Experimental study of melting of the voznesenka biotite and Li-F granites

A. M. Aksyuk, A. A. Konyshev Institute of Experimental Mineralogy RAS, Chernogolovka <u>aksyuk@iem.ac.ru</u>, <u>konyshev@iem.ac.ru</u>, fax: 8 (496) 524 6205, tel.: 8 (496) 522 5861

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On the territory of the Voznesenka ore area, located in the south-western part of Primor'e, are known some fluorite deposits (Pogranichnoye, Voznesenka, Lagernoye), tin (Pervomaiskoye, Yaroslavka, Chapayevskoye), Ta, Be, iron (skarn) and polymetallic (hydrothermal) ores, which formation is associated with the voznesenka granites. The Voznesenska complex consists of two phases of biotite and lithium-fluorine granite.

In forming the biotite and Li-F granite and related deposits (fluorite, tantalum, tin, beryl, etc.) fluorine played an essential role. In gas-liquid inclusions can be met fluorine levels up to 0.6m [*Govorov*, 1977]. Li-F granite are the richest in fluorine, and enclosed Ta-Nb mineralization and deposits and in which the halo exocontact of carbonate rocks are converted to fluorite deposit (Voznesenskoye, Pogranicnoye, etc.).

According to geological data the formation of Ta-Nb deposits of the Voznesenska area took place at the fluid-magmatic stage of crystallization of molten Li-F granite, but fluorite, and Sn-W deposits were formed in the post-magmatic greisen or hydrothermal stages connected with the formation of biotite and lithium-fluorine granite [Govorov, 1977; Kononets et al, 2008; Ryazantseva et al, 1994; Rub and Rub, 2006].

According to our preliminary estimation, the HF concentration in the aqueous fluid of the voznesenska granite could reach $0.5-1.0 \text{ M}_{\text{HF}} \text{ (mol/dm}^3)$ or $0.8-2.3 \text{ m}_{\text{HF}} \text{ (mol / kg H}_2\text{O})$ at a pressure of 200 MPa and 600–800°C. These estimates were obtained using the experimentally based geofluorimeters [*Aksyuk*, 2002; *Aksyuk*, 2009] and the composition of the mica, were published in works [*Ryazantseva et al*, 1994; *Rub and Rub*, 2006].

If we compare these data to estimates of fluorine concentrations of rare metal deposits in other regions, it can be seen (Fig. 1) that voznesenska deposits were mainly at the level of fluid in the Ta-Nb deposits Etyka and Orlovka in East Transbaikalia or topaz-quartz veins in Akchatau (Kazakhstan), i.e. at the third, the most fluorine-rich trend.

Thus, it is evidently that the melting of voznesenka granite, at least their second Li-F phase took place or could happen with the HF concentration in the fluid around the granite 0,1-1,0 m (mol / kg solution). It's used us as one of the prompt for the experiments. Solidus of granites show the T-P parameters are the boundary of transition from magmatic to post-magmatic stages of formation voznesenska deposits.

The experiments to study the solidus were carried out on hydrothermal apparatus with powder Li-F granite of the Voznesenska and biotite granite from the Yaroslavska-massifs at temperatures of 600, 625, 650, 675 and 700°C, and pressures of 50, 100, 150, 200 and 300 MPa, as in pure water as well as with concentrations of 0.1 and 1 m HF in the initial solution.

The position of the solidus of granite in the experiment was determined by the appearance of the first traces of glass in experimental products determined by optical and electron microscope.

The obtained results clearly shown with reference to in relation to gaplogranite the voznesenska granite begin to melt at lower temperatures and pressures (Fig. 2). This shift in temperature is below at least 40°C for the biotite granite and from 80 to 90°C for the Li-F granite. Hence the crystallization of granite of phase II for voznesenska granite was completed at temperatures below 40-50°C. In this regard, the formation of deposits in the ore-magmatic stage, which is connected with Ta-Nb mineralization, – was going for a long time, and area around the lithium-fluorine granite massif remained favorable for physical-chemical conditions.

Compared with Li-F voznesenka granite, the Li-F granite of Orlovka Ta-Nb deposit (Eastern Transbaikalia) was melted at a temperature some higher than Voznesenka.



Fig. 1 Concentrations of HF (M, mol/dm³) in the fluid of voznesenska Li-F granite, estimated by geofluorimeters



Fig. 2 solidus voznesenka - biotite and Li-F granite compared with the solidus of other granite

Products of quenching experiments were analyzed by EPMA, the results were recalculated to 100%. Content of fluorine in the glasses ranged from 0.5 wt% in experiments with pure water, to 3-4% in experiments with 1m HF in the initial solution (Fig. 3, 4, 5). Fluorine-rich mica and topaz were formed. Composition of the glasses was calculated for the wt% of model phases: - albite, anorthite, orthoclase and quartz. All compositions in which there is a lack of one of these phases, as well as those much escaping outside the main distribution of compositions - were excluded. Getting the number of Ab + An, Or, Q - were recalculated to 100%.

In experiments on the melting of Li-F granite in 0.1 m_{HF} ,- a dependence on temperature and pressure. By increasing temperature of the experiment, the compositions of glasses are displaced in orthoclase corner of the triangular diagram. With increasing pressure - there is a shift to the eutectic region for gaplogranite system. As compared to melting in pure water - glass compositions are also shifted to the orthoclase corner (Fig. 6, 7, 8).



0.1mHF init 700°C-200 MPa 700°C-100 MPa 675ºC-100 MPa 650°C-200 MPa 650ºC-100 MPa 625ºC-200 MPa 600°C-200 MPa Bt granite 650°C-200 MPa % 2 1 0 64 68 72 SiO2%

Fig. 3. Contents of F and SiO_2 wt% in glass Li-F granite after melting in pure water

Fig. 4. Contents of F and SiO₂ wt% in glass Li-F and Bt granite after melting at 0.1 m_{HF} initial solution.



Fig. 5. Contents of F and SiO_2 wt% in glass Li-F granite after melting in a m_{HF} init. sol.



Fig. 7. Ab + An, Q, Or weight% in glass Li-F granite after melting at $0.1 \text{ m}_{\text{HF}}$ init. sol.



Fig. 6. Ab + An, Q, Or weight% in glass Li-F granite after melting in pure water



Fig. 8. Ab + An, Q, Or weight% in glass Li-F and Bt granite after melting in a 0.1 m_{HF} init. sol.

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