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Experimental study of greisenization of granite in water and HF solution at 400–600°C

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An experimental simulation of greisenization of the voznesenka biotite and lithium-fluorine granites at 400–600°C and 100 MPa in water and water-fluoride fluids showed that during the experiments, the sharp frontal diffusion of substitution did not occur in powder rocks, as observed in the dissolution of the individual grains and the formation of new minerals. There was "infiltration" process in a confined space capsule. According to microprobe analysis that is due to the relatively high porosity of the initial powders (tens of %) and the gradient of the component concentrations in the pore solution, as opposed to natural processes, where the porosity is usually up to 2–5 %. The results of analyzes of solid products, the experiments shown that the "metasomatic" alteration of granites in the course of the experiments clearly observed, depending on experimental conditions, but clearly apparent statistically.

Key words: experiment, greisenization, granite, fluorine, Voznesenka

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Greisenization rare-metal granite is a widespread process in nature and develops in the form of rims for cracks in the granite, quartz-filled, with a hydrothermal process. In the fluid-magmatic stage in the rare-metal granites, especially with the fluorine-rich fluid, evolving "avtometasomatoz" primarily in the apical parts of the ledges of granite massifs, which are sometimes formed thick zones greisenizaed granites. On the territory of the Voznesenka ore area (in the Primorye) are known different (Ta–Nb, W, Sn, etc.) deposits which formation are associated with granites greisenization of the voznesenka complex. The complex includes two phases: biotite and lithium-fluorine granites. Li-F granite make up a small (1–2 km) stocks, which are igneous or independent body, or transformed and greisenized projections underlying the more powerful (more than 10 km in diameter) of the massif of biotite granite. The source of ore-bearing fluids was a deep magma chamber. Fluoride has played a major role in the formation of greisen and greisen deposits of the Voznesenka area. According to our estimates obtained using geofluorimeters [*Aksyuk, 2002*], in fluid of the granite the concentration of fluoride was about 0.1–1 mHF. From the physicochemical point of view greisenization granites is, first and foremost, the reaction of hydrolysis of feldspars and their replacement by quartz-mica-topaz. Transformations of biotite granites under the influence of fluoride fluids at high P-T conditions bring them closer to the composition of lithium- fluorine granites.

Greisen zoning in granites simulated experimentally by *G.P. Zaraisky* [*1989*]. We have performed experiments on the formation of greisen in endocontact of voznesenka biotite and Li-F granites, which were carried out in autoclaves with automatic temperature control during the experiment. In an autoclave were placed containers sealed, lined with platinum, inside which an open platinum or quartz ampoule. Internal volume of the container was about 20 cm^3. Open platinum or quartz ampoule was jammed mashed powder of granite weighing about 0.3-0.4 g and container was filled with an aqueous solution of a given concentration of HF. Rock-fluid ratio was about 1:25. The duration of the experiments was 15–30 days.

After the experiment products of runs were impregnated and sealed with cyanoacrylate without destroying (Fig. 1), ground to the required depth and studied by x-ray (microprobe) Cam Scan MV2300 (VE GA TSS130MM).

Fig. 1. The columns after the experiment

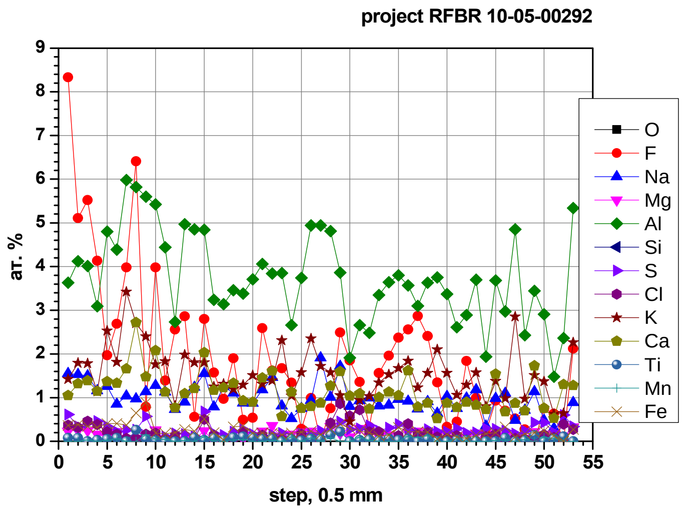

Fig. 2. The composition of the column at 600°C, H_2O

Recording of spectra was carried out on areas with a side of about 0.5x0.5 mm in increments (steps) of approximately 0.1–0.5 mm. According to the microprobe analysis of the experimental greisen columns, a sharp frontal diffusion replacement of powder rocks was not observed, and there was the dissolution of the individual grains and the formation of new minerals. There was "infiltration" process in a confined space capsule. That is due to the relatively high porosity of the initial powders (tens of %) and the gradient of the component concentrations in the pore solution along the length of the column, as opposed to natural processes, where the porosity of the rock is usually up to 2–5 %.

Analysis of the composition of solid products of the experiments shows that the "metasomatic" alteration of granites in the course of the experiments clearly observed, depending on experimental conditions, but these relationships manifested statistically. This required measurements of rock compositions by the microprobe on sites with size we used the most often 0.5x0.5 mm.

At 600°C and 100 MPa in H_2O (Fig. 2, open to a solution on the left) and 1m HF solutions after the experiments the pH was shifted markedly to 2.2 in the water and 2.45 in 1m HF. In experiments of long duration (more than 30 days) crystals of potassium feldspar and albite are completely dissolved. In the platinum-lined canisters at 500°C and a pressure of 100 MPa, in 1m HF solutions contents of Al and F drastically changed in the column to open to solution end (Fig. 3, right).

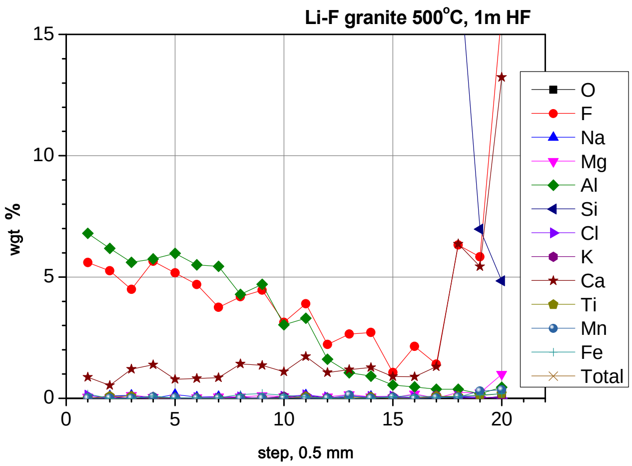

Fig. 3. Greisen column by voznesenka Li-F granites (open to the solution of the-right)

The upper (open to solution) part of metasomatic columns were encountered clusters of grains of fluorite, some grains of sellaite ($Mg(OH, F)_2$), topaz, mica flakes with distinct cleavage, and quartz grains increased in size.

In experiments at 400–500°C and 100 MPa, 0.5 m_{HF} +0.5 m_{HCl} (Fig. 4, 5), albite and K-feldspar also completely dissolved and the chemical composition of granite dramatically changed.

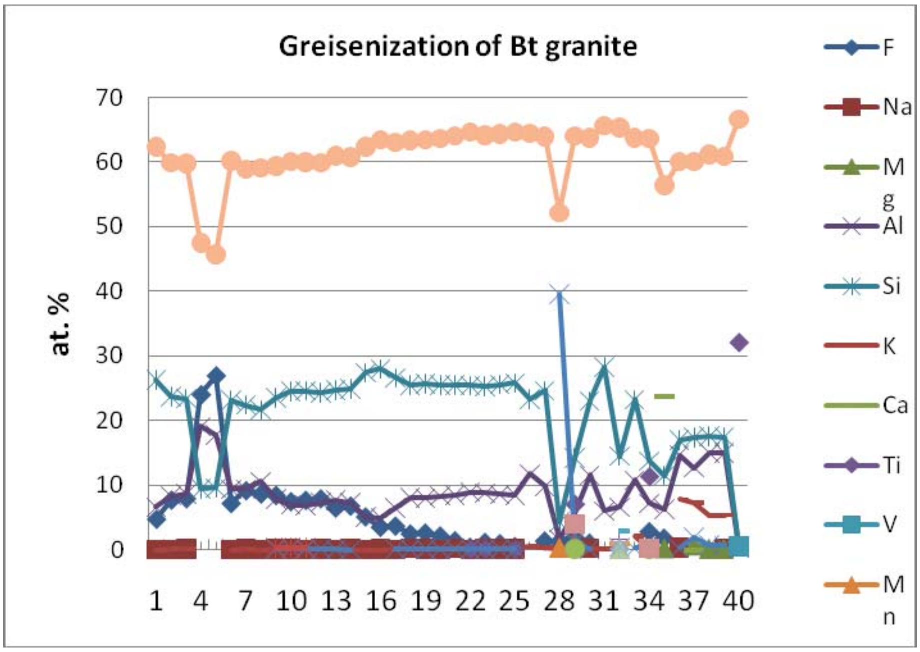

Fig. 4. Greisenization of biotite granite, measured in 1 mm increments (open to the solution of the columns is at the left)

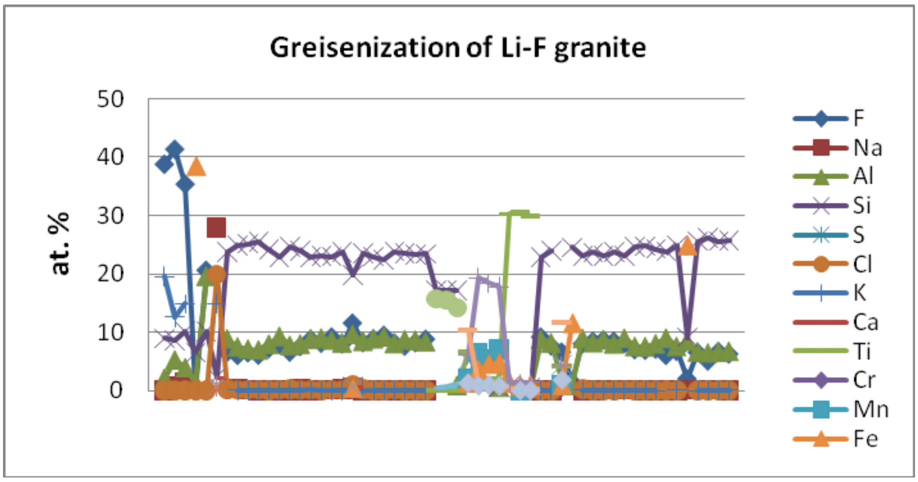

Fig. 5. Greisenization of Li-F granite, measured in 1 mm increments (open to the solution of the columns is at the left)

Sometimes the inside of the column began to form quartz veins. At the open end of the metasomatic column formed separate grains hieratite (K_2AlSiF_6), elpasolite (K_2NaAlF_6). Voznesenka Li–F granites throughout the column converted to zwitter (quartz + topaz). There were retained only rare grains of oxides Fe, Ti and Ta–Nb and sometimes preserved grains of zircon with Zr/Hf ratio of 13-17 typical to high evolved granite. Biotite granite in front of the column converted to zwitter over one third of length, where among the remaining and newly formed grains of quartz crystals grows F-topaz. Then instead of the topaz were formed andalusite, which is marked on the Voznesenka fields. The initial solution (0.5 m_{HF} +0.5 m_{HCl}) had pH = 1.45. After the runs with the Li–F granite, it has changed to pH 1.69, with the biotite granite it was up to pH = 1.80. This indicator has changed little during the experiment. The concentration of fluoride in quenched solution was m_F = 0.0155 mol/kg H_2O for the Li-F granites and m_F = 0.0204 mol/kg H_2O for the biotite granite. Fluoride solutions in granitic fluids voznesenka ore district contributed to the dissolution and transport of tantalum-niobates in the endocontact aureole. According to mineralogical data [*Lugovskoy, 1968*] on the Voznesenka ore field there was developed tantalbearing struverite $(Ti,Ta,Fe)_3O_6$), which is present in the predominantly ferric iron. This indicates the important role of redox conditions during formation its, that is confirmed by our experimental data on the solubility of tantalum-niobium minerals [*Korzhiskaya, Kotova, 2012*].

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