

A comparison between compositions of fluorine saturated experimental melts and cryolite-bearing granites

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The question of the cryolite-bearing granites genesis and related deposits of cryolite (Na_3AlF_6) so far is debatable. On the one hand there is an obvious evidence of magmatic crystallization of cryolite, on the other – hydrothermal-metasomatic one. When considering the magmatic hypothesis, we relied on data from experiments conducted in the granite system, saturated aqueous and fluorine fluid, at temperatures ranging from 650 to 800 °C and $P_{\text{H}_2\text{O}} = 1000$ bar. It was shown [Gramenitskiy, *et al*, 2005] that the equilibrium field of cryolite with aluminosilicate melt on the phase diagram ranges from quartz-normative to nepheline-normative area. In peraluminous part of the system it is limited by equilibrium with topaz, corundum and aluminofluoride melt (close to chiolith – $\text{Na}_5[\text{Al}_3\text{O}_{14}]$), and in agpaitic part of the system it is limited by equilibrium with villiaumite.

Most of the occurrences of cryolite is directly related to intrusive rocks of the alkali-granite series, attributed to the A-type. Cryolite-bearing granites make up small intrusive massifs of columnar forms ranging from a few hundred meters to 2–3 kilometers. They are located in the rupture of the platforms basement, consisting of ancient granite rapakivi complexes or in the middle massifs in regions of the complete folding; occur within volcano-plutonic systems, in pegmatites and among the metamorphic rocks. These granites are of different age from Precambrian to Mesozoic.

The paper discusses those occurrences in which cryolite crystallized from magma as an accessory or minor rock-forming mineral, but also forms a virtually mono mineral lenticular and vein body. Among the manifestations magmatic cryolite the best widely known examples are large deposits: Ivigtut in South Greenland, Pitinga in Brazil, the Jos plateau in Nigeria, Ulug-Tanzek in Tuva, Zashihinskiy in East Sayan, Utulikskiy in SW Baikal, the district of Hamar-Daban. The most of the bulk compositions cryolite-bearing rocks belong to the moderate- and high-silica, rarely to ultra-silica granites, fit into the interval on SiO_2 from 66 to 78 wt.% on the classification diagram SiO_2 -($\text{Na}_2\text{O} + \text{K}_2\text{O}$). On the amount of alkali $\text{Na}_2\text{O} + \text{K}_2\text{O}$ from 8 to 13 wt.% they can be carried over to moderately alkali or alkaline range. Most of the rocks compositions of Brazil, Ivigtut and Ulugh-Tanzek and partially Perzhanskiy, Nigerian are in the field of moderately alkaline granites. Most of the granites of Nigeria, Zashihinskiy deposits, partially Brazil belong to the alkaline range. Only granites and ongonites Urugdey-Utulikskiy belt, where cryolite coexisting with topaz, are referred to normally alkaline series. At a rate of agpaitic granites of different objects differ more clearly. Most of the granites of Brazil, Nigeria and Zashihinskiy deposits are agpaitic. Ivigtut granites have coefficients agpaitic close to unity or slightly less than it; the compositions of Ulugh-Tanzek granites slightly deviate from $K_{\text{agp}} = 1$ in both directions. Perzhanskiy, part of Brazilian and Hamar-Daban granites, in which cryolite coexisting with topaz belong to peralununous series of compositions. In the ratio of Na / K (at.%) is observed excess of sodium over potassium in 1.5 - 2 times in all cryolite-bearing granites. Agpaitic character of granites is always expressed in the appearance of dark minerals presented by alkali pyroxene and amphibole (aegirine, ribekite, arfvedsonite). Mica is often represented by a lithium species – polyolithionite, lepidolite, etc.

Reported petrochemical peculiarities show that cryolite crystallization occurred from granitic melts in a wide range of compositions of silica and alumina and alkali components ratio. Necessary condition for the formation of cryolite in the rocks is their high alkalinity of more than 8 wt.% and high levels of fluoride, causing the possibility of the formation of saturated with fluorine phase – cryolite. The rocks agpaitic coefficient can be both larger and smaller of units.

Comparison of the compositions of cryolite-bearing granites and of glasses of fluorine containing system (with SiO₂ from 63 to 83 wt.%) showed that the most of glass compositions in equilibrium with Na- and K-Na- cryolite phases in the classification diagram SiO₂ – (Na₂O + K₂O) fall into the same area of alkaline and moderately alkaline granites, which formed cryolite-bearing rocks. The most closely correspond to real rocks with cryolite - the experimental glasses composition with the alkali content of 8 to 12 % of that in equilibrium with cryolite and quartz in the Na and K–Na parts of the system at 650–800° C or aluminofluoride melt in LiK–Na part of the system at 800° C. By agpaite coefficient in the range from 0.8 to 1.3 of glasses are closed to the real cryolite-bearing granites as agpaite and peraluminous type.

Results of experiments in the system Si–Al–Na–K–Li–O–H–F showed that cryolite can be crystallized as a liquidus phase at temperatures from 650 to 800 ° C, P_{H₂O} = 1000 bar in a much wider range of compositions of aluminosilicate melt compared with compositions cryolite-bearing granites. This suggests that only a limited of the possible equilibria of melt + cryolite, identified in our experiments, are realized in nature. On the experimental diagram, representing the projection of the phase stability area of the system under study at the triangle SiO₂–AlO_{1.5}–NaO_{0.5}, points of cryolite-bearing granites compositions fall in the fields of equilibrium aluminosilicate melt with cryolite, quartz + cryolite, cryolite + fluoride melts. They are grouped mainly along the line corresponding agpaite coefficient equal to unity between the points of the temperature minimum system Q–Ab–Or at 730 ° C, 1 kbar H₂O and eutectic Q–Ab–Or with 4 wt.% F, 1 kbar H₂O at 630 ° C [Manning, 1981].

The above comparison of experimental and natural data relates mainly to the equilibrium of the silicate melt with cryolite in the experiments and to granites interspersed with cryolite, which crystallized from saturated fluorine magmatic melts. At the same time the particularly important result of experiments is the detection of alkali aluminofluoride (salt) melt resulting from immiscibility of silicate and salt melts in the fluoride saturated system. Much wider field of immiscibility was found in the system by replacing the sodium and potassium of lithium in Li at content from 0.5 to 2.5 wt.%. Salt melt is in equilibrium with the aluminosilicate one, as well as quartz and feldspar up to 650 ° C and probably at lower temperatures.

In our opinion similar to that salt melt is a medium from which nests, lenses, veins, and large bodies of cryolite under natural conditions crystallized. They usually have a clear phase boundaries with the host or attendant bodies of alkali granites and pegmatites. Examples of such large structures can serve cryolite deposits associated with granites: Ivigtut, Ulugh Tanzek, Zashihinskoe; with pegmatites – Zapot (Nevada, USA), Ilmensky mountains, Morefield (Virginia, USA, Sangilen), St. Peters House (Colorado, USA). As a rule cryolite body accompanied by a lithium-bearing minerals (mica, cryolitionite, simmonsite), indicating that high Li concentration, along with fluorine in natural environments. According to our experimental data aluminofluoride salt melt, especially if it contains Li, has the ability to concentrates of ore elements such as Li, W, Nb, Hf, Sc, U, Th, REE. It is this set of trace elements which is typical for the investigated objects of alkali-granite formation.

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