Experimental study of phosphorus and fluorine influence on the superliquidus differentiation of granite melts: preliminary data

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Abstract

Experiments conducted at 800°C and 2 kbar show that interaction of phosphorus and fluorine with granitic melts under H-O-C fluid presence (X_{H2}=0.03-0.04) induces a liquid cluster differentiation of melt into peraluminous and silicic compositions. The enrichment of phosphorus, fluorine, and other volatiles in residual granitic melts might result in the cryptic and contrasting liquid differentiation, with formation of layers as a mechanism of the magma evolution and ore concentration of extremely fractionated Li-F-P granite massifs.

Introduction

The behaviour of phosphorus and fluorine in silicate melts have been the subject of intensive study in recent years in connection with a magmatic evolution of P, F-enriched rare-metal granites (London et al. 1993; Breiter et al. 1997; Webster et al. 1997; Zaraisky et al. 1997).

The mechanism of phosphorus and fluorine enrichment in granite rocks is explained by magmatic processes and/or postmagmatic metamorfism with hydrothermal elements redistribution. However, exactly how the P,F -mineralization formed remains mostly uncertain on account of the absence of experimental data obtained at conditions of complex magmatic fluid.

The aim of this study is to assess experimentally the influence of phosphorus and fluorine on liquid evolution of granitic magma (at superliquidus conditions) under pressure of H-C-O system fluid.

Experimental technique

All experiments were run in the internally heated gas-media pressure vessel at 2 kbar and 800°C. The initial charges were homogeneous glasses obtained by melting rock at 1300°C and 1 atm. The starting granitic melts were powders of glasses of granite from an extremely fractionated Li-F(+P) massifs of Eastern Transbaikalia (Orlovka) and Krusne Hory / Czech Republic (Podlesi). The glasses were pressed into Pt-capsules (25 mm long, 5 mm in diameter, 0.2 mm wall thickness). In general, the starting charge contained 150 mg of glass and fluid (Table 1): water or solution of 10 wt% HF, teflon (C_nF_{2n}), P_2O_5, paraffin (C_nH_{2n}), which were fed into the capsules. The Pt-capsules were sealed and inserted into the gradient-free zone of a tungsten reactor of hydrogen cell (Fig. 1). The hydrogen fugacity was controlled by an argon-hydrogen mixture in the reactor (Bezmen et al. 1992) and was 280 bar, $X(H_2)^{Ar-H}$ = 0.1. As distinct from Ar-H_2 mixtures at 800°C and 2 kbar a relation of gasses in the H-O-C system is strongly unideal. For accurate calculation of other gasses fugacities we must control the oxygen fugacity or fugacity of any C-bearing gas in addition. Since the investigation is preliminary we decided not to complicate experiment and appreciate the oxygen fugacity and the molar fraction of hydrogen approximately. The calculated molar fractions of hydrogen in the capsule were $X(H_2)^{H-O-C}$ = 0.03-0.04 without consideration of C-bearing gasses solubilities in the melts. The oxygen fugacity therein was $\log f_{O2}$=NNO-1,5(2) that corresponds to magnetite stability. The experiments were

kept to 7 days after which the isobaric quenching was performed. The run products were analyzed by optical and electron microprobe (broad beam, 15-20 µ).
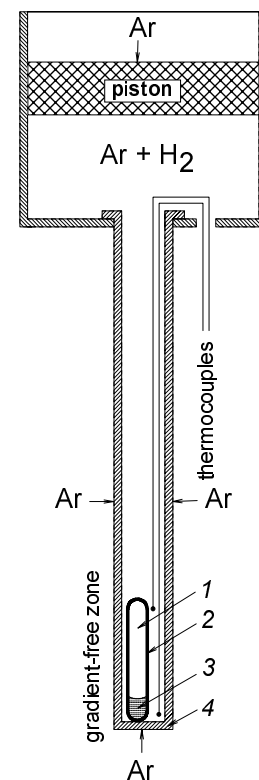
Fig. 1. Reactor set up for conducting experiments under controlled hydrogen fugacity in a gas-media pressure vessel. *1* - hydrogen-bearing fluid, *2* - Pt-capsule, dia. 5 mm, *3* - studied charge, *4* - W or Re reactor.

Experimental results. Before considering the obtained data one must note that all experiments were carried out at the temperatures exceeding of the superliquidus by 100-150°C at least. The water solubility increases in the presence of fluorine (Holtz et al. 1993) and hydrogen (Bezmen et al. 1991) and the melting temperatures decrease accordingly. At X_{H2}=0.04 the solidus curves of albite (Bezmen et al. 1998) and Qz-Ab eutectic (Bezmen et al. this volume) have a pronounced minimum with temperature depression about 30°C. It is known that CO_2 and CO are poorly dissolved in the silicate melt, but the CH_4 behaviour is not obvious. C-bearing gasses have an essential influence on the differentiation of basic-ultrabasic melts (Bezmen et al. 1992) as a consequence of the carbon addition in the experiment.

Table 1. Content of the fluid components in charges

Fluids charge (mg)	Podlesi	granite	Orlo-vka	granite
	Gr-5	Gr-7	Gr-6	Gr-8
Teflon, C_nF_{2n}	10	10	30	15
P_2O_5	5	5	-	-
Paraffin, C_nH_{2n}	10	15	-	-
Water	50	50	-	-
Solution of 10wt%HF	-	-	70	70
F (wt%)*	5.06	5.06	20	12.33
P_2O_5 (wt%)*	3.4	3.4	-	-

* bulk content relative to silicate charge (150 mg)

In experiments under a hydrogen-bearing fluid pressure a very low solubility of the silicate in the fluid was observed (Bezmen, 1992) that gives evidence for the absence of extraction of the components from the melt by the fluid.

At the interaction of phosphorus and fluorine with Podlesi granite melt (Gr-5 and Gr-7 runs) in the presence of H-O-C system fluid in the absence of the thermal gradient and constancy of all other thermodynamic parameters, these develop cryptic layering, a gradual alteration of liquid composition along the sample height and appearance of layers ("lenses") enriched in silica (Fig. 2a, b). The upper boundary of the layers and "lenses" is more sharp and the lower part is diffuse. One can see on Figure 2 that in accordance with an increase of P_2O_5 content in the glass the Na_2O concentration increase relative to K_2O as well as in London et al., 1993. An increase of C-bearing gasses content in fluid phase causes an accumulation of Qz-enriched melt in the upper part of the sample (Fig. 2b).
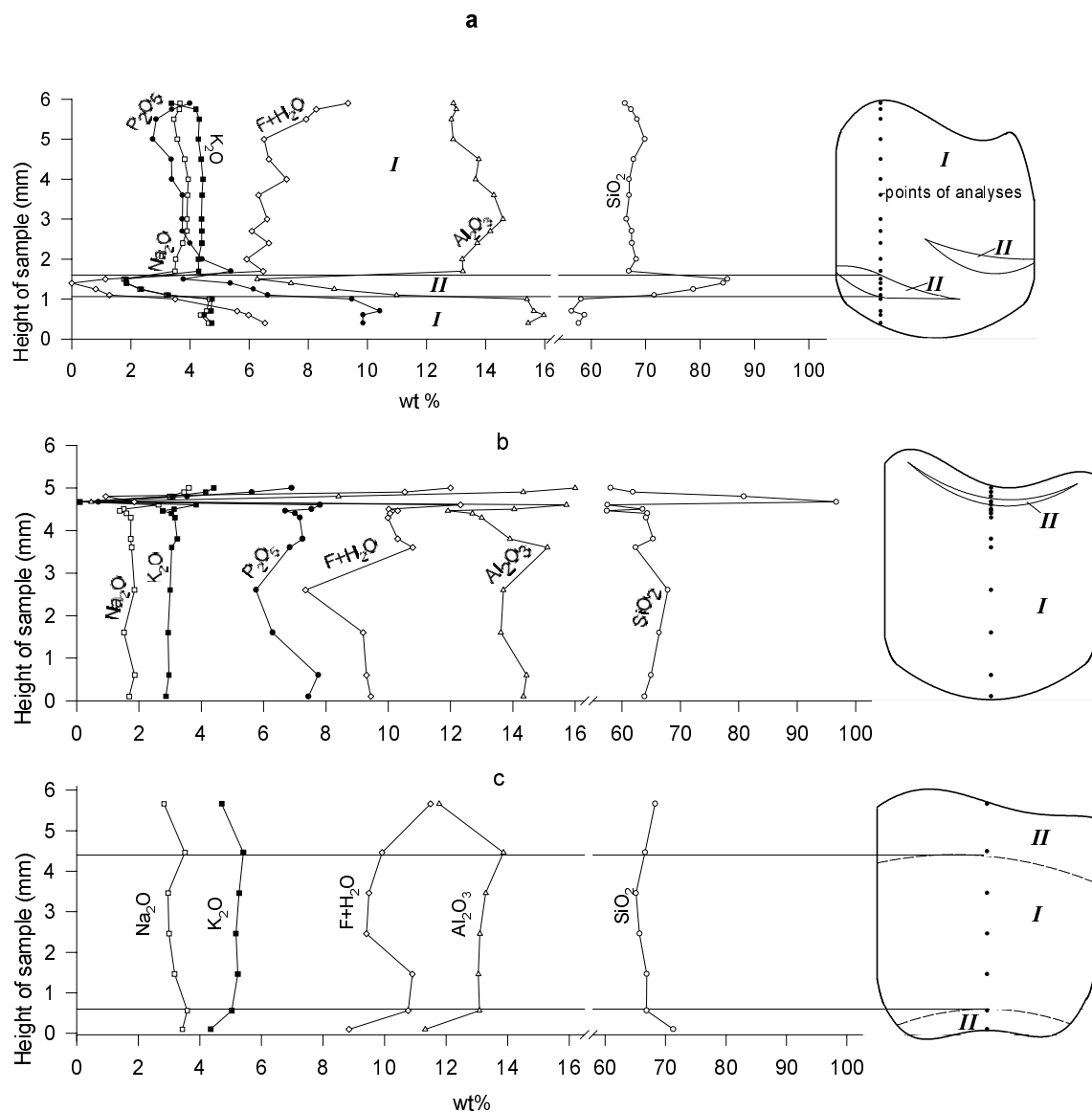
Fig. 2. Cryptic and contrast layering of Podlesi (a,b) and Khangilay (c) granite melts obtained at its interaction with H-O-C-F-P system fluid at 800°C and 2 kbar at duration 7 days. *I* - zones of peraluminous granite; *II* - zones, layers or "lenses" of silicic granite. a-Gr-5 run, b-Gr-7, c-Gr-8 (Table 1).

Table 2. Analytical data of the starting charges and the separated melts of cluster aggregates and matrixes of Khangilay (Orlovka) granite runs (microprobe Camebax data calculated on 100 wt%).

Sample	1	2	3	4	5	6	7	8	9
SiO_2	74.50	87.25	70.12	54.33	52.99	64.66	74.48	79.87	76.09
TiO_2	0.20	0.12	0.32	0.17	0.14	0.27	0.25	0.19	0.21
Al_2O_3	13.80	6.90	18.91	26.33	26.53	13.44	15.18	13.13	13.54
FeO	1.19	0.38	0	0	0.06	0	0.03	0.18	0
MnO	0.03	0	0.15	0.07	0.16	0	0.07	0.23	0.05
MgO	0.29	0.08	0.30	0	0.19	0.87	0	0	0
CaO	0.29	0.25	0.30	0.51	0	0.09	0	0.19	0
Na_2O	3.64	1.59	4.86	11.95	4.81	1.93	3.82	1.6	3.4
K_2O	4.51	3.38	5.01	6.64	15.05	18.68	6.11	4.56	6.64
P_2O_5	0.06	0.05	0.04	0.01	0.07	0.06	0.06	0.05	0.07

1 - starting composition for experimental research (corresponds to Khangilay (Orlovka) biotite-muscovite granite; analyzed glass produced from molten whole rock pulver of sample Z-73)

2-9- experimental melt compositions obtained at interaction F-rich fluid with granite melt under pressure of H-O-C system volatiles (Gr-6: 2 - matrix; 3-5 - cluster aggregates; Gr-8: 6,7 - matrix, 8,9 - cluster aggregates).

The interaction of F-strongly enriched fluid with Orlovka granite melt (run of Gr-6, Table 1) results in the layering in a state of loop form extremely inhomogeneous cluster aggregates placed into silicate-enriched matrix. Three type aggregates are distinguished (Table 2): peraluminous (17-18 wt% Al_2O_3) and strongly peraluminous with predominance of Na_2O (26% Al_2O_3, 15% Na_2O) and K_2O (26% Al_2O_3, 12% K_2O). Unfortunately, we can not analyze fluorine. However, according to sums the matrix is more enriched in fluid (35-40 wt% H_2O +F) then inclusions (20-25 wt %). The cluster aggregates have a disarranged fibrous structure without interface, that is characteristic of solidified colloidal liquids. A decrease of F concentration (run of Gr-8, Table 1) in the run leads to the cryptic layering with formation of zones: upper, middle and lower (Fig.2c). The upper and lower zones are enriched in silica and became poor in alkalis and alumina. There are cluster aggregates and matrix in the every zone. Cluster aggregates are enriched with silica, matrix with alkalis (Table 2).

Discussion. There are numerous data on water, fluorine and phosphorous solubilities in silicate melts. At 800°C equilibrium between fluid and melt is attained during 3.5-4 days incidentally melt is homogeneous. At high concentration of F or P liquid immiscibility form of salt-silicate type. Salt and silicate are separated by interface. At increase of run duration homogeneity in the drops and matrix increases. Speed of quenching depending on the equipment type do not influence on crystals formation in the granite melt practically. In the presence of hydrogen, $X_{H2O}=0.03-0.04$, silicate-silicate layering is developed. (Fig.2). The time of experiments is 7 days and the more duration of H_2-enriched runs the more inhomogeneity (Bezmen 1992).

In our experiments at superliquidus conditions the drops or inclusions with clear interface are absent. What is the mechanism of differentiation?

It is well known that silicate melts have a heterogeneous structure, i.e they are composed of silicon-oxygen complexes whose structure matches that of minerals. The fluidless silicate melts are 3-dimensional reticular polymers which are not capable of the layering. The NMR, IR, and Raman spectroscopy data suggest that hydrogen interacts with the framework oxygen with formation of OH-groups and molecular water, during which event the effective charge of silicon alters (Bezmen 1992). The breakdown of bridge silicon-oxygen bonds gives rise to intensive depolymerization of hydrogen-bearing fluid magmatic melts.

The origin of heterogeneities is connected wih the formation of fluctuating more ordered structures-clusters, which exchange particles and energy with matrix of melt. The depolymerization of melt affects the cluster formation. The degree of silicate melt depolymerization is stipulated by dissolution in the latter of volatiles, specially of hydrogen, phosphorus and fluorine: their presence increases water solubility (Surapure and Hamilton 1984; Holtz et al. 1993; Bezmen at al. 1991). Clusters are intermediate state between liquid and crystal. The popular way to describe clusters is the 'jellium' model (Cohen and Knight 1990) in which the cluster is seen as having a central ordering core of atoms surrounded by a cloud of total electrons. The structure as a whole is uncharged. Moreover, clusters are put together in the associations as a package, spheroids and chains which have the end molecules capable to exchang with matrix (Strepiheev and Derevitzkaia 1976). Clusters are stabilized by the presence of appropriate ligands (Schmid 1985; Pruchnik 1990). Most of the pioneering experimental work has been done using complex organic reagents (see Schmid 1985), but theoretically most

of the ligands (such as F, P_2O_5, OH) should be suitable to effect such stabilization. The ligands do not form 'formal' chemical bonds with the cluster core, but rather arrange themselves as symmetrical (usually nearly spherical) envelopes around the cluster in such a way that repulsion is minimized (Schmid 1985). The atoms in the ligand layer are highly mobile, so that the structure as a whole develops a solid-like core with a liquid-like surface (Schmid 1985). The behaviour of clusters cannot be predicted by 'classical' chemical principles: various studies on such diverse properties as ionization potentials and nearest neighbour distance has shown that the values for clusters of an element is intermediate between that obtained for its individual atoms and the bulk crystal (Stace 1988). As it was shown experimentally under certain critical thermodynamical conditions the aggregate of clusters are capable of the gravitational movement (Bezmen 1992) with the accumulation of colloidal liquids which after quenching have the disarranged fibrous solidified structures.

Experimental data have shown that P and F in the presence of hydrogen and other gases of H-O-C system bring about cryptic and contrasting layering of granite melt of silicate-silicate type (peraluminous granite-silicic granite, Fig.3). Unfortunately, we can not analyze the F distribution along height of samples, but preliminary data revealed essential increase in F concentration in hydrogen-bearing silicate melts (up to 9 wt%). After crystallization owing to high F affinity to hydrogen it should be redistributed to the gas phase and abandons the silicate. We are going to verify that experimentally.
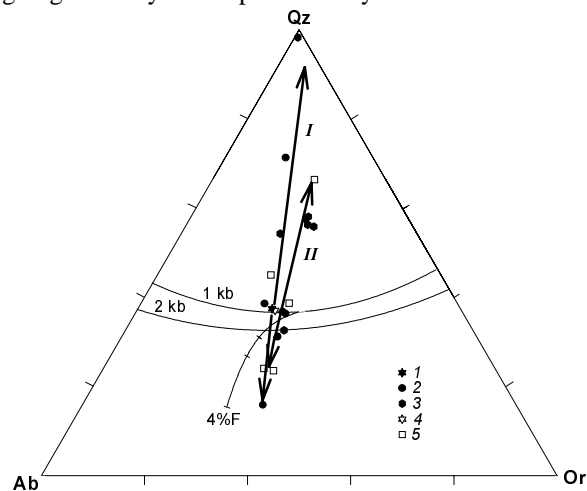
Fig. 3. The Ab-Or-Qz normative diagram of the experimental data. Solidus curves of haplogranite system in the presence of H_2O (2 kb) and H_2O-F fluid were constructed from experimental data given in Manning (1981) 1-starting compositions of Podlesi granite, 2-Gr-5, 3-Gr-7, 4- starting compositions of Khangilay granite, 5- Gr-6,8.

Conclusion. In the evolution of granite massifs a residual melt enriched in P,F and other volatiles. While reaching the concentration of fluid enough for a cluster differentiation this melt develop with formation of the layered rocks between which fluid and other components including Li, Ta, Nb, ets are distributed .

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