### The Limiting Contents of Fluorine and Water in Highly Differentiated Granite Melts

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**Abstract**—The content of water was estimated in acid aluminosilicate and brine aluminofluoride melts in equilibrium. The solubility of water reaches 7-8 wt % in a silicate melt and 15-19 wt % in an aluminofluoride melt. The maximum concentration of fluorine in an aluminosilicate melt increases with increasing water content in the system.

*Keywords:* highly differentiated granite melts, fluorine-rich granite systems, silicate-brine liquid immiscibility, water content

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### **INTRODUCTION**

The role of highly differentiated, salt-rich magmatic melts in the processes of the formation of raremetal endogenic deposits is an important problem in modern geology. In this relation, it is necessary to provide qualitative and quantitative characteristics for physicochemical equilibria in fluorine-rich magmatic systems. These equilibria are significantly controlled by the temperature, fluid pressure, and concentration of water fluid in melts.

The natural representatives of such systems are differentiated complexes, in which the final phases are characterized by the higher concentrations of many incoherent rare elements in comparison with their clarke values.

Topaz-bearing granite and ongonite, as well as cryolite-bearing granite are major objects of the study. Among silicates in these rocks are minerals with a high concentration of fluorine: micas, amphiboles, and especially topaz. The high concentration of fluorine is typical of melt inclusions in rock-forming minerals as well. At the same time, the bulk concentration of fluorine in rocks may not exceed the clarke values and does not indicate high-fluorine systems. As a rule, a certain rare-metal mineralization associates with all rocks containing fluorides that formed from fluorinerich magmas.

Accumulation of fluorine at the end of the magmatic stage may result in the formation of fluoride brine melts. Some researchers consider that these melts formed via silicate—brine liquid immiscibility as the most likely phases that accumulate many rare metals. The brine melt may transport and accumulate oreforming elements at the magmatic stage of the formation of massifs (Alfer'eva et al., 2011; Devyatova et al., 2007; Gramenitskii and Shchekina, 1993; Gramenitskii et al., 2005, 2008; Shchekina et al., 2013).

According to the data of different authors, the concentration of fluorine in the bulk composition of highly differentiated granite ranges from a few hundredth of a percent to 1-2 wt %. However, these data do not reflect the real content of fluorine in a melt during its crystallization. The study of melt inclusions in rockforming minerals provides the data closest to the real concentration of fluorine in a melt. The concentration of fluorine in melts from inclusions in minerals of Li-F granite rarely falls below 1 wt %. Different massifs show a wide compositional range of melt inclusions. Thomas et al. (2005) reported the compositions of 60 inclusions in guartz from rocks of the Zinnwald Province. The concentration of fluorine in homogenized silicate melts of inclusions varies from 1.9 to 6.4 wt %. These values are much higher than the concentration of fluorine in the bulk composition of crystalline rocks, which does not exceed 0.93 wt %.

As is evident from the study of the composition of melt inclusions in quartz and topaz, the concentration of fluorine in Li–F granite from the Orlovskoe deposit reaches 6.7 wt % (Reyf, 2009). At the same time, the average bulk concentration of fluorine in rocks does not exceed 1.1 wt % (Badanina et al., 2010; Syritso, 2002). The maximum fluorine content (8.9 wt %) was registered in melt inclusions in quartz from granite of

the Krushna Gora (Thomas and Klemm, 1997). At such a high concentration of fluorine in a granite melt, the state of saturation should be gained for one fluorine-rich phase. As is evident from the study of the haplogranite system with fluorine (Gramenitskii et al., 2005), such phases may include topaz, cryolite, williomite, and aluminofluoride melt depending on the composition of the silicate melt (L).

The occurrence of topaz is typical of quartz-normative, highly plumasitic melts; villiaumite is formed in highly agpaitic melts. Cryolite (or its K- or Li-bearing analogs) and aluminofluoride melt are formed in equilibrium with near-normal, moderately plumasitic, and moderately agpaitic silicate melts. As is evident from the experimental data, separation of a brine aluminofluoride melt (*LF*) at a temperature of 800°C and pressure of 100 MPa is probable at a fluorine content in silicate melt of 5–6 wt % (Gramenitskii et al., 2005). With a further decrease in temperature, the concentration of fluorine required for liquid immiscibility decreases rapidly.

The products of aluminofluoride melt quenching usually form round segregations (globules) with a diameter from 5  $\mu$ m to 2 mm (Gramenitskii et al., 2005); sometimes they form a continuous layer located in the upper part of the ampoule, often with evidence for merging of melt drops.

Addition of fluorine to the model granite system results in increase in water solubility in melt. According to the data of Holtz et al. (2001) and Burnham (1975), the solubility of water in quartz-normative fluorine-free silicate melt is 3-4 wt %. It increases by 0.5-0.8 wt % per each 1% of fluorine added (Holtz et al., 1993; Webster at al., 1998). Experiments performed by Holtz et al. (1993) are characterized by the conditions of saturation with water and by a fluorine content up to 5 wt %. In this case, the aluminosilicate melt obtained is not saturated in relation to high-fluorine phases.

Based on the above, our study was aimed at experimental estimation of the solubility of a brine aluminofluoride melt in a haplogranite silicate melt at T =800°C, P = 100 MPa, and a variable starting water content in the system, as well as estimation of the water content in a silicate melt of the fluorine-rich haplogranite system, and calculation of the probable water content in an equilibrium aluminofluoride melt.

# THE METHODOLOGY OF EXPERIMENTAL MODELING AND ANALYTICAL STUDY

The starting compositions were selected with account for the previously determined phase relationships in order to simulate the equilibrium between aluminosilicate and aluminofluoride melts under the hydrous rich conditions of experiment. The composition of the silicate melt ranged from quartz-normative granite to syenite with predomination of alumina over alkalis. The starting water content was 4 and 10 wt % from the dry-sample weight.

Experiments were performed in platinum ampoules by the quench method on a high-pressure apparatus at the Chair of Petrology of the Department of Geology at Moscow State University on a highpressure hydrothermal apparatus with external heating and a cool shutter. The ampoules had a length of 15– 25 mm, an outer diameter of 3.0 mm, and a wall thickness of 0.1 mm. The runs were performed at a temperature of 800°C and a pressure of 100 MPa. The accuracy of pressure maintenance was  $\pm 3$  MPa; the temperature was estimated with an accuracy of  $\pm 5^{\circ}$ C. The weight of the content of each ampoule was controlled before and after a run. The experiment was considered successful if the weigh difference did not exceed 0.001 g.

SiO<sub>2</sub>, NaAlO<sub>2</sub>, AlF<sub>3</sub>, NaF, LiF, gel mixture Al<sub>2</sub>SiO<sub>5</sub>, and distilled water were used as starting materials.

The textural relationships and chemical composition of experimental glasses were studied at the Local Methods of Matter Study Laboratory at the Department of Geology of Moscow State University on a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Energy 350 spectrometer.

To minimize statistical errors in analysis of the concentrations of light elements, we developed a methodology for the optimization of profiles of analyzed elements. Calibration was performed using the standards of natural minerals, namely chiolite (Na<sub>5</sub>Al<sub>3</sub>Si<sub>14</sub>), cryolite (Na<sub>3</sub>AlF<sub>6</sub>), cryolithionite (Na<sub>3</sub>Al<sub>2</sub>Li<sub>3</sub>F<sub>12</sub>), MgF<sub>2</sub>, and feldspars. The accelerating voltage was 10 kV at a current of 0.7 nA. According to this methodology, the error of fluorine analysis was  $\pm 1\%$  from the element concentration.

We used the samples that contain aluminosilicate glass without quenched phases and boiling upon quenching in order to study the distribution of water between aluminosilicate and aluminofluoride melts. Analysis of the water content in globules from aluminofluoride melt quenching products is pointless, since they are composed of quenched fluoride phases only and do not contain traces of glass of an alumofluoride melt at all. The fluid phase was not studied.

The concentration of water in aluminosilicate glasses was analyzed at the Center of Geological Studies (Potsdam, Germany) using Raman spectroscopy. The Raman spectra were obtained on a Jobin-Yvon LabRam HR800 spectrometer equipped with an Olympus optical microscope with an LMPlanFI  $100 \times long$ -focus objective. Radiation was formed by an Ar+laser with wavelengths of 514 and 488 nm. Each spectrum was taken 11 times with an acquisition time of 20 s or longer. Glass with a known water content (8.06 wt %) was applied as a key standard. The water content in the glass was determined by Dr. R. Thomas using the method described in (Thomas and Davidson, 2006; Thomas et al., 2000).

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| Sample no. | Start.<br>H <sub>2</sub> O | Phase composition          | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | F     | O=2F | Meas.<br>H <sub>2</sub> O* |  |  |
|------------|----------------------------|----------------------------|------------------|--------------------------------|-------------------|------------------|-------|------|----------------------------|--|--|
| W4F9       | 4                          | L, LF                      | 72.16            | 18.67                          | 3.08              | 0.21             | 10.15 | 4.27 | 3.2                        |  |  |
| W4F10      | 4                          | L, LF                      | 64.50            | 16.42                          | 0.11              | 12.93            | 10.44 | 4.39 | 4                          |  |  |
| W4F9-2     | 4                          | L, LF                      | 72.42            | 18.77                          | 2.86              | 0.18             | 9.95  | 4.19 | 3.95                       |  |  |
| W10F10     | 10                         | <i>L</i> , <i>LF</i> , ±f1 | 73.12            | 13.10                          | 6.85              | 0.56             | 11.00 | 4.63 | 5.8                        |  |  |
| W10F12     | 10                         | L, LF, Cry, Qtz, ±fl       | 71.24            | 14.52                          | 6.09              | 0.62             | 13.00 | 5.47 | 6                          |  |  |
| W10F14     | 10                         | <i>L</i> , <i>LF</i> , ±f1 | 57.34            | 20.58                          | 12.53             | 0.42             | 15.77 | 6.64 | 7.4                        |  |  |

**Table 1.** The composition of silicate glasses (wt %) normalized to 100% in the samples and the water content in them obtained by Raman spectrometry (\*)

Table 2. Microprobe analyses of the bulk compositions of the products of aluminofluoride melt quenching (wt %)

| Sample no. | Si   | Al    | Na    | К    | Ca   | F     | 0    | Total | H <sub>2</sub> O |
|------------|------|-------|-------|------|------|-------|------|-------|------------------|
| W4F9       | 0.11 | 8.52  | 11.99 | 0.01 | 0.30 | 82.42 | _    | 80.6  | 8.7              |
| W4F10      | 0.12 | 7.66  | 0.22  | 8.30 | 0.22 | 77.16 | —    | 70.0  | 8.9              |
| W4F9-2     | 0.08 | 8.20  | 11.87 | 0.00 | 0.32 | 77.34 | —    | 76.9  | 9.5              |
| W10F12     | 1.50 | 12.11 | 17.93 | 0.14 | 0.34 | 57.35 | 2.44 | 93.2  | 15.0             |
| W10F14     | 1.27 | 11.25 | 16.82 | 0.13 | 0.21 | 53.66 | 3.70 | 90.5  | 18.5             |

(-) The data are absent; the water content was calculated.

## THE RESULTS OF EXPERIMENTAL MODELING

*Run products.* The samples obtained in our runs consist of aluminosilicate glass, products of alumino-fluoride melt quenching, and sometimes, quartz and Li-bearing variety of cryolite (simmonsite) (Tables 1 and 2).

Aluminosilicate glass, the product of aluminosilicate melt L quenching, was the phase that occupied a significant volume of the sample and was contained in all other phases. The run conditions corresponded to the liquidus part of the system. All obtained glasses were high-alumina (Table 1).

The aluminofluoride melt *LF* consisted of an aggregate of quench crystals (Fig. 1). The most abundant minerals among them are cryolite (Na<sub>3</sub>AlF<sub>6</sub>), simmsonite (Na<sub>2</sub>LiAlF<sub>6</sub>), and cryolithionite (Na<sub>3</sub>Li<sub>3</sub>Al<sub>2</sub>F<sub>12</sub>). The potassium-bearing analogs of these minerals are formed in experiments with potassium. Griceite (LiF), chiolite (Na<sub>5</sub>Al<sub>3</sub>F<sub>10</sub>), and others are less abundant. The bulk composition of the entire mixture of quench phases is the most consistent with cryolithion-ite and differs in the low (up to 2%) concentrations of silica and oxygen.

Lithium-bearing analog of cryolite (simmsonite) usually form around crystals in run products. The size of crystals in different runs varies from 50 to 500  $\mu$ m (Fig. 2). The edges of crystals are sharp and even; sometimes they are uneven, similar to resorbed contours (Fig. 2b). Rarely, crystals have well-formed faces (Fig. 2a). The internal structure of crystals is homoge-

neous with the constant atomic proportions of Na/Al/F corresponding to those of simmsonite.

*Water content.* The water contents in aluminosilicate glass are given in Table 1.

The experimental series form two groups of points on the  $C_{\rm F}^{\rm L} - C_{\rm H_{2O}}^{\rm L}$  diagram (Fig. 3). One of them characterizes the compositions of silicate glasses with the initial 10% water content in the system plots slightly below the continuation of the trend obtained by Holtz et al. (1993). It is possible that in these runs saturation by water fluid occurred and the equilibrium between aluminosilicate (*L*) aluminofluoride (*LF*) melts, and fluid (fl) was achieved.

The second group of runs with the initial 4% water content plots significantly below the trend obtained by Holtz et al. (1993). This group does not show a correlation between the concentration of water and fluorine in aluminosilicate glass. It is most likely that the low water content did not allow fluid to form the proper phase and water was totally dissolved in silicate and brine melts.

With account for the two-phase equilibrium (L-LF) in these three runs and using the method of mass balance, we can estimate the approximate water content in the aluminofluoride melt under the run conditions. Based on the known initial and analyzed concentrations of Si, Al, and other elements, we should calculate the weight of silicate and aluminofluoride melts. Knowing the starting water content and its concentration in a silicate melt and with account for the



**Fig. 1.** Products of aluminofluoride melt quenching (LF) and aluminosilicate glass (L) with pores and crystalline phases of quench origin. (a) merging of a drop of fluoride melt with a larger globule; (b) round inclusion of aluminosilicate glass in products of aluminofluoride melt quenching.

absence of an equilibrium fluid phase, we may easily calculate the water content in an aluminofluoride melt.

Table 2 contains the calculated water contents in *LF*. Using these data, we may calculate the coefficients of water partitioning between two melts:  $K_p = C_{\rm H_2O}^{\rm L}/C_{\rm H_2O}^{\rm LF}$ . The values of  $K_p$  obtained for runs W4F9, W4F10, and W4F9-2 are much lower than 1 (0.37, 0.45, and 0.42, respectively), which provides evidence for significant accumulation of water in an alumino-fluoride melt.

Accepting that the partitioning coefficient almost does not depend on the water content and melt composition and that the average  $K_{pH_{2}O}$  is 0.41, we may calculate an approximate water content in the aluminofluoride melt for three other experiments in which the three-phase equilibrium L-LF-fl occurred. Our calculations show that the water content in alumino-



**Fig. 2.** Crystals of a lithium-bearing analog of cryolite (simmsonite) with various shapes. Cry, a lithium-bearing analog of cryolite; Qtz, quartz; *LF*, products of alumino-fluoride melt quenching.

fluoride melt in runs W10F10, W10F12, and W10F14 is  $\sim$ 15–19 wt %.

Figure 4 and Tables 1 and 2 show the relative variation in the concentrations of Si, F, and water in silicate glass and products of aluminofluoride melt quenching. Increasing the water content in a silicate melt in equilibrium with an aluminofluoride melt results in an increase in the limiting fluorine content and, therefore, in an increase in solubility in an aluminofluoride melt.

### DISCUSSION

An increase in water solubility in an aluminosilicate melt with increasing fluorine content was found in several studies (Holtz et al., 1993; Koster van Groos and Wyllie, 1968). It was shown that addition of fluorine into a melt resulted in transition of some Al from four-fold to six-fold coordination and in the formation

of  $AlF_6^{3-}$  complexes in the aluminosilicate melt (Manning et al., 1980; Mysen and Virgo, 1985; Shaller et al.,

1992). These complexes most likely play the net-forming role in aluminofluoride melts.

Gramenitskii et al. (2005) established the dependence of the solubility of high-F phases on the composition of an equilibrium silicate melt. With increasing  $SiO_2$  content in a melt (from nepheline- to a quartznormative melt), the limiting fluorine content in it decreased from 13-18 to 3-5 wt %. In general, our trend of the dependence of the maximum fluorine content in silicate glass of the SiO<sub>2</sub> concentration (Fig. 5) is consistent with the previously obtained trend (Gramenitskii et al., 2005). However, as shown in Fig. 5, the solubility of fluoride phases is controlled by the water content in the system as well. Melts with a starting water content of 4 wt % are saturated by an aluminofluoride melt at a fluorine content of ~10 wt %. With increasing water content, the limiting fluorine content in a silicate melt with the similar SiO<sub>2</sub> concentration may increase up to 12-14 wt %.

The limiting fluorine content required for the formation of high-fluorine phases under the dry conditions will most likely be slightly lower than that under the water-rich conditions.

According to the data of Baker and Alletti (2012), pressure is an important factor that affects the solubility of water in a silicate melt. A pressure of 100 MPa corresponds to water solubility of 4-5 wt % in an acid silicate melt; 6 wt % of water dissolves at a pressure of 200 MPa (Baker and Alletti, 2012). The presence of fluorine in the system influence significantly the data. An acid silicate melt with a water content of 6 wt % may be formed at relatively low pressure (100 MPa) and a temperature of 800°C under aluminofluoride-saturated conditions.

The occurrence of fluorine-rich phases limits increase in the concentration of fluorine in silicate melt as a result of crystallization differentiation. Fluorine is accumulated as an incoherent element until the formation of such high-fluorine phases. Therefore, an increase in the water content controlled by fluorine may proceed until that moment.

The formation of aluminofluoride melt as a highfluorine phase at the final stages of magmatic crystallization is controlled by the composition of a silicate melt (Gramenitskii et al., 2005). Such an aluminofluoride melt may be formed in equilibrium with both agpaitic and moderately plumasitic silicate melts. The melt in the recrystallized state may be easily weathered; therefore, there are only a few reports on its finding (Peretyazhko and Savina, 2010) and indirect evidence for its probable presence in rock are described (Gramenitskii, 1986; Gramenitskii et al., 1998; Shchekina et al., 2013; Syritso, 2002; Thomas at al., 2000).

The data on the water content in aluminosilicate glasses that coexist with the products of aluminofluoride melt quenching and the estimate of the water content in an aluminofluoride melt under the conditions



**Fig. 3.** The correlation between the water and fluorine contents in the aluminosilicate melt: (1) in the haplogranite water-saturated system with the low fluorine content at  $T = 850^{\circ}$ C and P = 100 MPa (Holtz et al., 1993); (2, 3) in the system saturated to aluminofluoride melt: (2) at a starting water content of 10 wt %, (3) at a starting water content of 4 wt %.



**Fig. 4.** The relationship between the concentrations of Si, F, and water (at % from the total) in aluminosilicate glasses and products of aluminofluoride melt quenching (the water content in *LF* was calculated).



**Fig. 5.** The dependence of the limiting fluorine content in experimental glasses on the concentration of  $SiO_2$  in systems with different initial water contents. See Fig. 3 for symbols.

of the experiment show that the water content in a brine alumofluoride melt of the hydrous granite system may be two times higher than that in equilibrium aluminosilicate melt. We may assume its higher mobility in magmatic systems and additional ability for dissolution and transportation of some ore components.

### CONCLUSIONS

(1) An increase in the water content in the haplogranite magmatic system results in an increase of the limiting fluorine concentrations in silicate melt and in an increase of solubility of brine aluminofluoride melt.

(2) The water content in an aluminosilicate melt under the conditions of its equilibrium with fluoride phases (aluminofluoride melt) in the model granite system at 800°C and 100 MPa may reach 7.4 wt % at a fluorine content in melt of 14.6 wt %.

(3) The water content in a brine aluminofluoride melt reaches 15-19 wt %, which is approximately two times higher than that in an aluminosilicate melt.

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