

COMPARISON OF NATURAL DATA WITH EXPERIMENTAL RESULTS IN MODEL FLUORINE BEARING GRANITE SYSTEM WITH LITHIUM AND WITHOUT LITHIUM

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Experiments were conducted in quartz- and nepheline normative parts of the model system Si-Al-Na-F-H₂O [1, 2] and in the same system but with lithium addition under T=800C and pressure 1kbar. Li was entered to the system instead of equivalent atomic quantity of Na in the ratio Na/Li=2/1 or 1/1. The ratio F/O in the start composition without water was equal to 1. New series of experiments cover wider area of Si, Al and alkaline metals ratios than the previous one. New data allow making comparison of experimental phase relations with natural highly evolved fluorine systems, in particular with cryolite and topaz bearing granites.

It was shown that lithium influences greatly on phase relations in run products. Lithium is the very important component of granites, syenites and nepheline syenites. In some kinds of rocks such as rare metal Li-F granites, alkali granites and pegmatites lithium is the major element as Li entered into composition of micas, alkali fluorides, and spodumene. All these types of rocks are connected with different complex metal deposits and lithium is often named ore forming elements [3]. Lithium mineralization is of great importance in the fluorine saturated granite systems in relation with pegmatites, albitites and graisens formation. The direct correlation is found between concentrations of Li and F in igneous rocks. Therefore the investigations of lithium influence on phase relations in fluorine saturated granite system are of interest for geologists.

All experiments were conducted in platinum capsules by quenching method in the high-pressure hydrothermal vessel with external heating. The pressure was maintaining accurate to ± 30 a bar, the temperatures - $\pm 5^\circ$. The duration of experiments was from 3 up to 7 days. Starting materials for experiments were prepared as gels of stoichiometric composition NaAlSi₃O₈, Al₂SiO₅, SiO₂ by a standard technique or used reagents NaAlO₂, AlF₃, NaF, LiF, Na₃AlF₆. The weight of solid charge was 60-100 mg. The amount of water made up 4-7 % from the weight of the charge. On the basis of the known literary data we considered, that the system is saturated with water at its content is higher than 4 %.

The contents of the main components and fluorine in phases was conducted with the help of microprobe complex on the basis of a raster electronic microscope « Jeol ISM-6480LV » with the combined system X-ray spectral microanalysis, uniting energy dispersion « INCA-Energy 350 » and wave diffraction a spectrometer « INCA-Wave 500 » at the petrology department of the Moscow State University. A fluid phase did not investigate.

Analyses of lithium were executed in VSEGEI by means of a measuring complex which consists from ICP mass - spectrometer Element-2 equipped with a source of ions with is inductive - connected plasma and systems laser sampling DUV193, equipped ultra-violet laser COMPex-104 (length of a wave 193 нм). The washer was located in a cell ablation of the system of laser sampling of a measuring complex. The choice of a point of the analysis and positioning of sample were carried out by means of the software of system laser ablation, with visual increase of display of a surface of a washer at the screen of a computer. Diameter of the laser beam made from 10 up to 250 microns, frequency of impulses following - from 2 up to 20 hertz. The maximal depth of a crater formed at the analysis is usually comparable to diameter of a beam. As the "external" standard the reference glass NIST-611 with concentration of elements ~ 450 ppm was used. As the internal standard were used Al and in some cases Si, contained in phases of investigated samples. At such approach relative sensitivity (from Li up to U) turns out from measurement of reference glass NIST, and absolute - from comparison of a mass - spectrometer signal of the internal standard to the data of its concentration received independently. As a whole for most of points of the analysis correct enough result is received that follows at the rate of balance of lithium contents of the phases and initial material of experiences.

Three main phases contain lithium: aluminosilicate melt (L), aluminofluoride melt (LF) and cryolite (Cry). In some cases two more quenched phases with lithium were found – LiF and cryolithionite. It is

established that a field of existence aluminosilicate melt L it is kept approximately in former borders [2] at the presence of lithium and with the same oxide phases (Qtz, Toz etc.), except for sodalite. Phase relations in the system with participation of fluoride phases considerably change at introduction of lithium. Villiaumite is in equilibrium with the peralkaline low silica content aluminosilicate melt. Topaz occurs with peraluminous high silica content aluminosilicate melt. The same villiaumite and topaz stability fields were determinate for Li free conditions.

The presence of lithium essentially enlarges aluminofluoride melt stability field (the field of liquid immiscibility). Compounds of aluminosilicate melt which is in equilibrium with aluminofluoride melt occur in peralkaline and peraluminium part of the system and can be as quartz-normative so nepheline-normative (fig. 1a, b). The ratio Al/Na in the aluminofluoride melts changes from 10/90 to 50/50. The LF compositions with high Al content enlarge LF stability field as compared with one found in system without lithium. The liquid immiscibility area extends due to significant contraction of cryolite stability field. Cryolite remains stable in equilibrium with the most high silica aluminosilicate melt compositions. According to X-ray phase spectrometry the main quenched phase forming from aluminofluoride melt is cryolithionite. It was not noted the influence of lithium on fluorine solubility in aluminosilicate melt.

In a qualitative sense both lithium and lithium free parts of the system satisfies to the natural data: the topaz field of stability is in the peraluminium areas of the system. The compositions of cryolite bearing granites fall within an outlined field of cryolite stability. Villiaumite coexists in equilibrium with agpaite aluminosilicate melts. In this case, despite of significant narrowing of the cryolite field of stability in lithium-containing area of the system, total compositions of cryolite bearing granites [2, 4, 5, 6, 7] correspond to experimentally received data.

A comparison experimental melts with compositions of topaz-bearing rocks (lithium - fluorine granites of Etyka, Orlovka deposits, ongonits) [2, 4] shows that the last correspond better to borders of topaz field of the lithium free part of the system. According to the experimental data in the lithium system the field of melt, equilibrium with topaz, is further from a line corresponding to the agpaite coefficient equal to unit, in comparison with its position in lithium free part of the system. This result demands an explanation and the further studying of phase relations in the field of existence melt with a topaz and specifications of borders position of appropriated fields.

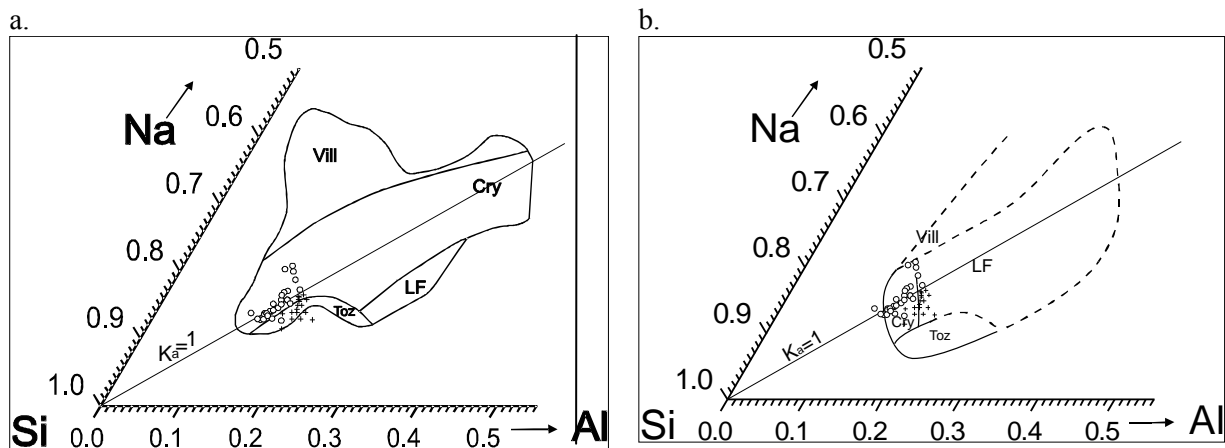


Fig.1. Projection Si-Al-Na on root of a prism Si-Al-Na-F of aluminosilicate melt compositions which are in equilibrium with fluoride phases: Vill-villiaumite, Cry-cryolite, Toz-topaz, LF - aluminofluoride melt. a) in part of the system without Li [2], b) in part of the system with Li. Points-compositions of cryolite bearing granites from different sources [2, 4, 5, 6, 7], crosses-compositions of Li-F granites from different sources [2, 4]

At this stage of works the step aside explanations relatively small-scale occurrence cryolite in a nature is made. At the previous stage, during studying lithium free parts of system, cryolite occupied an extensive field of stability and it was in equilibrium with aluminosilicate melts, appropriate on composition to a plenty of calcium free acid and alkaline rocks. The field of topaz stability was far less than cryolite field.

These facts are in contradiction with occurrence of magmatic cryolite and a topaz in a nature. In lithium-bearing part of the system cryolite is stable in small area of compositions equilibrium aluminosilicate melts, existing only in quartz - normative area. The received disagreements of experiments with topaz bearing granites demand the further studying and, probably, updating of the starting compositions.

The destiny of a salt melt phase LF occupying the most extensive field of stability in lithium - bearing part of system is not clear to the end at temperature decrease and the further evolution magmatic melt. Its existence in a natural environment is confirmed by studying fluid and melt inclusions in minerals [8]. Difficulties of its detection in a nature are connected with its small amount and with possible big mobility aluminofluoride melt. At present the most plausible represents the version about the further evolution of this salt melt to the concentrated water fluid and its possible participation in meta-somatic processing of magmatic massifs and country rocks.

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