

**Topaz, cryolite and villiaumite crystallization conditions in the system  
 $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O-Li}_2\text{O-H}_2\text{O-F}$  and in nature**

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It is shown that the composition of rocks containing high fluorine minerals, corresponds to the composition of the melts in the experimental phase diagram of the granite and nepheline-syenite system at 650–800 ° C and 1 kbar. This is a proof of the magmatic nature of accessory cryolite, topaz and villiaumite, as well as of the cryolite large bodies crystallization from the molten salt.

*Key words: cryolite-, topaz- bearing granites, villiaumite-bearing rocks, saturated with fluoride melts, aluminosilicate and aluminofluoride melts, liquid immiscibility, the total composition of rocks*

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A sequential increase in the concentration of volatile components, including water and fluorine will occur in the process of magmatic melts differentiation. As the limit of solubility of fluoride-bearing phases is reached, they are crystallized from a magmatic melt in the form of accessory, sometimes minor rock-forming minerals. In the system we have studied ( $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O-Li}_2\text{O-H}_2\text{O-F}$ ) at temperatures from 650 to 800 ° C and pressure of 1000 bar, the high-fluorine of these phases would be cryolite  $\text{Na}_3\text{AlF}_6$ , elpasolite  $\text{NaK}_2\text{AlF}_6$ , villiaumite  $\text{NaF}$  and topaz  $\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$ . [Gramenitskiy et al, 2005].

In addition to these minerals, fluoride melt may occur in the system at the equilibrium with aluminosilicate melt. The stability field of fluoride melt expands substantially in the presence of Li [Alferieva et al, 2011]. Each silicate melt in the system has a fixed content of fluorine, thus demonstrating the solubility of fluoride in it. It has been established that in the experimental glasses, as well as in the bulk composition of the rocks, containing high-fluorine minerals, there is a tendency for the concentration of fluoride, to decrease, when contents of  $\text{SiO}_2$  increases.

The chemical composition of phases obtained in the experiment was studied by means of the electron microprobe energy dispersive micro analyzer based on scanning electron microscope Jeol JSM-6480LV (INCA-Energy Spectrometer 350) of Department of Petrology, Moscow State University.

Most of the bulk compositions of cryolite-bearing rocks belong to the normal- and moderate-alkali or alkaline series, i.e. to a group of subalkaline, and alkaline leucogranites, respectively. Most of them fall in the category of the agpaitic, and some to peraluminous series. The alkali sum ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) varies from 8 to 13 wt.%. The ratio of Na / K (at.%) is always in favor of sodium and usually equals 1.5–2. Topaz-bearing granites are acidic plutonic rocks of moderately alkaline or subalkaline series and belong to the microcline-albite granites. All topaz-bearing (Li-F) granites and their subvolcanic equivalents - ongonites and elvanes - belong to peraluminous series of rock compositions with agpaitic coefficients from 0.65 to 0.98. Villiaumite-bearing rocks are represented by sodium-potassium alkaline medium rocks – nepheline- and feldspathoid-syenite. Villiaumite is found in agpaitic nepheline syenites and their pegmatites only. Usually in the rocks with villiaumite  $\text{SiO}_2$  content varies from 51 to 58%, the alkali sum ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) from 14 to 21%.

In general, the experimental data in the system  $\text{Si-Al-Na-O-F}$  at 800 ° C and 1 kbar are confirmed in the petrochemical features of rocks: a) the topaz-, cryolite and villiaumite-containing rocks form a separate field of figurative points of the compositions; b) fields position themselves in that order with progressively increasing agpaitic coefficients; c) fields of rocks with topaz and villiaumite don't touch each other, the paragenesis of these minerals is prohibited. Bulk composition

of cryolite- and topaz-bearing rocks are consistent with well-defined compositions of melts in equilibrium with these minerals in the experimental diagram.

On the other hand, there is some controversy, since the experimental data refer to the phase relations in the simplified composition, moreover, they are tied to certain conditions. Thus, most of the figurative points of compositions of villiaumite-bearing rocks, as well as of inclusions in them, fall in the agpaitic part of the field of equilibrium cryolite + melt, stretched along the line of joint crystallization of cryolite and villiaumite, rather than in the melts in equilibrium with villiaumite. The field of cryolite + melt at the experimental diagram is distributed in the region of nepheline-normative area and is much wider than field of real cryolite-bearing rocks.

If Na is substituted by Li in the system, the field of cryolite is replaced by field of equilibrium of aluminosilicate and fluoride melt (liquid immiscibility) in nepheline normative area. Confirmation of these relationships have not been identified in nature. The equilibrium of cryolite-villiaumite doesn't occur on the border of the suitable fields, but it is well defined in the experiments in the system without Li. It is possible that other components, besides lithium, may influence the change of phase relations. The displacement of field boundaries of cryolite and villiaumite towards a less agpaitic area, according to schematic reaction – cryolite+ agpaitic melt → villiaumite + aluminous melt, - may be attributed to the presence of a component in the system which enters into villiaumite and expands the field of its stability, or to a change in temperature, or in pressure. Verification of these hypotheses requires further experiments.

The experimental data show the presence in the high-alumina part of model system of an immiscible area of aluminosilicate with fluoride melt, while the solidus of fluoride liquid refers to much lower temperatures than in the case of aluminosilicate melt. This field corresponds to the rich in fluorine corundum nepheline syenites, very rarely found in nature. As already mentioned, the field of liquid immiscibility significantly expands with the replacement of sodium (and potassium) by lithium. The concentration of 1% of Li in the system would suffice to replace the field of cryolite by the field of fluoride melt, which overlaps compositions of most natural granites and syenites. It has been traced up to 650 ° C. Liquid immiscibility manifests itself by the formation of large-scale isolations (salt globules) in the silicate melt. Manifestations of immiscibility process may occur also in nature.

These include the segregation of cryolite in the form of large, almost monomineralic bodies found in a number of cryolite-bearing granites, of great economic value. Examples of such formations are: Ivigtut deposit in Greenland, Pitinga in Brazil, Ulug-Tanzek and Zashihinskoe in Eastern Siberia. Undoubtedly, a cryolite crystallization from a melt (or highly concentrated brine) occurred in these deposits. Similar formations were discovered in alkaline rocks. In the Khibiny massif are found syenitic pegmatites with the villiaumite core, constituting up to 30% of the pegmatite. Schlieren-like segregations of villiaumite form big blocks in association with natrolite, sodalite and gaskmanite, and are encountered in pegmatite horizon of the same complex. Apparently, separation processes of magmatic melts in the liquid silicate and essentially salt compositions have played an important role during villiaumite bodies formation.

Thus, the magmatic nature of accessory topaz, cryolite and villiaumite in granites and nepheline syenites has been proved by way of comparison between petrological and experimental data. It has been shown that the large ore bodies of cryolite and villiaumite geologically connected with granites and pegmatites may be formed from the fluoride salt melt, created as a result of liquid immiscibility with the fluorine saturated silicate melt.

## References

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