Fluorine, along with water, carbon dioxide and chlorine, are major components of natural hydrothermal fluid. The highest concentration of natural fluid in the formation of fluorine reached at the lithium-fluorine granite and associated pegmatite, in greisen, as well as in pegmatite of high alkaline rocks. Concentration of fluorine and silica in the fluid were the main factors of formation of quartz veins and zones of silicification in metasomatites in greisen and pegmatite of rare metal deposits.

According to the authors, the T-P conditions and the concentration of fluorine in the fluid for various natural objects associated with greisen or rare-metal mineralization, were different. Rocks of Khangilay pluton (Eastern Transbaikalia) were formed at pressure close to 100 MPa (at depth of about 6-8 km) [Zaraisky et al., 1997; Aksyuk, 2002]. In Khangilay pluton there are three intrusion phases: the earliest, which formed bt granite of the Khangilay massif; later leucogranite phase, which formed the Spokoynensky stock and the final phase of the lithium-fluorine granites, which formed the Orlovka stock. According to our estimates, the concentration of fluorine in fluid at formation of biotite granite of the Khangilay massif was about 0.037-0.075 M HF (mol/dm³) (or 0.157 - 0.234 m HF (mol/kg)). In the formation of leucogranite and associated Sn-W deposit Spokoyninskoe, characterized by magmatic fluids with concentration of fluorine of about 0.024 -0.064 M HF (or 0.1 - 0.2 m HF) at 790-650°C [Korotaev, 1994]. Concentration of HF was much higher, up to 0.43 M HF (1.226-1.697 m HF) and typical for ore-bearing lithium-fluorine-amazonite-albite granite of Orlovka stock. Estimates of the temperature of the formation of biotites and lithium micas in granitic rocks Orlovka stock given interval of temperature 620 - 750°C [Aksyuk, 2002]. Related fluorine concentration were typical for the fluid at the formation of ongonite-like dike in W-Mo deposit Akchatau (Kazakhstan) - about 0.45-0.63 M (1.8 m), and for the fluid involved in the forming of lithium-fluorine granites at Ta-Nb deposit Etyka about 0.73 M (2.08-2.88 m), T-P conditions for their formation were similar [Aksyuk, 2009].

Based on these evaluations, the experiments were carried out to find the dissolved silica amount in fluorine aqueous fluid in equilibrium with quartz. Dissolved silica was determined by weight loss of quartz after the experiment. The experiments were carried out in high-pressure vessel, in sealed gold or platinum ampules with a fluorine-containing aqueous solution, with concentrations in the initial solution from pure water to 2.5 m HF. The pressure was set by filling the vessel with the calculated amount of water. The duration of the experiments was 2-4 weeks at temperature ranging from 200 to 600°C and pressures of 50-150 MPa. The quartz was taken from the quartz core of ceramic pegmatite from north Karelia.

The experimental results were fitted by equations [eqs. 1-10] and [eqs. 17-21]. In the same way the data were processed by other authors [eqs. 10-14] [Shapovalov and Balashov, 1990], [eqs. 15-16] [Aksyuk and Zhukovskaya, 1998]. Calculations for the temperature 700 - 1000°C were performed on the equations taken from [Aksyuk and Korzhinskaya, 2008]. Lowering the temperature and pressure are often used as a universal cause of precipitation of quartz, although in the system quartz-water, according to data published in [Kennedy, 1950], at pressures below 75 MPa were observed zone of retrograde solubility, when instead of precipitation of quartz obtained its dissolution (Fig. 1). A similar phenomenon for the quartz also was noted [Balitsky et al., 1999].

Table.
The resulting experimental data showed (Fig. 2, 3, 4, 5) that with increasing fluorine concentration in the fluid retrograde solubility of silica (mol/kg solution) manifested in pressure greater than 75 MPa, since under these T – P conditions, the influence of changes in the density of the solution began to dominate over the effect of fluorine. That is just in the range of pressure and temperature, which was formed by fluorine-rich granite and associated metasomatic rocks. Also, with increasing concentration of fluorine, region of retrograde solubility shifted to lower temperature region.

Which implies that the natural objects with low fluorine content in the fluid, the amount of silica
in the fluid, an equilibrium with quartz, was compared with fluids without fluoride. And at the same time, their dependence on T and P will be close to the purely aqueous fluids.

For example, when the HF concentration in the initial 0.1 m solution (Fig. 2, typical of tin-tungsten deposits and occurrences) at constant pressure and falling temperature from 800 to 400°C will dissolved 15.5 wt. % quartz, with a further fall from 400 to 200°C it should be precipitated about 65% of the dissolved silica. When the HF concentration in the initial 2 m solution (Fig. 4, a typical Orlovka lithium-fluorine granite) at constant pressure and falling temperature from 800 to 400°C quartz was dissolved about 74 wt. % with a further falling in temperature from 400 to 200°C was deposited as soon as about 13% of the dissolved silica. With further increase of fluorine in the fluid (2.5 m in initial solution) but precipitation of silica practically does not occur.

Hence with a higher content of fluoride in the fluid, silica can become more mobile component in a wider range of T-P parameters with respect to the low fluoride fluid. In this case, directly in the apical parts of massifs with low fluorine content in the fluid could happen or not intense silicification. Perhaps this was one of the main factors of forming a "quartz hat" on Spokoynenskoe deposit or its absence on Orlovka. Even if consider the reduction of the equilibrium fluorine and silica concentrations in greisen and hydrothermal stages, due to a decrease in temperature and, mainly, by dilution of magmatic fluids by meteoric waters, the amount of dissolved silica at 200 °C in objects with elevated levels of fluoride can still prevail over the drop-silica precipitated, compared with the beginning of the dissolution process. Of course, one should bear in mind that the proposed model Of course, one should bear in mind that the proposed model is a extreme case, not reflective of all natural processes as so far unknown form of finding the silica and fluoride in the fluid some of these sites and
there was boiling fluid [Bychkov et al., 2010].

In addition, as shown in the G.P. Zaraisky [Zaraisky, 1999], contribution to the dissolution of silica can contribute also feldspars, possessing greater solubility relative to quartz, resulting in a fluid may be supersaturated with respect to crystalline quartz to the level of equilibrium with the metastable amorphous silica.

The proposed model, despite the above limitations, yields, although approximate, since the calculations are for a system of qtz-H₂O-HF, but still quantifying silicification and main factors influencing this process in rare-metal deposits.

**Literature**


Aksyuk A. M., T. N. Zhukovskaya (1998), Solubility of quartz in aqueous solutions of hydrofluoric acid at temperatures of 500 - 1000°C and pressures of 100-500 MPa. DAN, 301, № 2, p. 244-247.


