 1:25. The duration of runs was 15–30 days. Initial rocks and greisenized granite were studied on the electronic x-microprobe Cam Scan MV2300 (VE GA TSS130MM). The hardening solution was analyzed on F-ion by fluorine-selective electrode and additionally its pH was measured. In the photo 1a initial Li-F granite, containing quartz, K-feldspar, albite, muscovite, fluorite, and topaz are shown. The photo 1b shows initial biotite granites, containing also quartz, potassium feldspar, albite, orthoclase, biotite, apatite, topaz, struverite $(Ti, Ta, Fe^{+3})_3O_6$, etc. After experiments products without destruction became impregnated and fastened with cyanoacrylate, then grinded on demanded depth. The photo 2 shows the products after the experiments in the form of columns impregnated with cyanoacrylate, of which subsequently were ground and studied by microprobe.

The experiments at 600^o and 100 MPa, in water and in 1m HF are carried out by method of double ampoules. After runs value of pH solution shifts considerably to 2.2 in initial water and to 2.45 in 1m HF. In the runs of the long duration (more than 30 days) crystals K-feldspar and albite were completely dissolved. T = 400^o and 500^{o}C experiments were carried out in hermetically sealed containers. The open densely filled platinum ampoule (4x0.1x40 mm) was placed inside with the pounded powder of a granite. As an initial solution 0.1m, 1m HF, and (0.5m HF+0.5m HCl) solution were used. At T = 500^{o}C and P = 100 MPa, in 1m HF sharply varied pH. The hardening solution has 1.68pH in experiments with Li-F granite and 2.1pH with biotite granite. Fluorine concentration in these solutions varied to 0.0111m in contacte with Li-F granite and 0.00683m with biotite granite. In this case, at the top of metasomatic columns clusters of fluorite grains, grain sellaite $(Mg(F,OH)_2$, topaz, mica flakes with a pronounced cleavage, and quartz grains increased in size were observed.

In experiments at 400°C and 100 MPa in the (0.5mHF+0.5mHCl) solution albite and K-feldspar were also completely dissolved, and a chemical compound of granite sharply changed (Fig. 2). At the open end of metasomatic columns (on Fig. 2a at the left) separate grains of hieratite (K_2AlSiF_6) or elpasolite (K_2NaAlF_6) were formed. The voznesenka lithium-fluoric granite were transformed in zwitter (quartz+topaz) on all extent of a column. Only rare grains of of Fe, Ti and Ta-Nb oxides remained. Zircons were sometimes marked with Zr-Hf relation about 13-17. Biotite granite in front column parts (on Fig. 2b on the right) are transformed in zwitter throughout 1/3 lengths where F-topaz grows among the remaining and neogenic quartz crystals. Furthermore, instead of a topaz andalusite is formed. The initial solution had pH of 1.45. After the run with Li-F granite pH was 1.69, or pH was1.80 with biotite granite, i.e. this indicator in the course of experiment has changed little. Concentration of fluorine in hardening solutions has made m_F = 0.0155 for Li-F granite and m_F = 0.0204 for biotite granite.



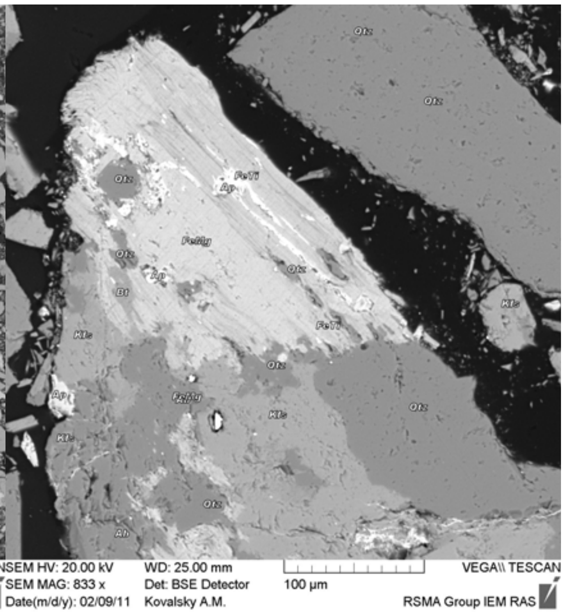


Photo 1a Initial Li-F granite **Photo 1б Initial Bi-granite**

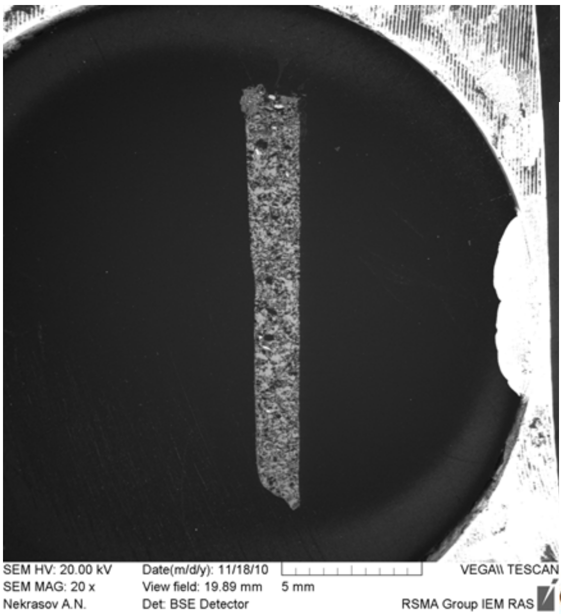


Photo 2 General view of "column" of greisenized granite, impregnated cyanoacrylate

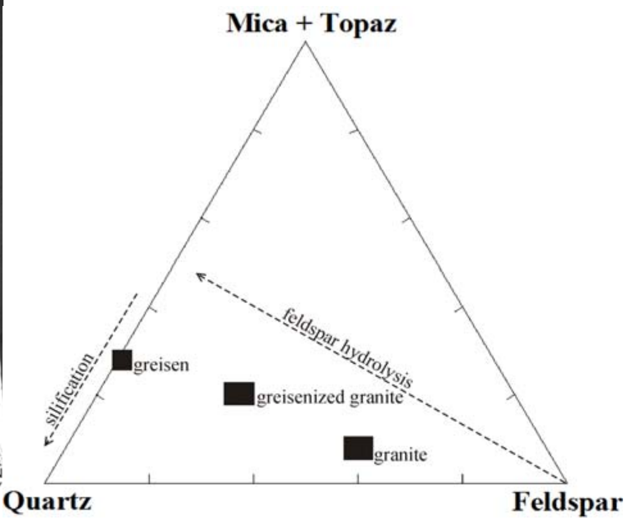


Fig. 1 Path of greisenization of a granite

Fluoride solutions in granite fluids of Voznesenska ore area promoted dissolution and carrying over tantalum-niobium minerals in endocontact zone or galo. Mineralogical data [Lugovskoy, 1968], on the Voznesenka ore field showed that Ta-bearing struverite $(Ti,Ta,Fe)_3O_6$) was developed which consists mainly of trivalent iron, that indicates about the major role of oxidation-reduction conditions in its formation and proves to be true in our experimental data of solubility of tantalum-niobium minerals [*Zaraisky end Korzhinskaya*, 2005].

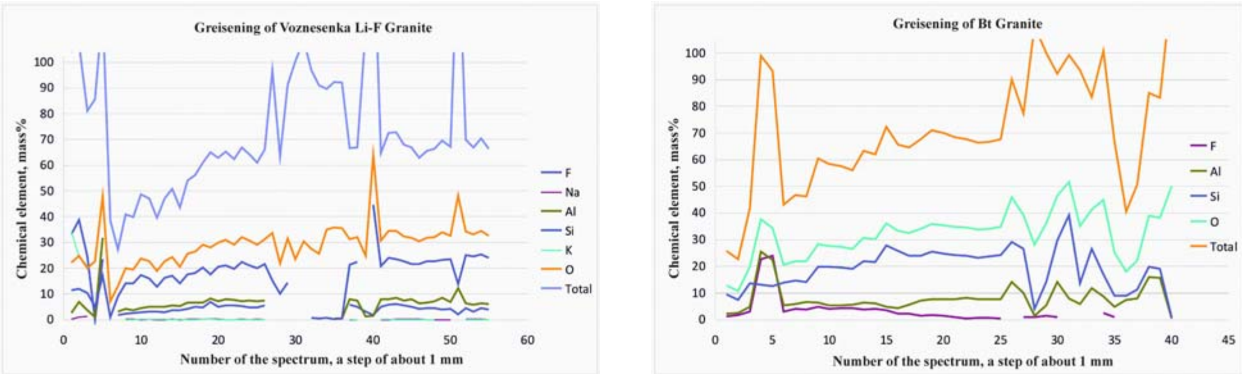


Fig. 2 a, b Experimental modelling greisenization of voznesenka granite

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