

## Interaction in systems of fluid-melt-crystal

### Zubkov<sup>1</sup>E.S., Kotelnikov<sup>1</sup>A.R., Kovalskaya<sup>1</sup>T.N., Konyshv<sup>1</sup> A.A. Effective solubility of fluorine in the aluminosilicate melt (system Si-Al-Na-F-O-H) at 650-750°C and 0.1 GPa

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**Abstract.** Study of the system Si-Al-Na-F-O-H were performed on the rapid-quench cold-seal high-pressure vessel at the temperatures of 650, 700 и 750°C and pressure of 0.1 GPa. All compositions were water-saturated and had maximum fluorine content which was indicated by occurrence of fluorine-bearing minerals in equilibrium with aluminosilicate melt. Dependence of fluorine solubility from a composition of the system, water content and a temperature were investigated. Two local maximums of fluorine solubility were found. Composition of each maximum strongly depends on temperature.

*Key words:* fluorine, cryolite, villiaumite, granite, melt.

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We investigated influence of temperature, system composition and water content on effective fluorine solubility in the model granite and nepheline-syenite melts based on the system Si-Al-Na-O-F. We define term “effective solubility” as maximum fluorine content in aluminosilicate melt of known composition in equilibrium with such fluorine-bearing minerals as cryolite (Na<sub>3</sub>AlF<sub>6</sub>), villiaumite (NaF) and topaz (AlSiO<sub>4</sub>(F,OH)<sub>2</sub>). This is concentration of saturation because with further increasing of fluorine content in the system the amount of fluorine-bearing phase in equilibrium with melt will grow.

Fluorine content in acidic aluminosilicate melt were broadly investigated. In the system granite-HF at pressure of 0.1 GPa villiaumite occur at fluorine content of 1.5-2 wt% [Gluk & Trufanova, 1977]. According to data [Kovalenko, 1979] maximum fluorine content in water-bearing granite melt is 3-3.5 wt%. In water-saturated haplogranite melt at 0.1 GPa and temperature range 680-780°C fluorine-bearing phases were not reported up to fluorine content of 4 wt% [Manning, 1981]. Fluorine content in water-saturated haplogranite melt at 0.1GPa in equilibrium with cryolite was reported as high as 11 wt% [Gluk & Anfilogov, 1973]. Based on study of water-saturated topaz rhyolites [Webster, 1990] in the temperature and pressure range of 770-1000°C and 50-500 MPa, respectively, even at maximum fluorine content in aluminosilicate melt of 6.9 wt% no fluorine-bearing phases were observed.

Despite on significant amount of published data, only few studies contains regular data on effective fluorine solubility in a wide range of acidic aluminosilicate melt compositions. For the water-saturated system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O systematic data on fluorine solubility in the melt were reported at temperature 800°C and pressure 0.1GPa [Gramenitskiy et al, 2005]. Dependence of effective solubility on system composition is complex with maximums of F content (up to 15%) related to quartz-albite and albite-nepheline eutectics. Influence of fluorine-bearing phase on fluorine content in the melt was shown.

In another study of water-saturated system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-K<sub>2</sub>O-Na<sub>2</sub>O at 0.1GPa and temperature range 500-1000°C [Dolejs and Baker, 2007] data on fluorine solubility was not summarized. Data on fluorine content reported for the eutectics granite-cryolite (4 wt% at 640°C), granite-topaz (2 wt% at 640°C) and for the compositions near the granite-topaz-quartz (3.6-5.9 wt% at 580°C). Thus, it was shown that at triple eutectic point fluorine solubility increases.

Dependence of effective fluorine solubility in aluminosilicate melt on temperature are currently poor studied. According to [Webster, 1990] fluorine solubility in melt is independent on temperature in the range of 800-995°C at 2 kbar, but this melt was fluorine-undersaturated. Fluorine solubility is increasing with temperature [Kovalenko, 1977], but this could be referred not only for temperature influence, but to changing composition of melt as well. On the contrary, based on homogenisation temperature of melt inclusions, increasing of fluorine solubility with dropping temperature was reported [Naumov et al, 1977].

This study is based on data of 107 experiments (Table 1). Starting compositions were prepared from the extremely pure reagents (“OSCH” in Russian terminology) and mixed in agate mortar under spirit cover and were placed in platinum tubes with external diameter of 3 mm. Distilled water were added at the amount of 7% of the mixture weight and tubes than were flat-welded. According to data [Holtz et al, 1993] at this water content system is water-saturated under parameters of experiment. For the 2 starting compositions experiments were performed with water content of 30% of a mixture weight. In these experiments equilibrium of melt with significant amount of fluid phase were modelled. Experiments were performed at temperatures of 650, 700 and 750°C and pressure of 0.1GPa on the cold-seal rapid-quench high pressure vessel [Ivanov et al, 1994], which provide cooling to temperatures above 200°C within 5-10 seconds. Some of 20% of experiments were performed on the high-pressure vessels (UVD-10000).

**Table 1. Number of experiments performed under various T - parameters**

| Temperature, °C | Water content, wt% |    |
|-----------------|--------------------|----|
|                 | 7                  | 30 |
| 650             | 15                 | 5  |
| 700             | 27                 | 4  |
| 750             | 54                 | 2  |

All phase assemblages were verified by electron microprobe CAMSCAN MV 2300 (IEM RAS). Analyses were carried out at E<sub>0</sub>=20 kV, τ =70 c, I = 516 pA. Concentrations of elements were calculated with the PAP corrections. Detection limit for fluorine was estimated as 0.5 wt%, relative error for concentration lower than 2 wt% was about 40%, and greater than 2 wt% - 15%.

**Influence of melt composition on effective fluorine solubility**

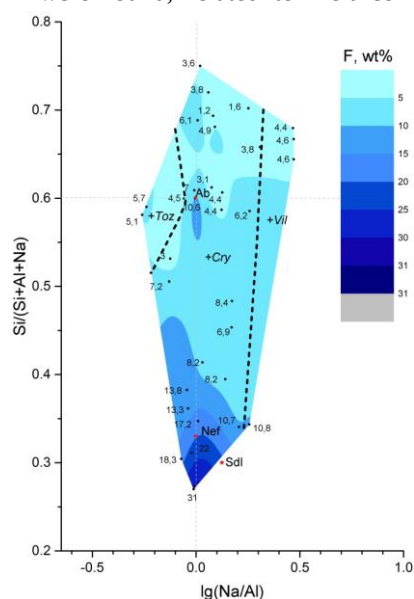
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Experimental results are shown on the fig. 1-3. Y-axis represents silica content in the system, X-axis show logarithm of Al/Na ratio (agpaitic). Different fluorine content is shown in different shades of colour with a range of 5 wt%, lighter colour shade correspond to lower fluorine content and darker – to higher. Following conclusions could be made within studied temperature range:

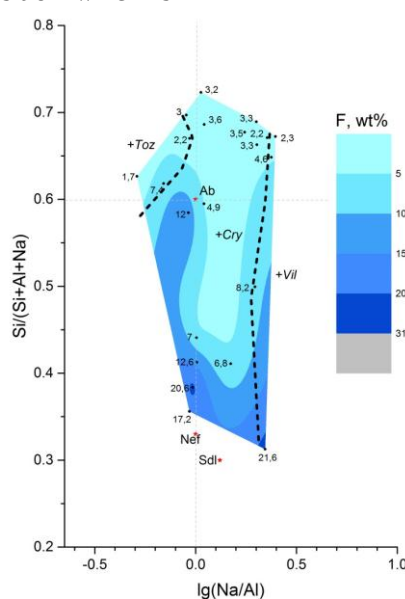
- Fluorine solubility in the system increases from 3 wt% to more than 20 wt% along with decreasing of SiO<sub>2</sub> content from 68 to 32 wt%;
- Two local maximums of effective fluorine solubility were found, related to melt composition which is

approximately correspond to stoichiometry of albite and nepheline;

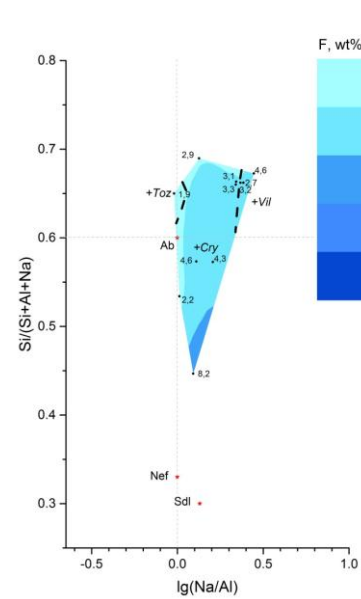
- Area of maximum fluorine solubility related to melt of albite composition are surrounded by melt with fluorine content less than 5 wt% and nearly disappear at 650°C;
- Fluorine content in melts, saturated by topaz and villiaumite is generally higher than in melts of similar compositions saturated by cryolite;
- Magnitude of effective fluorine solubility retained for the melt of given composition as temperature drops from 750 to 650°C.



**Fig. 1. Dependence of effective fluorine solubility from the melt composition. T=750°C.**



**Fig. 2. Dependence of effective fluorine solubility from the melt composition. T=700°C.**



**Fig. 3. Dependence of effective fluorine solubility from the melt composition. T=650°C.**

### Influence of temperature on effective fluorine solubility

As shown on the Fig.1-3, change of temperature significantly effect on the size of a melt field, i.e. for the given system composition at different temperatures different melt composition will formed. Thus, we study fluorine content in the melts of the same composition rather than fluorine content in melts, generated from the same starting composition. In the latter case composition of melt could influence on effective fluorine solubility. For the temperature of 800°C we used data [Gramenitskiy et al, 2005] which were collected in the same system by the same method. Total of 10 melt compositions represents following part of the system:

- Quartz-normative melt in equilibrium with villiaumite (2 compositions);
- Quartz-normative melt in equilibrium with cryolite (3 compositions);
- Quartz-normative melt in equilibrium with topaz (1 composition);
- Nepheline-normative melt in equilibrium with cryolite (4 compositions).

For quartz-normative melt in equilibrium with villiaumite temperature influence on effective fluorine solubility are insignificant – only one melt composition at 650°C has 1.4 wt% less fluorine than melts generated from

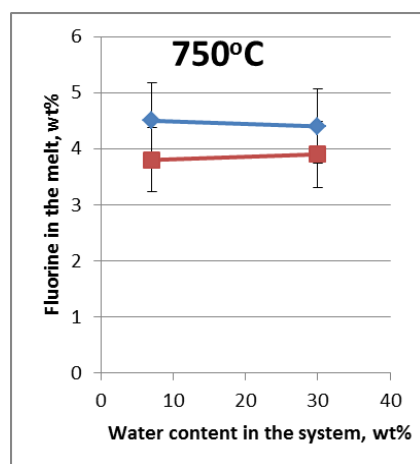
the same starting composition at higher temperatures. For the second melt composition fluorine content is equal in the whole temperature range, and thus no temperature dependences was observed.

For quartz-normative melt in equilibrium with topaz effective fluorine solubility is growing as temperature increases from 2 wt% at 650°C to 12 wt% at 800°C and well approximates by parabolic function.

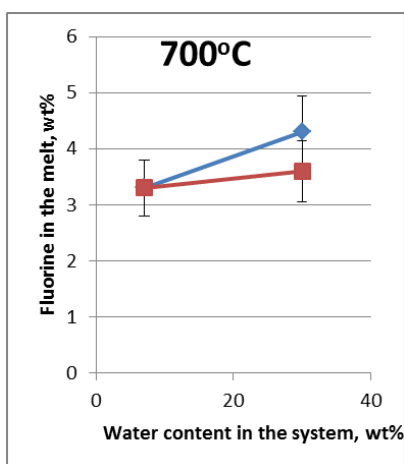
Fluorine solubility in quartz-normative melts in equilibrium with cryolite is increasing from 3-3.5 wt% at 650 and 700°C to 4-7 wt% at 750-800°C. Influence of temperature is growing with decreasing Na/Al ratio in the melt.

For nepheline-normative melt effective fluorine solubility is increasing for 2-3 wt% on average as temperature grows from 650 to 800°C. Inconsistency in this tendency between our data (650-750°C) and data for 800°C [Gramenitskiy et al, 2005] is observed for two melt compositions:

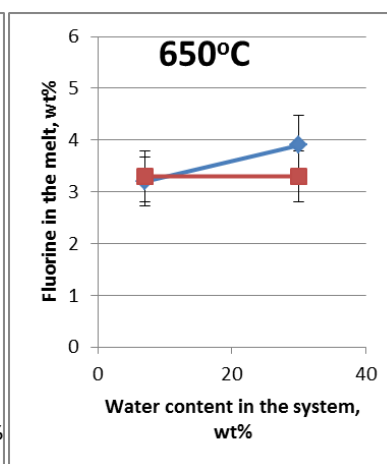
- Increasing of effective fluorine solubility from 5 wt% (750°C) to 12 wt% (800°C) for the first;
- Decreasing of effective fluorine solubility from 6wt% to 5 wt% for the second.



**Fig.4. Influence of water on effective fluorine solubility in the melt, 750°C.**



**Fig.5. Influence of water on effective fluorine solubility in the melt, 700°C.**



**Fig.6. Influence of water on effective fluorine solubility in the melt, 650°C.**

Apart of this data, effective fluorine solubility is increasing with temperature for all melt compositions, except the most silica-depleted. For this composition solubility slightly decreasing from 8.2 wt% at 650°C to 7.5 at 750-800°C.

#### **Influence of free fluid phase amount on effective fluorine solubility**

Two starting compositions forming quartz-normative melts were selected for this study. Run products of all experiments were include aluminosilicate melt, quartz and cryolite. Existence of cryolite indicates that melts were saturated by fluorine. Effective fluorine solubility is shown on Fig. 4-6. As follows from figures, presence of significant amount of fluid phase has weak influence on effective fluorine solubility in melt: for composition 1 solubility is the same in all temperature range, for composition 2 solubility slightly increases for water-oversaturated conditions. It should be noted that that all results are within measurement error of fluorine detection.

**Conclusions.** Complex nature of effective fluorine solubility is shown, including influence of temperature and melts composition. Effective fluorine solubility generally increasing with decreasing silica content in the melt with two local maximums. These maximum are migrate with temperature decreasing from quartz-albite and albite-nepheline eutectics to melts with albite and nepheline stoichiometry, respectively. This dependence is complicated by temperature influence on effective fluorine solubility, especially for quartz-normative compositions in equilibrium with topaz and cryolite.

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**Zubkov<sup>1</sup>E.S., Shchekina<sup>2</sup>T.I., Alferyeva<sup>2</sup>Ya.O., Gramenitskiy<sup>2</sup>E.N., Kotelnikov<sup>1</sup> A.R. Influence of quenching rate on experimental results in the system Si-Al-Na-K-Li-F-O-H at 700–750° and 1 kbar**

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**Abstract.** Sodium, potassium-sodium and lithium-potassium-sodium parts of the system Si-Al-Na-K-Li-F-O-H was investigated on two types of high-pressure vessels. Quenching

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rate up to the temperatures below 200°C was estimated as 3–5 seconds and 2–5 minutes, respectively. All compositions were water-saturated and had fluorides in equilibrium with aluminosilicate melt. Experiments with “slow” cooling contains quenching phases, aluminosilicate melt was enriched by silica and depleted by alkali elements and fluorine, distribution coefficients between alumina-fluoride and aluminosilicate melts vary significantly in comparison with experiments with “rapid” quenching

**Key words:** phase relations, quenching rate, fluorine, cryolite, melt.

**Citation:** Zubkov E.S., T.I. Shchekina, Ya.O. Alferyeva, E.N. Gramenitskiy, A.R. Kotelnikov (2014). Influence of quenching rate on experimental results in the system Si–Al–Na–K–Li–F–O–H at 700–750° and 1 kbar.

System Si–Al–Na–K–Li–F–O–H was investigated in sodium, potassium-sodium and lithium-potassium sodium parts. Starting materials were prepared from extremely pure reagents (“OSCH” in Russian terminology), which were homogenized in agate mortar under the spirit. Each starting composition was loaded in platinum capsule with diameter of 3 mm, 7 wt% of distilled water was added, capsuled than were welded. Based on data [Holtz et al, 1993] we suppose that under experimental conditions system was saturated by water. All experiments were performed under pressure of 1 kbar and temperatures of 750°C and 700°C for sodium and potassium-sodium and lithium-potassium sodium parts of system, respectively.

Two types of cold-seal high-pressure vessels (UVD) with different quenching rates were used. Vessel of a first type is quenched by compressed air, which provide cooling of a system to temperatures below 200°C in 2–5 minutes. In the vessel of a second type [Ivanov et al, 1994] reactor is located on rotary mount and placed in horizontal position during the experiment, and capsules are hold by stainless steel cap. During quenching, reactor is rotated to vertical position, and cap with capsules fall down to cold seal. Thus, quenching to temperature below 200°C performed in less than 5 seconds. Hereinafter vessel of the first type will be referred to as vessel with “slow” quench. And the second one – vessel with “rapid” quench. The chemical composition of phases was studied by electron-probe energy dispersive microanalyzer based on scanning electron microscope Jeol JSM-6480LV (spectrometer X-Max N-50, Oxford Instruments) of Department of Petrology, Moscow State University and electron-probe energy dispersive microanalyzer in IEM RAS.

Experiments were performed with total of 12 starting compositions (Table 1), each composition on both types of vessels (table 2). After experiment capsules were demolished, and each sample was divided on two parts. First part were powdered for X-ray analyses, second was mounted in epoxy for microprobe analyses.

**Table 1. Chemical compositions of starting materials.**

| No of starting material | Composition, at.% |       |       |      |      |       |       |
|-------------------------|-------------------|-------|-------|------|------|-------|-------|
|                         | Si                | Al    | Na    | K    | Li   | F     | O     |
| A-36/11                 | 15.19             | 8.29  | 5.76  | 4.07 | 4.91 | 23.16 | 38.62 |
| A-37/11                 | 15.60             | 8.25  | 8.47  | 5.87 | 0.00 | 22.18 | 39.64 |
| A-38/11                 | 9.28              | 12.51 | 7.87  | 4.77 | 6.32 | 24.92 | 34.34 |
| A-39/11                 | 9.47              | 12.56 | 11.73 | 7.00 | 0.00 | 24.21 | 35.03 |
| A-40/11                 | 17.24             | 6.92  | 5.07  | 3.84 | 4.46 | 21.82 | 40.65 |
| A-41/11                 | 17.41             | 6.77  | 7.35  | 5.49 | 0.00 | 23.18 | 39.80 |
| 1                       | 10.91             | 4.44  | 26.59 | 0    | 0    | 32.58 | 25.48 |
| 2                       | 12.95             | 7.66  | 18.33 | 0    | 0    | 29    | 32.06 |
| 515                     | 7.5               | 8.18  | 27.97 | 0    | 0    | 30.15 | 26.19 |
| 516                     | 13.87             | 9.88  | 16.75 | 0    | 0    | 17.1  | 42.39 |
| 517                     | 13.51             | 10.65 | 16.21 | 0    | 0    | 17.09 | 42.55 |
| 518                     | 11.07             | 12.38 | 18.25 | 0    | 0    | 16.94 | 41.36 |

**Table 2. Number of experiments with different system composition.**

| Composition of the system          | Quenching rate |        |
|------------------------------------|----------------|--------|
|                                    | “Fast”         | “Slow” |
| Si-Al-Na-O-F (quartz-normative)    | 2              | 2      |
| Si-Al-Na-O-F (nepheline-normative) | 4              | 4      |
| Si-Al-Na-K-O-F                     | 3              | 3      |
| Si-Al-Na-Li-O-F                    | 3              | 3      |

### Sodium part of the system

Experiments with two starting compositions were performed in the quartz-normative part of a system (Table

3, Fig.1). Run products are consist of aluminosilicate melt, cryolite and quartz. Villiaumite is only crystallized in experiments performed on the vessel with “slow” quenching rate. Following specific characters of “slow” quenched glass compositions in comparison with “fast” quenching should be noted:

- Depletion by Na with coefficients 1.5 and 1.9 for compositions 1 and 2, respectively;
- Depletion by fluorine with coefficients 3.1 and 8.7 for compositions 1 and 2, respectively;
- Enrichment by silica with coefficient 1.07 for both compositions;
- Si/Al rate for each composition weakly affected by quenching rate and is within 10–15%.

## Abstracts

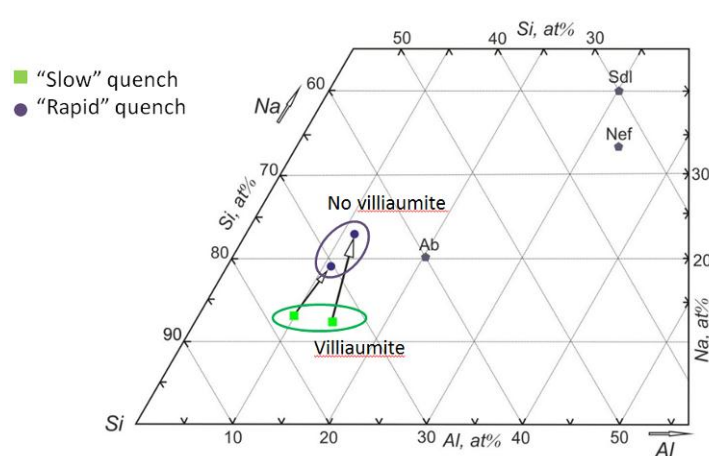
**Table 3. Phase compositions of individual runs and chemical composition of aluminosilicate glasses, quartz-normative area.**

| No of composition | Quenching rate | Composition of aluminosilicate glass, at% |      |      |       |      | Phase relations |
|-------------------|----------------|-------------------------------------------|------|------|-------|------|-----------------|
|                   |                | Si                                        | Al   | Na   | O     | F    |                 |
| 1                 | "slow"         | 27.84                                     | 3.55 | 4.74 | 63.13 | 0.62 | L+Cry+Qtz+Vil   |
|                   | "rapid"        | 26.14                                     | 3.98 | 7.12 | 60.84 | 1.93 | L+Cry           |
| 2                 | "slow"         | 26.63                                     | 5.14 | 4.51 | 63.07 | 0.48 | L+Cry+Vil       |
|                   | "rapid"        | 24.78                                     | 4.25 | 8.64 | 58.17 | 4.16 | L+Cry           |

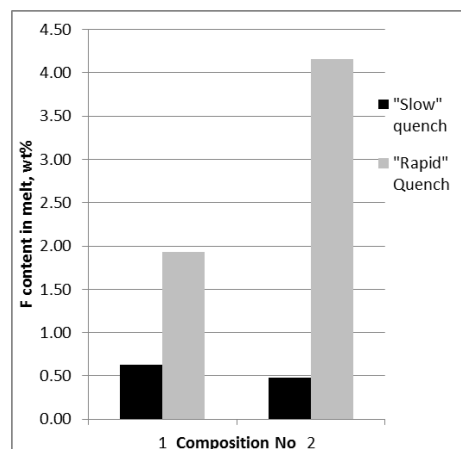
Legend: L - aluminosilicate glass, Cry - cryolite ( $\text{Na}_3\text{AlF}_6$ ), Qtz - quartz ( $\text{SiO}_2$ ), Vil - villiaumite ( $\text{NaF}$ )

Experiments with four starting compositions were performed in nepheline-normative part of the system (Table 4). Typical sign of experiments with "slow" quenching is absence of phase of aluminosilicate melt. That means that melt was completely crystallized during

quenching with formation of such quenching phases like albite and fluorine-sodalite. Nevertheless, experiment 523 confirms stability of fluorine-sodalite under parameters of experiment [Yakubovich et al. 2011].



**Fig 1. Compositions of aluminosilicate glasses.**



**Fig. 2. Fluorine content in glasses, produced on both types of vessels.**

**Table 4. Phase composition of run products. nepheline-normative area.**

| "Slow"     |                   | "Rapid"    |                   |
|------------|-------------------|------------|-------------------|
| Run number | Phase composition | Run number | Phase composition |
| 515        | Sdl+Cry+Vil       | 523        | Sdl+Cry+Vil       |
| 516        | Sdl+Cry+Ab        | 524        | L+Sdl+Cry         |
| 517        | Sdl+Cry+Ab        | 525        | L+Cry             |
| 518        | Sdl+Cry+Vil       | 526        | L+Vil+Cry         |

Legend: L – aluminosilicate glass. Cry – cryolite ( $\text{Na}_3\text{AlF}_6$ ). Qtz – quartz ( $\text{SiO}_2$ ). Vil – villiaumite ( $\text{NaF}$ ). Ab – albite ( $\text{NaAlSi}_3\text{O}_8$ ). Sdl – sodalite ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{F}_2$ )

### Potassium and lithium parts of the system

Experiments were performed with six starting compositions for sodium-potassium and sodium-lithium potassium parts of a system. (Table 1). Experimental results are shown in the Table 5. In all experiments aluminosilicate melt in equilibrium with fluorine-bearing phases was formed. Following points are noted for experiments with "rapid" quench in comparison with "slow" quench:

Absence of quenching metastable phases, represented by chiolite, K-Na feldspar and quartz for sodium-potassium part of system and K-Na feldspar, cryolite and lithium fluoride for sodium-potassium-lithium part of the system;

- Fluoride melt is quenched to homogeneous globules and not decomposed for several quenching phases, which allows to determine composition more precisely;
- Agpaitic coefficient increases by 1.2-1.3;
- Silica content in the melt decreases by 1.05-1.08;
- Effective solubility of fluorine decreases by 1.5-2.1.

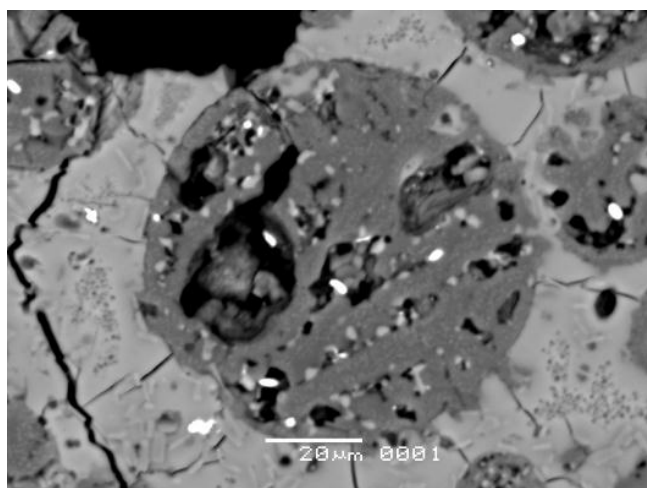


Fig.3 "Slow" quench of LF phase.

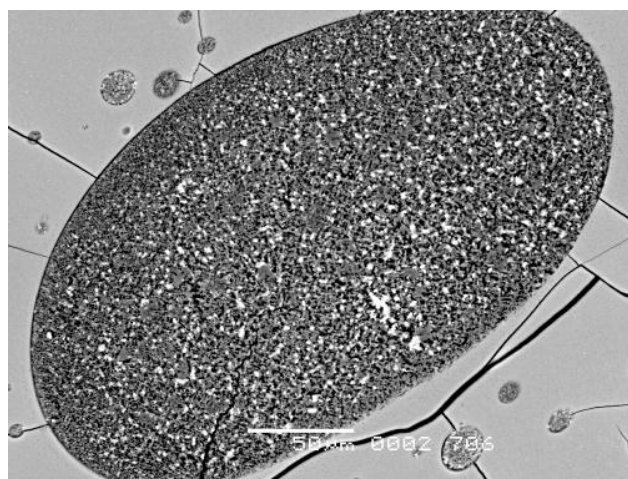


Fig.4 "Rapid" quench of LF phase.

Table 5. Experimental results. Potassium-sodium and lithium part of the system.

| Start composition | Run No. | Quench rate | Phase composition | Composition of aluminosilicate glass. at% |       |      |      |       |       | (Na+K)/Al in L | (Na+K)/Al in LF or FP |
|-------------------|---------|-------------|-------------------|-------------------------------------------|-------|------|------|-------|-------|----------------|-----------------------|
|                   |         |             |                   | Si                                        | Al    | Na   | K    | F     | O     |                |                       |
| A-36/11c Li       | 700     | "slow"      | L+LF+Crl+Fsp      | 22.10                                     | 7.14  | 1.19 | 5.34 | 10.56 | 53.66 | 0.91           | 1.88                  |
|                   | 706     | "rapid"     | L+LF              | 19.63                                     | 7.61  | 4.26 | 4.37 | 16.82 | 47.30 | 1.13           | 1.73                  |
| A-37/11           | 701     | "slow "     | L+Cry+Qtz         | 24.48                                     | 5.42  | 2.01 | 3.99 | 6.36  | 57.74 | 1.11           | 3                     |
|                   | 707     | "rapid"     | L+Cry             | 22.19                                     | 5.79  | 3.01 | 5.14 | 11.89 | 52.00 | 1.40           | 2.91                  |
| A-38/11c Li       | 702     | "slow "     | L+LF+FP           | 14.72                                     | 12.44 | 3.99 | 6.73 | 16.17 | 45.95 | 0.86           | 2.43                  |
|                   | 708     | "rapid"     | L+LF              | 12.43                                     | 12.11 | 6.61 | 6.03 | 25.69 | 37.12 | 1.04           | 1.49                  |
| A-39/11           | 703     | "slow "     | L+Fsp+Cry         | 17.11                                     | 11.37 | 4.71 | 5.50 | 9.24  | 52.07 | 0.90           | 2.97                  |
|                   | 709     | "rapid"     | L+Cry             | 15.32                                     | 10.45 | 5.71 | 7.36 | 15.10 | 46.07 | 1.25           | 2.94                  |
| A-40/11c Li       | 704     | "slow"      | L+Cry             | 25.56                                     | 4.92  | 2.09 | 2.95 | 6.07  | 58.42 | 1.02           | 3.01                  |
|                   | 710     | "rapid"     | L+LF              | 22.16                                     | 6.04  | 3.12 | 4.25 | 13.40 | 51.02 | 1.22           | 1.71                  |
| A-41/11           | 705     | "slow "     | L+Qtz+Chi+Cry     | 25.33                                     | 5.57  | 0.72 | 3.53 | 6.87  | 57.98 | 0.76           | 2.86                  |
|                   | 711     | "rapid"     | L+Cry             | 23.68                                     | 4.65  | 2.68 | 4.61 | 11.14 | 53.23 | 1.57           | 2.9                   |

Legend: L-aluminosilicate melt, LF-alumofluoride melt, FP – crystal fluoride phases, Cry-cryolite ((K.Na)<sub>3</sub>AlF<sub>6</sub>). Qtz-quartz. Fsp-K-Na feldspar. Chi-chiolite (Na<sub>5</sub>Al<sub>3</sub>F<sub>14</sub>)

**Conclusions.** Obtained data show significant influence of quenching rate on the experimental results, both on phase composition of experiments (crystallization of quenching phases) and on chemical composition of aluminosilicate melt in equilibrium with fluorine-bearing phases (depletion by fluorine, enrichment by silica, increasing of agpaite coefficient). Nevertheless data obtained with "slow" quenching rate could be used with correlation coefficient for melt composition and accounting of quenching effects on fluorine equilibrium.

#### References

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