Experimental testing of line rocks in Li-F granites: evidence from superliquidus experiments with F and P added

ALEXEI FEDKIN[1]* – REIMAR SELTMANN[2] – NIKOLAI BEZMEN[1] – GEORGE ZARAISKY[1]

[1]Laboratory of Ore Deposits Modelling, Institute of Experimental Mineralogy RAS, 142432 Chernogolovka, Moscow District, Russia
*Corresponding author: Present address: Dept. of Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637, USA;
e-mail: avf@uchicago.edu
[2]Centre for Russian and Central Asian Mineral Studies, Department of Mineralogy, Natural History Museum, Cromwell Road, London SW7 5BD,
United Kingdom

A b s t r a c t . New experimental data on the simulation of layered textures typical of some highly evolved granites are presented. In the experiments, low-evolved and high-evolved granite systems were compared, both doped with F and F+P. Most of the runs exhibit zones of quartz crystallization within a chemically heterogeneous granite glass. The experiment using typical material from the Li-F-P-rich Podlesí granite stock (Krušné hory Mts., Czech Republic) as a starting charge, with added F and P, resulted in discrete microlayering. In the quenched glass, rhythmically alternating thin (5–10 μm) bands either enriched or depleted in alumina occurred. The experimental result simulates natural analogs of granitic line rocks, which occur locally in the Podlesí stock as well as in the Orlovka and Etyka granite massifs, Eastern Transbaikalia (Russia).

K e y   w o r d s : alkali feldspar granite, layered intrusion, fluorine, lithium, phosphorus, melting experiment, melt, X-ray data

Introduction (previous models of line rocks)

The highly fractionated Li-F granites are among the final products of granite magma evolution. Some of them contain so-called line rocks – layered textures due to variable modal composition of the individual layers corresponding totally to the melting temperature minimum composition in the Qtz-Ab-Or-system with 2% F (Manning 1981). Such textures were reported and studied geochemically in many granitoid massifs within pegmatite aplite units (London 1987), as comb-quartz layers in the granite-aplites (Povilaytis 1990, Kirkham and Sinclair 1988, Lowenstern and Sinclair 1996), as rhythmical thin-banded textures in granitic rocks (Rockhold et al. 1987, Zaraisky et al. 1997). There are abundant hypotheses on the genesis and formation mechanisms applied to any kind of granitic line rocks due to powerful theoretical modelling, experimental studies, and from using a geochemical and petrological approach.

A. A. Yaroshevsky (1970) studied a process of zonal melting and oriental crystallization in near-eutectic systems. The possibility for creating a pattern of rhythmical zoning by crystallizing the near-eutectic magma as layered zones conforming to a contact surface was proven.

McBirney and Noyes (1979) associate rhythmical layering with oscillatory supersaturation of a boundary layer in front of crystallization front.

According to Povilaytis (1990) accumulation of the fluid phase as a trigger of the layering process shifts the eutectic composition and provides crystallization of mineral present in excess. During crystallization the system composition approaches the eutectic, which results in the formation of a layer of eutectic composition. At some distance from the cooling front this process also occurs. A sharp temperature gradient between the cool surface of the host rocks and the intruded hot magma causes the layered texture formation. Low viscosity magma at a temperature close to the liquidus is important in this model whereas the undercooled acid magmas are normally highly viscous and tend to form homogeneous glass.

Shannon et al. (1982) considered a variety of unidirectional solidification textures (USTs) mostly as comb-quartz layers or comb-feldspar layers developed in aplite granite groundmass. Such textures are due to quartz crystal growth at fluid saturation conditions; the possible fluid pressure drop results in undercooling of the system and crystallization of granite-aplites in association with comb layers (Lowenstern and Sinclair 1996, Carten et al.1998, Kirkham and Sinclair 1988). This crystallization sequence reflects the shift of the quartz-feldspar eutectic in response to a change in fluid pressure (Tuttle and Bowen 1959, Jahns and Burnham 1969).

Webber et al. (1997) developed an oscillatory diffusion model for the layered dike bodies within pegmatite-aplite systems. In their study the complex dikes characterized by zones enriched in garnet or alternatively in albite-quartz-muscovite were formed through oscillatory nucleation and crystallization. Any factor that triggers undercooling under non-equilibrium crystallization is able to provide heterogeneous nucleation and oscillatory crystal growth. This will result in the formation of excluded components in front of the crystallization front and line rock formation. In this model the role of mafic components is significant. The latter are not involved in the crystallizing liquidus phases and are pressed out by the advancing crystallization front. The supersaturation by mafic components favours crystal-

Fig. 1. A representative rock sample of Li-F granitoids from the Orlovka Ta deposit, Eastern Transbaikalia: layered texture (line rock) of the topaz-Li-mica-albite-amazonite granite showing alternating pegmatoid (amazonite-rich) and aplitic (albite-rich) bands.

- pegmatoid amazonite-rich zone
- albite-rich microgranite
- quartz
- amazonite
- albite-rich layer
- quartz-mica rich layers

Fig. 2. A dike like body from the Orlovka Ta deposit, Eastern Transbaikalia. The marginal part (1) near the contact with the host metasedimentary rocks is layered: thin mica-quartz and mica-albite bands are rhythmically alternating. The central part of the dike is represented by massive albite-rich microgranite (2) with no layering.

lization of garnet or other Fe-Mg minerals. Line rock formation ceases when the volatiles accumulated in the residual melt decrease the degree of undercooling. The pressure drop within the dike can be considered as a destabilization factor.

Quartz-feldspar rhythmically layered texture was experimentally simulated by London (1998) from a boron-rich aqueous melt affected by strong undercooling (~150 °C). This texture is explained as formed by accumulation of excluded components along an advancing crystal-melt interface, creating a boundary layer of evolved or highly fluxed melt.

The layered dike formation may be due to fractional crystallization (Morgan and London 1999) where the equilibrium distribution of elements occurs at the crystal/melt boundary. The melt composition evolves based on the compatibility or incompatibility of elements. The composition of the boundary layer changes while the crystallization front moves.

The coexisting aplite layering and pegmatoid quartz-K-feldspar zones can be explained by a different growth-diffusion ratio (Baker and Freda 1999) at undercooling conditions.

Balashov et al. (1999, 2000) developed a model of "swinging eutectic" for the albite-quartz and albite-K-feldspar systems. In the case of the albite-quartz system fluid pressure oscillation resulted in expanding of either the quartz field at high pressure or the albite field at low pressure and further crystallization of alternating albite-quartz line rock. The pressure oscillation was due to granite melt degassing.

In this study, we made an attempt to simulate the layered texture of a granitic glass through the superliquidus experiment. Based on previous publication of this material (Bezmen et al. 1999, Fedkin et al. 1999, Fedkin et al. 2000) we present the data on major element distribution in the experimental glass specimen as a result of a rapid quench run in the F-P-Li-rich granite system. The experiments in high-evolved and low-evolved granite systems are compared in this paper. Granite melting with boron in a water-saturated system resulted in rhythmic layering at a certain degree of undercooling (London 1998). We suppose that also F or maybe a F+P-rich fluid can also result in formation of rhythmical textures in the highly evolved granite systems at superliquidus conditions or during rapid quench. The experimental work would also help evaluating the influence of fluorine and phosphorus on granite evolution with respect to the genesis of fluorine-rich (Orlovka, Transbaikalia) or F+P-rich (Podlesí, Czech
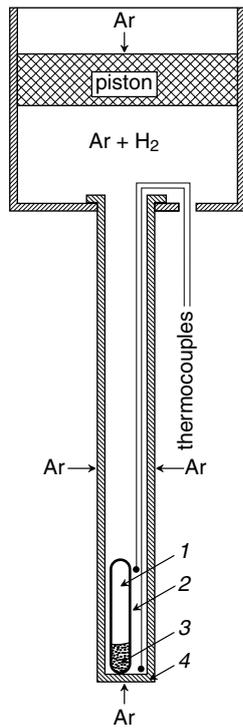
Fig. 3. Scheme of the internally heated pressure vessel (IEM RAS): 1 – hydrogen-bearing fluid, 2 – Pt-capsule of 5 mm in diameter, 3 – studied charge, 4 – W or Re reactor.

Republic) mineralized granites, which is also a subject of discussion (Breiter et al. 1997, Dolejš and Štemprok 2001).

Geological and petrological base

Orlovka and Etyka tantalum deposits, Eastern Trans-baikalia, were the subjects of recent geological and petrological research (Zaraisky et al. 1997, 1998, Fedkin et al. 1998, Seltmann et al. 1998, 1999, Reyf et al. 1999, Balashov et al. 2000), the main focus of which was on the genesis of the layered granitic textures typical of both deposits. Geologically, they are Late Jurassic bt-ms-granite – Li-F granitoid series rocks emplaced in a Triassic metasedimentary sequence (Beskin et al. 1994a,b, Lugovskoi et al. 1972). Granite line rocks (fig. 1) are widely common within the upper parts of the Li-F granite cupola as thin lenses (from several cm to 1–1.5 m in thickness) in massive granites or as dike-like bodies in the host metamorphic rocks (fig. 2). Alternating quartz-rich, albite-rich or K-feldspar (amazonite)-rich zones normally represent such rocks with a highly variable modal composition of the individual layers. Generally, the rocks are enriched in albite in contrast to quartz and K-feldspar. The albite content can reach up to 90–95 vol% within the line rock units, however, the K-feldspar content usually does not exceed 20 vol%. There is a large range in quartz contents reaching 80–85 vol% within the comb-quartz layered rocks.
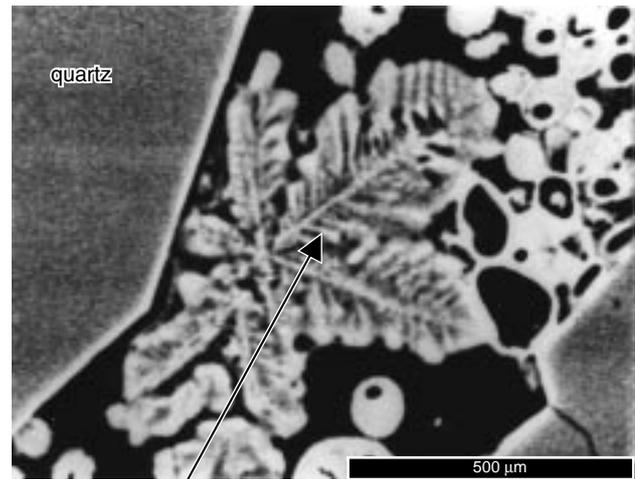
dendrites (comp.1)
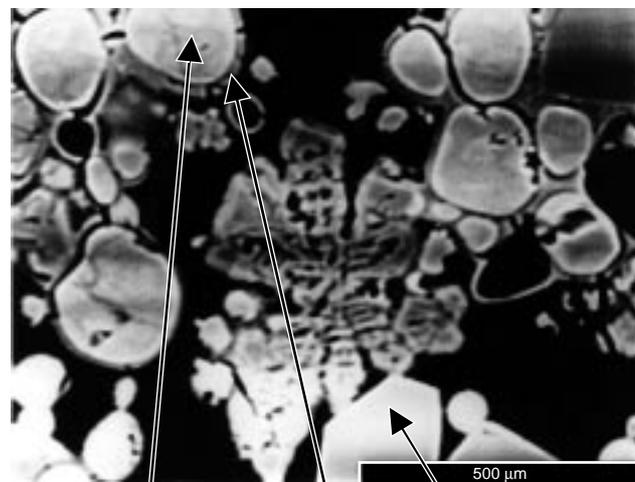
(Al, F)-globules (comp. 2)   rims (comp. 4)   quartz
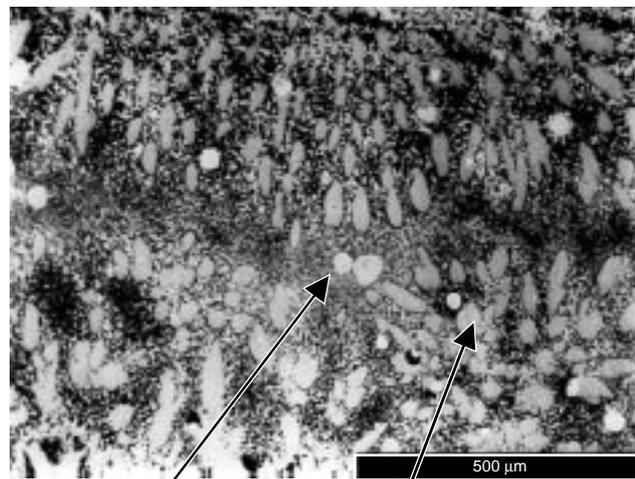
matrix (comp. 3)   globules (comp. 1)

Fig. 4. Back scattered electron (BSE) images (CAMECA SX-100, GFZ Potsdam) showing newly formed phases as a result of the experiment in the highly evolved granite system (G5): *upper* – skeletal growth in contact with an idiomorphic quartz grain (scale bar 20 μm); *middle* – liquid immiscibility (Al, F) globules with reaction films (scale bar 50 μm); *lower* – quench zone in the upper part of the specimen with silica-enriched globules (comp. 1) in the glass matrix (comp. 3; scale bar 500 μm).

Table 1. Whole-rock analyses (wt%, XRF and ISE, GFZ Potsdam) of the granite samples used as starting materials for the melting experiments.

Element	Li-F granite, Podlesí	Bt-ms granite, Khangilay
SiO_2	74.07	75.0
TiO_2	0.053	0.20
Al_2O_3	14.61	13.4
Fe_2O_3	0.80	1.28
MnO	0.01	0.02
MgO	0.08	0.30
CaO	0.50	0.70
Na_2O	3.66	3.67
K_2O	4.07	4.37
P_2O_5	0.558	0.06
H_2O^+	0.47	0.48
CO_2	0.15	0.05
F	1.289	0.123
$-O=F_2$	0.54	0.05
Total	99.78	99.56

phorus on melting and structural features of granite melts was intensively studied (Glyuk and Anfilogov 1973, Kogarko and Krigman 1981, Gramenitsky and Shchekina 1993, London et al. 1993). Enrichment of granite melts by volatile components is a result of magma fractional crystallization differentiation processes. However, their role in line rock formation and the associated mineralization process is not properly understood. The available petrological and geochemical data on Li-F granite complexes (Fedkin 2000) provide information for understanding magmatic differentiation in these systems, but are not, however, sufficient to explain the magmatic layering. An attempt to simulate line rock textures under various experimental fluid and thermodynamic regimes was initiated in this work.

Petrological interest in the genesis of line rocks is due to their association with rare-metal deposits. Experimental and theoretical development of the line rock formation mechanisms can contribute to an ultimate understanding of Li-F granitoid crystallization and related ore accumulating processes.

Melting experiments in fluid-rich granite systems

In some cases both phosphorus and fluorine enrich the residual granite melts during magmatic differentiation (Raimbault et al. 1995, Breiter et al. 1997). The main reason for this is the high peraluminosity in the system (Zaraisky et al. 1998): alumina is bound with phosphorus to form the berlinite molecule $Al[PO_4]$, and fluorine plus alumina form (Al, F) compounds. The Podlesí stock (Krušné hory Mts., Czech Republic) with widely common layered pegmatite-aplite textures is a perfect example of such fluorine- and phosphorus-rich systems. On the contrary, the more alkaline Orlovka and Etyka granites, Eastern Transbaikalia, are highly enriched in fluorine but poor in phosphorus. The influence of fluorine and phos-

Methods and starting materials

The experiments were run in an internally heated gas-media pressure vessel (fig. 3) in the H-O-C system (Bezmen et al. 1999) at P = 2 kbar and T = 800 °C in the presence of fluorine and phosphorus or only fluorine. The two series were: 1) F-P-Li-rich granite system using the Podlesí (Czech Republic) stock granite sample and 2) normal granite system using the barren two-mica granite sample from the Khangilay granite massif (Transbaikalia; Table 1). The starting powders were prepared by crushing the granite samples and carefully homogenizing them with a mortar and pestle. The homogeneous powders were melted at T = 1300 °C and P = 1 bar. The resulting glasses were analysed with a CAMEBAX electron microprobe (IEM RAS) for alkali loss, then doped with fluorine (as teflon C_nF_{2n}), phosphorus (as P_2O_5), hydrogen (as paraffin C_nH_{2n}) and water and pressed into Pt-capsules (25 mm long, 5 mm in diameter and of 0.2 mm wall thickness). In series 1 the calculated values for fluorine and phosphorus in the system were F 5.06 wt%, P_2O_5 3.4 wt%. In series 2 the values were 7.06 and 7.0 wt%, respectively. Where only fluorine was added its content was 12.3 wt% (series 2 only). In all the cases the bulk content of water was 33 wt%. The hydrogen fugacity was controlled by an argon-hydrogen mixture in the reactor and was 280 bar, $X(H_2)Ar-H = 0.1$. Unlike Ar-H_2 mixtures at 800 °C and 2 kbar the gas mixtures in the H-O-C system are strongly non-ideal. It is necessary to control oxygen fugacity and also the fugacity of other C-bearing gases. So as not to complicate the experiment we decided to estimate the oxygen fugacity and hydrogen molar fraction approximately. The calculated molar fraction of hydrogen in the capsule was $X(H_2)^{H-O-C} = 0.03–0.04$ not taking into account C-bearing gas solubility in the melt. The oxygen fugacity was approximately determined as $logfO_2 = NNO-1.5(2)$, which corresponds to the magnetite stability field. Isobaric quenching was performed after seven (fourteen) days of running the experiment.

The run products were examined by EMPA SX-50/SX-

Fig. 5. The experimentally formed rhythmical texture as alternating dark and light layers in the upper quench zone (G5). The length of the image is 1 mm.

Table 2. Microprobe analyses (average values) of the Podlesí experimental product (G5) phases, wt%.
(1 – dendrites, 2 – liquid immiscibility globules, 3 – glassy matrix, 4 – reaction films between globules and matrix)

Comp.	upper zone (1 mm in width)				middle zone (2 mm in width)					lower zone (2 mm in width)			
	1 (n=5)*	2 (n=3)	3 (n=2)	4 (n=1)	1 (n=2)	2 (n=6)	3 (n=4)	4 (n=5)	Bln (n=3)	1 (n=3)	2 (n=2)	3 (n=5)	4 (n=1)
P_2O_5	17.18	8.50	5.27	3.76	21.17	18.02	6.85	6.28	57.51	16.40	14.15	8.05	9.37
SiO_2	49.58	0.31	36.47	17.94	44.27	0.83	32.28	10.30	0.13	50.34	0.72	37.00	24.75
TiO_2	0.03	0.13	0.04	0.05	0.01	0.19	0.07	0.03	0.01	0.04	0.18	0.07	0.10
Al_2O_3	19.34	45.98	30.72	32.43	21.92	43.61	32.90	50.46	40.66	19.37	44.25	31.22	43.12
MgO	0.04	0.36	0.08	0.20	0.01	0.32	0.06	0.01	0.00	0.03	0.21	0.07	0.06
CaO	0.52	3.81	0.81	2.37	0.14	3.59	0.47	0.08	0.02	0.32	1.23	0.43	0.52
FeO	0.02	0.12	0.02	0.07	0.01	0.11	0.03	0.02	0.00	0.02	0.09	0.05	0.00
Na_2O	1.66	6.86	7.20	5.40	1.06	5.45	9.70	10.72	0.01	1.50	9.04	6.47	6.14
K_2O	2.40	4.88	5.21	4.13	2.24	3.30	5.96	5.66	0.01	2.39	6.58	3.13	1.84
Rb_2O	0.23	0.13	0.25	0.17	0.31	0.10	0.23	0.19	0.01	0.26	0.13	0.26	0.27
F	7.88	38.83	27.89	30.93	4.40	39.98	31.90	45.69	0.00	7.71	41.43	30.26	39.80
O=F	-3.32	-16.35	-11.75	-13.02	-1.85	-16.83	-13.43	-19.24	0.00	-3.25	-17.44	-12.74	-16.76
Total	95.6	93.6	102.2	84.4	93.7	98.7	107.0	110.2	98.4	95.1	100.5	104.3	109.2

*1 (n=5) – composition group, in brackets – a number of averaged analyses, bln – berlinite Al[PO4]

100 (GFZ Potsdam). Two regimes were used. Firstly, detailed point analyses of the resulting phases were made under beam conditions of 15 kV and 20 μm spot size. The second step was area scanning of the representative parts of each zone of the run product. The scanning proceeded for six elements: F, P, Si, Al, Na, and K, which allowed a comparison of phase compositions to be made. The beam conditions for the scanning were 15 kV and 2–5 μm spot size, 4–8 μm pixel step.

Results of the runs in the highly evolved granite system (G5)

The electron-probe point analyses revealed four compositions corresponding to the glassy phases with phase borders well distinguished in the BSE images (fig. 4). The abundant dendrites correspond to composition 1 (Table 2). Due to high volatile (F) enrichment during the superliquidus evolution of the melt, liquid immiscibility globules (composition 2) were developed. These are enveloped by thin films (composition 4). The glassy matrix corresponds

Table 3. Chemistry of the vertical zones (upper, middle and lower) in the Podlesí run product (G5) calculated from the X-ray images (wt%).

	upper	middle	lower
P_2O_5	11.36	6.07	9.99
SiO_2	39.65	63.84	59.85
TiO_2	0.05	0.03	0.03
Al_2O_3	25.90	14.54	15.52
MgO	0.07	0.02	0.03
CaO	0.74	0.24	0.19
FeO	0.02	0.01	0.02
Na_2O	5.56	3.26	2.23
K_2O	4.33	2.34	2.35
Rb_2O	0.24	0.13	0.16
F	21.55	11.06	8.29
-O=F	-9.07	-4.66	-3.49
Total	100.39	96.89	95.18

to composition 3. In general the resulting experimental glass specimen is very heterogeneous in texture and composition. Chemically and texturally distinguished phases form a rhythmical layering in the upper part of the specimen as alternating thin bands (dark and light bands in the photo, fig. 5). Chemistry of the experimental specimen was qualitatively analysed and presented as X-ray images

Table 4. Selected microprobe compositions of the experimental phases in the low-evolved granite runs (G12-13) with gradual cooling temperature regime.

	Glass near Qtz	Glass far from Qtz	Silica-poor Na-K-Al-F salts		Mica compositions			Topaz compositions	
	G12b.209*	G12b.247	G13m.73	G13t.85	G13t.86	G13t.87	G13t.92	G13m.79	G13m.256
P_2O_5	10.397	4.847	0.255	0.359	0.214	0.226	0.191	0.137	0.149
SiO_2	46.072	57.134	0.071	6.445	55.438	54.727	57.536	39.653	30.421
TiO_2	0.207	0.163	0.018	0.036	0.067	0.057	0.035	0.102	0.087
Al_2O_3	20.657	17.476	54.36	47.25	19.909	17.053	11.984	43.749	49.898
Cr_2O_3	0.022	0.006	0	0	0	0.012	0.031	0.009	0.024
MgO	0.26	0.07	0.025	0.014	0.002	0.019	0.043	0.027	0.021
CaO	0.252	0.119	0.122	0.017	0.058	0.048	0.087	0.063	0.028
MnO	0.022	0.024	0.117	0.132	0.056	0.045	0	0.011	0.039
FeO	0.007	0.009	0	0.017	0.016	0	0.018	0.015	0.027
Na_2O	3.748	3.468	20.972	5.966	1.853	0.96	0.772	0.245	2.259
K_2O	5.694	5.384	2.167	18.154	10.102	9.117	6.586	2.498	0.811
Rb_2O	0.046	0.083	0	0	0	0	0	0	0.02
F	12.077	9.525	52.407	44.055	14.787	8.035	5.601	16.672	25.747
O=F	-5.085	-4.011	-22.068	-18.551	-6.227	-3.383	-2.359	-7.02	-10.842
Total	94.38	94.30	108.45	103.89	96.28	86.92	80.53	96.161	98.689

*G12b – bottom part of the G12 run specimen (see text for explanation). G13m,t – the middle and the top zones of the G13 run specimen.
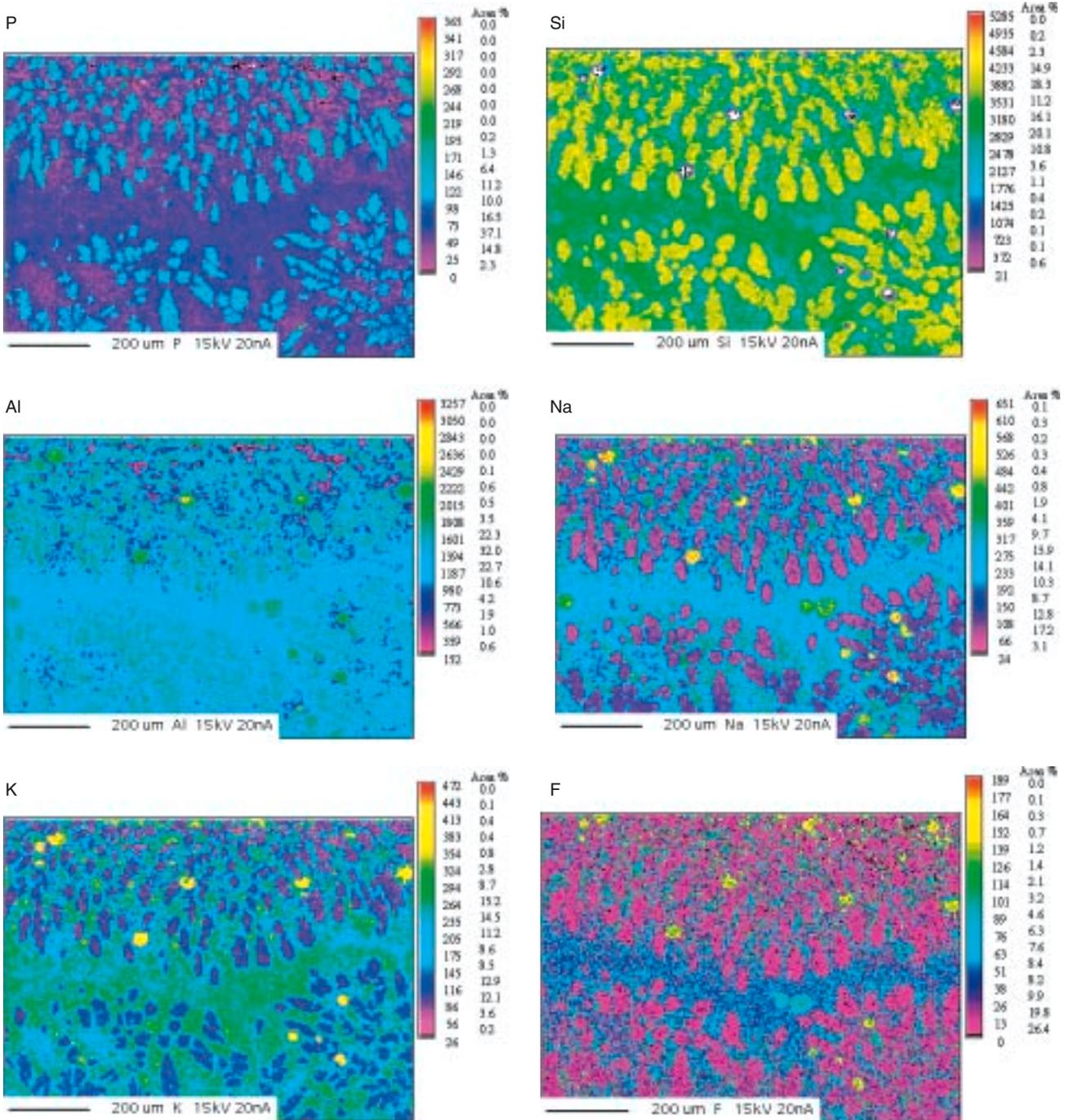
Fig. 6. X-ray images of the experimental specimen (G5) – upper zone. The higher colour intensity shown in the bar on the right side of the image exhibits relative enrichment of a certain phase in the indicated element. The distinguished oval globules are more enriched in phosphorus, silica and alumina and depleted in alkalis and fluorine compared to the coexisting glassy matrix. The white round spots in the Si map and yellowish in the other images represent (Al, F) liquid immiscibility globules with no silica.

for each analysed element performed by CAMECA SX-100 (GFZ Potsdam). These maps clearly represent differences in chemical composition of the resulting experimental phases. In the upper zone (fig. 6) approximately 1 mm wide there are oval globules that differ from the matrix in a higher content of silica (as shown by the higher colour intensity), phosphorus, and lower alkali and

fluorine concentrations. There is no major difference in alumina contents, though the Al map most clearly demonstrates the thin-banded layering in the upper quench part of the sample distinguished by alternating layers of more and less alumina enriched. Line zones of 5–10 μm in width are represented by globular aggregates enriched in alumina and alkalis and the glassy layers are enriched in phos-
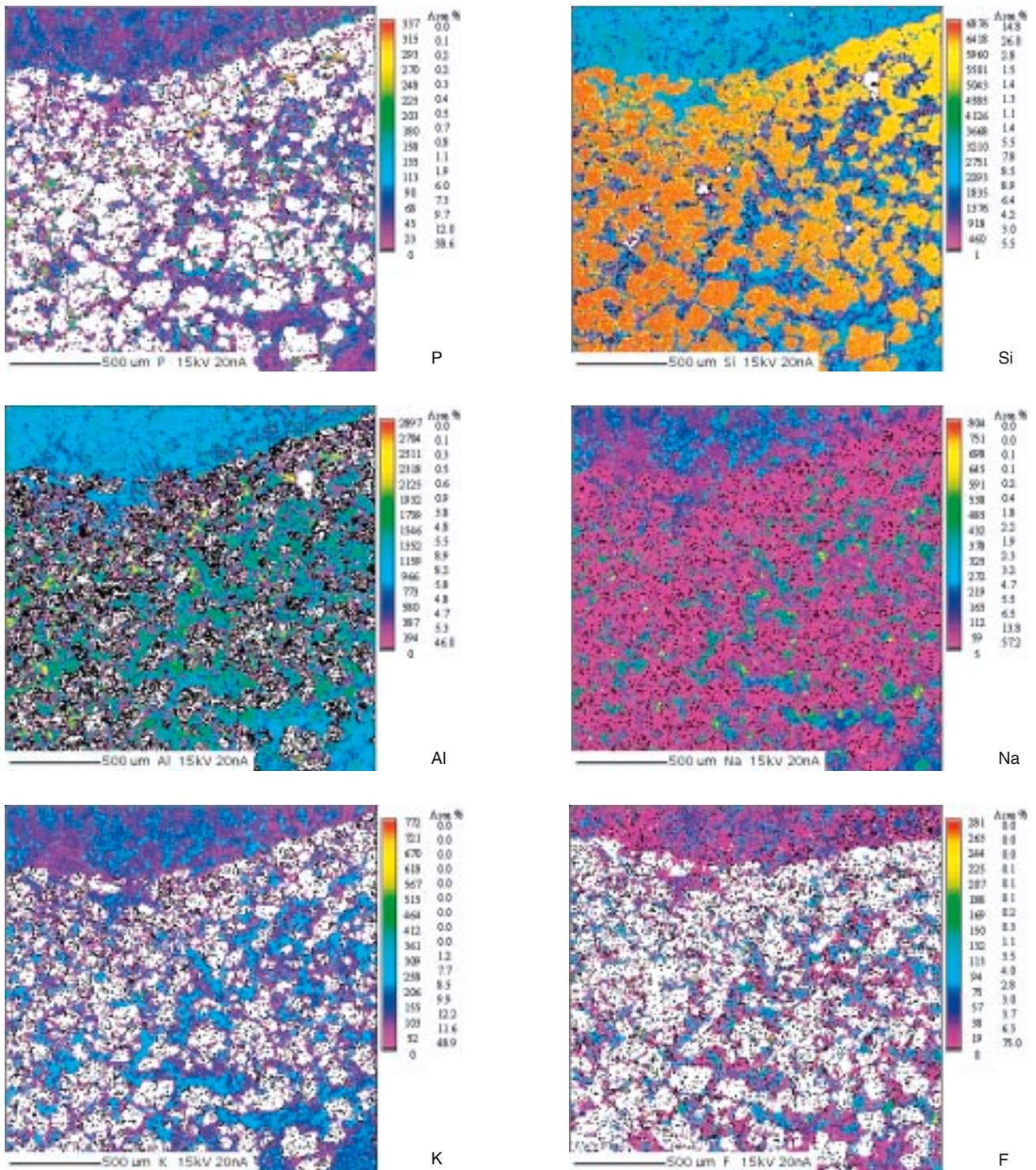
Fig. 7. X-ray images of the experimental specimen (G5) – middle zone. A sharp border between the upper quartz-free zone and the middle quartz-rich zone is visible. Quartz enrichment is shown in the Si-map as orange and in the P-map as white. The high-intensity collored spots just visible in the P- and Al-maps define the berlinite ($AlPO_4$) composition.

phorus and silica. The bands are too thin to be precisely detected by microprobe. However, the phases representing the first group of bands within the layered texture are also represented by coarser oval globules and dendrites (comp. 1) with relatively high silica and phosphorus contents (SiO_2 44–50 wt%, P_2O_5 16–21 wt%) and low alumina, alkali and fluorine contents (Al_2O_3 19–20 wt%, $\sum_{Na_2O+K_2O}$ = 3.3–4, F 4.4–7.8 wt%) in the same zone. The glassy matrix (comp. 3) representing the second group is relatively depleted in silica (32–36 wt%) and enriched in alumina
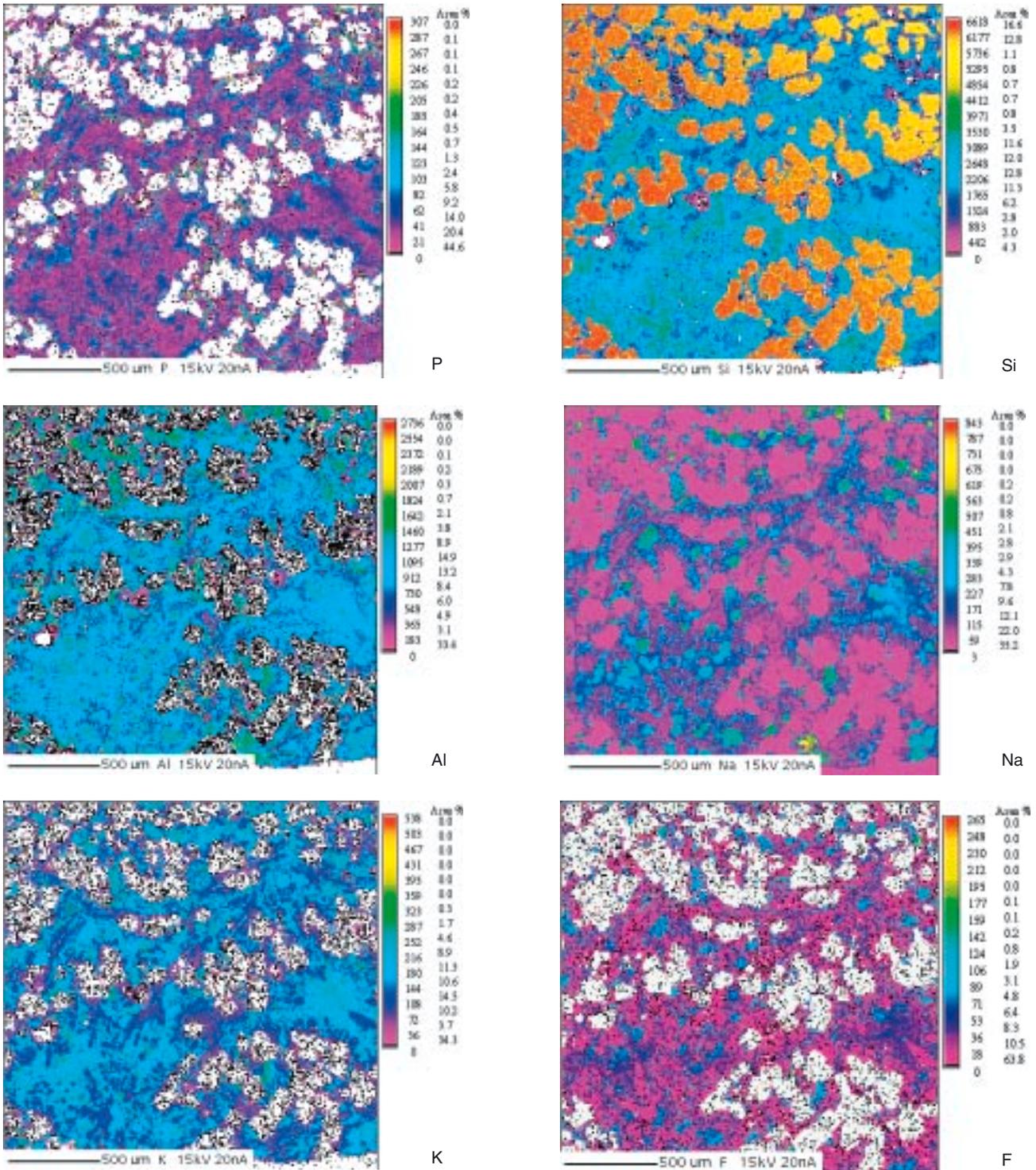
Fig. 8. X-ray images of the experimental specimen (G5) – lower zone – less quartz enriched compared to the middle zone. Dendritic crystals and globules of variable composition in the glassy matrix are abundant.

(30–32 wt%), alkalis ($\Sigma_{Na_2O+K_2O}$ = 9–15.5 wt%) and fluorine (27–30 wt%). Well-distinguished yellowish-white spots are the products of liquid immiscibility. Quartz enrichment in the middle zone (fig. 7) of approximately 2 mm in width is marked by a high colour intensity of the quartz idiomorphic grains. The phosphorus and alumina rich phases are slightly visible in the corresponding images reflecting berlinite compositions in the zone. The lower zone (fig. 8) of approximately 2 mm in thickness is relatively depleted in quartz. It is composed mostly of non-equilibrium glassy aluminosilicate phases slightly different in composition.

Upper zone

Middle zone

Lower zone
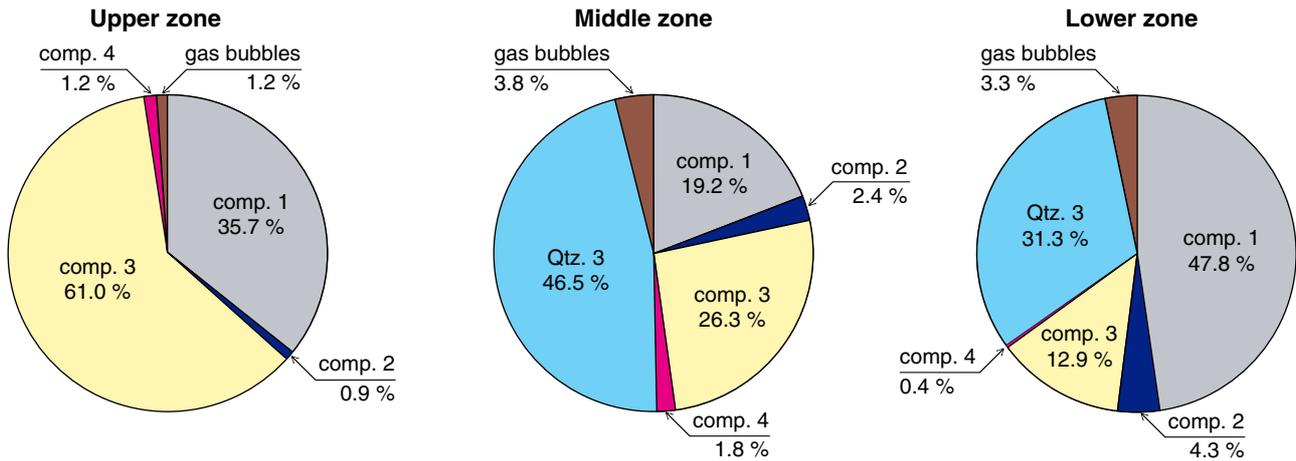
Fig. 9. Contents of the experimental phases (in vol%) of the defined four compositions (G5) calculated from the X-ray image area percent data for the three zones of the specimen.

The above images provide quantitative data in area percent of the distinguished resulting phases within an individual zone. In turn, the electron microprobe point analyses give us the compositions of those phases. Thus, it is possible to calculate the bulk chemical composition of the zones in order to highlight the distribution of the most important components during the experiment. The calculation results are presented in pie diagrams (fig. 9) for each of the zones and in table 3. The data show that the middle zone is mostly enriched in silica, whereas the upper zone is characterized by high concentrations of fluorine, phosphorus, alkalis, and alumina.

Results of the runs in the low-evolved granite system (G10-13)

The normal two-mica granite from the Khangilay complex (Transbaikalia) was used in this series of experiments. Unlike the Podlesí stock granite the Khangilay granite is not mineralized in rare elements and has no significant Li, F, P contents. Fluorine and also fluorine plus phosphorus were added to the glass charge. The run duration was 14 days at T = 800 °C, P = 2 kbar. Isobaric quenching was performed. For comparison, runs with a gradual temperature decrease from T = 800 °C to T = 685 °C (estimated liquidus temperature, Zaraisky 2000) were conducted.

Runs with gradual cooling

Added fluorine and phosphorus in the run (G12) resulted in heterogeneous glass and quartz crystallization. Quartz is usually distributed as line zones along the experimental specimen walls (fig. 10). A change in glass composition occurs when approaching quartz grains: the silica content significantly decreases, while the fluorine, phosphorus and alumina contents increase (table 4, fig. 11). The vertical profile for major components shows enrich-

ment in silica in the central part of the specimen. This was also demonstrated by the experiment in the highly evolved granite system (see above). The silica-enriched part corresponds to relatively low concentrations of phosphorus, alumina and fluorine.

The runs with only fluorine (without phosphorus G13) did not produce any kind of layered zones. Due to the high fluorine concentration salt globules accumulated in the upper part separated from the alumosilicate lower part. The salts are not stoichiometric in composition. However, they may be related to the cryolite – elpasolite series based on elevated F, Al, Na, and F, Al, K contents, respectively. Initially, high fluorine contents in the charge favoured topaz and Li-mica formation (cf. table 4) during the run.

Rapid quench runs

The rapid quench experiment in the presence of fluorine only (G11) resulted in homogeneous glass formation without quartz crystallization or formation of globules and "clusters". Substantial zoning in the glass was not observed.

Added fluorine and phosphorus led to quartz crystallization upon quenching (G10). Idiomorphic crystals formed along the margins of the homogeneous glass specimen (cf. table 4). Several line quartz zones can be distinguished (cf. fig. 10).

Due to more rapid quenching of the run compared to the previous case the glass product does not exhibit substantial changes in composition within the quartz areas.

Discussion

Interaction of added portions of phosphorus and fluorine in the aqueous phase with the Podlesí granite melt developed a cryptic layering of silicate-silicate type. The experiment showing disarranged fibrous solidified structures after quenching may be interpreted as controlled by
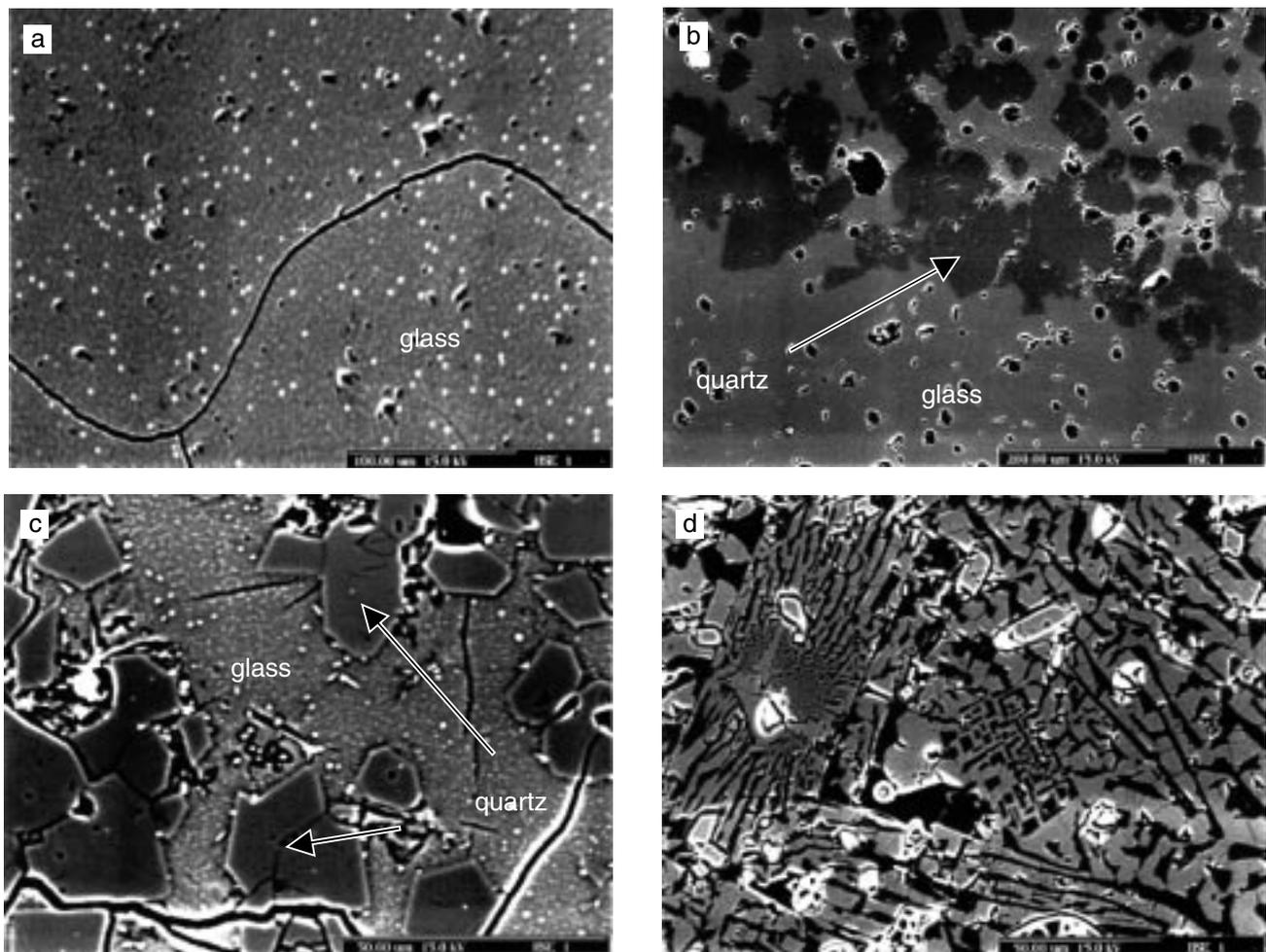
Fig. 10. BSE-images of the run products from the low-evolved granite studies (G10–13); a) homogeneous granitic glass with high fluorine content (up to 10–12 wt%) – the rapid quench run with added fluorine (G11); b) a quartz zone in the homogeneous granite glass with F content up to 6–7 wt% and P_2O_5 – up to 8–9 wt% – the rapid quench run with added fluorine and phosphorus (G10); c) quartz grains within heterogeneous glass – runs with added fluorine and phosphorus with gradual cooling regime (G12); d) Na-K-Al-F salts approaching cryolite and elpasolite compositions – runs with added fluorine with gradual cooling regime (G13).

cluster formation (Bezmen and Elevich 1998). Simultaneously, it may have resulted in separation of the relatively quartz-rich central zone and consequent quartz crystallization resulted in an abrupt increase of fluorine concentration that decreased melting temperature in the system and triggered liquid immiscibility. The silica poor globules are located predominantly near the quartz grains. Uneven distribution of the Al, F-globules is a result of disequilibrium quenching. Due to the latter, skeletal structures and thin-rhythmical layering develop in the upper zone of the specimen. These structures are evidence for strong undercooling in the system.

Other experimental results in granite systems with fluorine (Gramenitsky and Shchekina 1993, Marakushev and Shapovalov 1994) describe liquid immiscibility phenomena as two contrasting compositions represented by alkali-aluminofluoride or aluminofluoride globules in an aluminosilicate matrix under conditions close to equilibrium. However, in this paper we assume that the resulting phases of the four summarized groups of compositions are the product of rapid cooling of the granite melt and they exhibit a variety of textures (globules, dendrites, aluminosilicate matrix, reaction rims, rhythmical layering).

The rapid cooling (quenching) of the fluid saturated (F, P_2O_5) melt contributed to oscillatory nucleation of the quenched phases and layered texture formation. Formation of the layered texture may be due to spinodal decomposition (Skripov and Skripov 1979, Marakushev and Yakovleva 1993) and also due to depolymerization of silicate melts under the influence of not only hydrogen (Bezmen 1992) but also of fluorine and phosphorus (Mysen et al. 1999). Granite melt differentiation can result in separation of the fluid saturated silica-rich liquid causing quartz zone formation. This phenomenon is supported by natural analogs as comb-quartz layers developed in rare metal granites (Lowenstern and Sinclair 1996).

The low evolved granite system has no potential for layering even after significant amounts of volatile components (F+P) are added. However, some heterogeneities in the glass were noticed: the glass near the border with the growing quartz crystals is more enriched in volatiles than that in the remote parts. Such zoning reflects disequilibri-
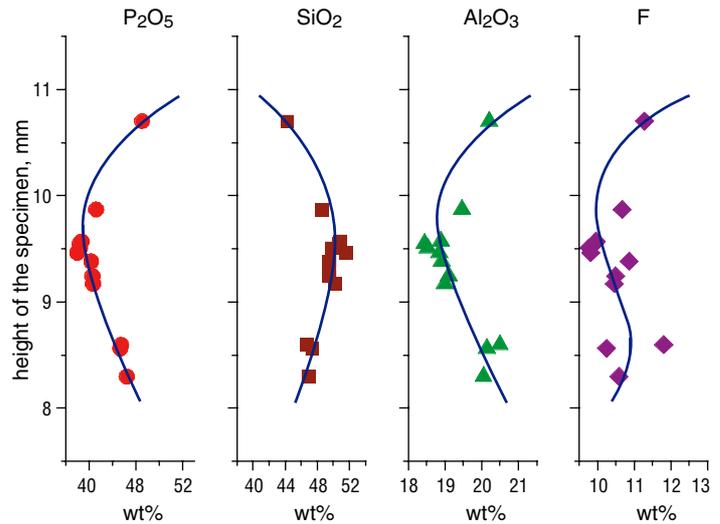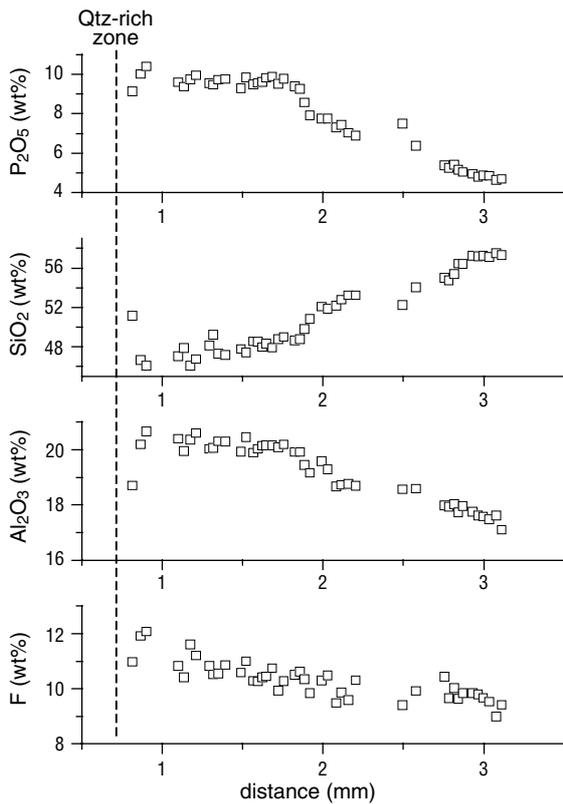
Fig. 11. Horizontal (left) and vertical (right) microprobe profiles through the experimental glass product – low-evolved granite system (G12). The horizontal profiles demonstrate a substantial silica depletion of the zone in contact with quartz grains in the left part of the specimen. The synchronous enrichment of this zone by the other components is observed. Vertical profiles exhibit a substantial silica enrichment of the central part of the specimen compared to the upper and lower zones.

um distribution of various components during quenching. A boundary layer enriched in excluded components is formed in front of the quartz crystallization. Due to the high quench rate the elevated concentrations of fluorine and other components did not reach equilibrium with the rest of the melt. In contrast to the run with the Podlesí stock granite the present series did not produce a thin-rhythmical layering in the quenched glass.

Totally different results of the runs with broadly similar compositions of the starting materials are due to differences in the initial contents of fluorine (1.29 wt% vs. 0.12 wt%) and phosphorus oxide (0.56 wt% vs. 0.06 wt%) in the granite samples used.

Analogies between natural systems and experimental products

Thin-rhythmical layering. The elevated volatile contents, decreasing melt viscosity (Aksyuk et al. 1999) and the significant degree of undercooling (London 1998) in the system favour line rock formation. This is reflected in one of the runs with the Li-F Podlesí granite sample (G-5), as alternating glassy line zones enriched in alumina and alkalis and aggregates and globules enriched in silica and phosphorus in the upper quenched part of the sample, demonstrated in some X-ray images for the upper zone (cf. fig. 6). The proposed layering mechanism is as follows. Firstly, when the temperature drops, nucleation of some phases begins. Secondly, components that make up these phases diffuse toward the growing crystals forming a zone

of depletion adjacent to the crystallization front that inhibits further nucleation. Initial growth must be rapid since nucleation requires a significant degree of supersaturation. Thus, the mechanism strongly depends on the degree of undercooling exhibited by the marginal parts of the experimental specimen or a sharp temperature gradient under natural conditions. As evidence for the latter we can observe the thin-banded Qtz-Ab dike-like bodies or more complex Qtz-Ab-microgranite rhythmic layering texture. In a multiply saturated system the supersaturation of each phase is affected by the nucleation and growth of other phases, so that formation of a layer rich in one mineral component may act to trigger formation of a following layer rich in another (Naslund and McBirney 1996).

The variable composition around the quartz zones (cf. fig. 10) reflects a disequilibrium rapid cooling that favours volatile supersaturation at the crystallization front. It is expressed as a change in glass composition in the experiment (G12). However, in more complex natural systems the same process results in the formation of multiple alternating silicate-silicate type line zones (Orlovka and Etyka Li-F granite systems) under similar thermodynamic conditions.

Quartz zones (comb layers). Volatiles play an important part in the layering process causing the temperature decrease and the minimum temperature composition shift, which determines the liquidus phase composition. Quartz is such a liquidus phase. The quartz line zones formed in some runs are evidence of granite melt enrichment in silica during superliquidus evolution. This occurs due to expansion of the quartz field stability favoured by the acidifying influence of

fluorine and phosphorus (Zharikov 1976). Nucleation and crystallization of quartz results in volatile saturation of the melt and a further decrease in liquidus temperature. This stops nucleation and results in glass formation and non-equilibrium liquid immiscibility phases upon quenching. Quartz zone formation in the experiment may be analogous to a certain stage of comb-quartz layered rock crystallization. Repeated comb layers within the albite-aplite matrix are typical for the Orlovka and Etyka granitic rocks. It is hardly possible to produce such a rhythmical texture experimentally although the physicochemical conditions for such phase relationships were realized during the experiment. The occurrence of the unidirectional solidification textures (USTs) in nature (Shannon et al. 1982) and the experimental studies support a magmatic genesis for the textures formed by the advancing cooling front in the system (Lowenstern and Sinclair 1996).

Fluorine-bearing phases (topaz, mica). Superliquidus conditions and high content of volatiles are possible causes of depressing the liquidus temperature and, thus, making the formation of feldspars impossible during the experiment. As a result, the experimentally produced layered zones are composed of glassy globules and clusters (Bezmen and Elevich 1998, Bezmen et al. 1999) enriched in various components and not by minerals. The fluorine concentration in the melt at late magmatic and magmatic-hydrothermal stages leads to crystallization of greisen-like quartz-topaz-zinnwaldite paragenesis (Xiong Xiao-Lin et al. 1999) typical of the Orlovka granitoids (Zaraisky et al. 1997). The experiments with high-doped fluorine contents confirm the formation of this mineral paragenesis through the occurrence of abundant quartz crystals and the experimentally newly formed phase compositions close to Li-mica and topaz (cf. table 4).

Experimentally obtained zones of different composition and features of rhythmic layering in granite systems reflect a simplified process or some certain stage of igneous layering in the natural analogues. The experiments were conducted based on detailed geochemical and petrological research of the Orlovka and Etyka granite systems (Zaraisky et al. 1997, Seltmann et al. 1999, Fedkin 2000) considering natural T-P conditions (Zaraisky 2000) and fluid regimes by melt inclusion studies (Webster et al. 1997, Reyf et al. 1999). This makes the experimental simulation applicable to the genesis and mechanism of most Li-F granitoids containing layered formations.

Conclusions

Rapid quench of the superliquidus experiment in the highly evolved F-P-Li-granite system (using the Podlesí stock Li-F-P granite, Czech Republic, as an example) produced line rock as rhythmically alternating thin bands in the upper part of the experimental glass specimen. The alternating bands exhibit differences in composition through major component analysis displayed by the corresponding X-ray images. The microprobe compositions of the globules, dendrites and glass constituting individual lines (5–10 μm in thickness) show that the two groups of bands within the layered texture differ from each other in the content of alumina (19–21 wt% vs. 30–32 wt%), silica (44–50 wt% vs. 32–37 wt%), fluorine (4–7 wt% vs. 27–31 wt%), phosphorus (16–21 wt% vs. 5–8 wt%), and alkalis ($\Sigma_{Na_2O+K_2O}$ 3–4 wt% vs. 9–15 wt%).

The low evolved granite system (using the Khangilay two-mica granite, Eastern Transbaikalia, as an example) doped additionally with F or F+P has no potential for layering. Instead, quartz zones form in the heterogeneous glass. The SiO_2 content of the latter substantially decreases at the quartz grain contacts showing the formation of a boundary layer at the crystallization front.

Formation of layered textures during the experiment reflects a certain stage of line rock crystallization in Li-F granites typical of the Orlovka-Etyka sites, Transbaikalia, and the Podlesí stock, Czech Republic.

Li-F granite line rocks form at the latest stage of granite magma evolution. Highly volatile (F)-saturated granite melt and a sharp temperature gradient between the host rocks and the intruded hot magma provide the necessary conditions for layered texture formation.

References

Aksyuk A. M., Fedkin A. V., Seltmann R. (1999): Micas from granites of the Orlovka and Etyka tantalum deposits and estimations of HF concentrations in endogenic fluids. Experiment in Geosciences, 8, 1–42.

Baker D. R., Freda C. (1999): Ising models of undercooled binary system crystallization: Comparison with experimental and pegmatite textures. Amer. Mineral., 84, 725–732.

Balashov V. N., Zaraisky G. P., Seltmann R. (1999): Fluid-magmatic interaction and oscillation fenomena during crystallization from melt. International Symposium "Physico-chemical aspects of endogenic geological processes" devoted to the 100-anniversary of D.S. Korzhinskii, Moscow, 1–26 (in Russian).

Balashov V. N., Zaraisky G. P., Seltmann R. (2000): Fluid-magmatic interaction and oscillation phenomena during granite melt crystallization with water-fluoride fluid gain-loss. Petrologiya, 8, 563–585 (in Russian).

Beskin S. M., Grebennikov A. M., Matias V. V. (1994b): The Khangilay granite pluton and the related Orlovskoe tantalum deposit, Transbaikalia. Petrologiya, 2, 68–87 (in Russian).

Beskin S. M., Zagorsky A. M., Kuznetsova L. G., Kursinov I. I., Pavlova V. N., Prokofev V. Yu., Tsyganov A. E., Shmakin B. M. (1994a): The Etyka rare metal ore field in Eastern Transbaikalia (Eastern Siberia). Geology of Ore Deposits, 36, 281–295.

Bezmen N. I. (1992): Hydrogen in the magmatic system. Experiment in Geosciences 1, 1–33.

Bezmen N. I., Fedkin A. V., Zaraisky G. P. (1999): Experimental study of phosphorus and fluorine influence on the superliquidus differentiation of granite melts: Preliminary data. Experiment in Geosciences, 8, 49–53.

Bezmen N. I., Elevich V. Ya. (1998): Petrochemical types of the PGE-bearing massifs and their petrogenesis. In: Laverov N. P, Distler V. V. (eds) International Platinum, St. Petersburg – Athens. Theophrastus Publications, 8–17.

Breiter K., Frýda J., Seltmann R., Thomas R. (1997): Mineralogical evidence for two magmatic stages in the evolution of an Extremely Fractionated P-rich rare-metal granite: the Podlesí Stock, Krušné hory, Czech Republic. J. Petrol., 38, 1723–1739.

Dolejš D., Štemprok M. (2001): Magmatic and hydrothermal evolution of Li-F granites: Cínovec and Krásno intrusions, Krušné hory batholith, Czech Republic. Bull. Czech Geol. Surv., 76, 77–99.

Fedkin A. V. (2000): Geochemical evolution and layering in Li-F granites from the Orlovka and Etyka tantalum deposits, Eastern Transbaikalia. PhD thesis (Moscow State University, Moscow), 1–161. (in Russian)

Fedkin A. V., Seltmann R., Zaraisky G. P. (1998): Geochemical evolution trends characterizing line rock formation in the Orlovka and Etyka tantalum deposits, Eastern Transbaikalia. Abstr. Int. Meeting "Problems of Genesis of Magmatic and Metamorphic Rocks". S.-Peterb., 144–145.

Fedkin A., Seltmann R., Rhede D., Zaraisky G., Bezmen N. (1999): Reaction of a granitic melt with fluorine and phosphorus enriched fluids at H-O-C conditions. In: Stanley et al. (eds) Mineral Deposits: Processes to Processing, Balkema, 1, 349–352.

Fedkin A., Seltmann R., Zaraisky G., Bezmen N. (2000): Experimental study of the effect of fluorine and phosphorus on layering in Li-F granites. Eighth International Symposium on Experimental Mineralogy, Petrology and Geochemistry (EMPG VIII), Bergamo, Italy, 5, p. 33.

Glyuk D. S., Anfilogov V. N. (1973): Phase equilibria in the system granite – H_2O-KF at water pressure of 1000 kg/cm^2. Doklady AN SSSR, 210, 938–940. (in Russian)

Gramenitsky E. N., Shchekina T. I. (1993): Liquidus phase relationships in the granite system with fluorine. Geokhimiya, 6, 821–840. (in Russian)

Jahns R. N., Burnham C. W. (1969): Experimental studies of pegmatite genesis. 1. A model for the derivation and crystallization of granitic pegmatites. Economic Geology, 64, 843–864.

Jahns R. N., Tuttle F. O. (1963): Layered pegmatite-aplite intrusives. Mineral. Soc. Amer. Spec. Pap. 1, 78–92.

Kirkham R. V., Sinclair W. D. (1988): Comb quartz layers in felsic intrusions and their relationship to porphyry deposits. In: Recent Advances in the Geology of Granite-Related Mineral Deposits. In: Taylor R. P., Strong D. F. (eds) Proceedings of the CIM Conference on Granite-related mineral Deposits, 1985, 50–71.

Kogarko L. N., Krigman L. D. (1981): Fluorine in silicate systems. Nauka, Moscow, 1–125. (in Russian)

London D. (1987): Internal differentiation of rare-element pegmatites: Effects of boron, phosphorus, and fluorine. Geochim. Cosmochim. Acta, 51, 403–420.

London D. (1998): Experimental simulation of a pegmatite texture (abstract). Inter. Mineral. Assoc. 17th Gen. Meet. Abstr., p. A144.

London D., Morgan G. B., Babb H. A., Loomis J. L. (1993): Behaviour and effects of phosphorus in the system Na_2O-K_2O-Al_2O_3-SiO_2-P_2O_5-H_2O at 200 MPa (H_2O). Contrib. Mineral. Petrol., 113, 450–465.

Lowenstern L. B., Sinclair W. D. (1996): Exsolved magmatic fluid and its role in the formation of comb-layered quartz at the Cretaceous Logtung W-Mo deposit, Yukon Territory, Canada. Transactions of the Royal Society of Edinburgh. Earth Sciences, 87, 291–303.

Lugovskoi G. P., Matias V. V., Timofeev I. N., Feldman L. G. (1972): Structure of the rare metal granite massifs and features of their genesis. In: Koptev-Dvornikov, V. S. (ed) Rare metal granites and problems of magmatic differentiation. Nedra, Moscow, 131–161 (in Russian).

Manning D. A. C. (1981): The effect of fluorine on liquidus phase relationships in the system Qz-Ab-Or with excess water at 1 kbar. Contrib. Mineral. Petrol., 76, 206–215.

Marakushev A. A., Shapovalov Yu. B. (1994): Experimental studies of ore concentration in the fluoride granitic systems. Petrologiya, 2, 4–23. (in Russian)

Marakushev A. A., Yakovleva E. B. (1993): The liquid immiscibility heterogeneity of the glassy matrix in the acidic effusives. Vestnik Moskovskogo Universiteta, 4, 78–92. (in Russian)

McBirney A. R., Noyes R. M. (1979): Crystallization and layering of the Skaergaard intrusion. J. Petrology, 20, 487–554.

Morgan G. B. V. I., London D. (1999): Crystallization of the Little Three layered pegmatite-aplite dike, Ramona District, California. Contrib. Mineral. Petrol., 136, 310–330.

Mysen B. O., Holtz F., Pichavant M., Beny J.-M., Montel J.-M. (1999): The effect of temperature and bulk composition on the solution mechanism of phosphorus in peraluminous haplogranitic magma. Amer. Mineralogist, 84, 1336–1345.

Naslund H. R., McBirney A. R. (1996): Mechanisms of formation of igneous layering. In: Cawthorn (ed.) Layered intrusions. 1–43.

Povilaytis M. M. (1990): Rhythmically layered granite intrusions and mineralization. M. Nauka, 1–240. (in Russian)

Raimbault L., Cuney M., Azencott C., Duthon J.-L., Joron J.-L. (1995): Geochemical evidence for a multistage magmatic genesis of Ta-Sn-Li mineralization in the Granite at Beavoir, French Massif Central. Econ. Geol., 30, 548–576.

Reyf F., Seltmann R., Zaraisky G., Fedkin A. (1999): Inclusion derived data on features of tantalite-saturated melt and its responsibility for the formation of the Orlovka tantalum deposit, Transbaikalia. Terra Nostra 99/6 ECROFI XV, GeoForschungsZentrum Potsdam, Germany, 250–252.

Rockhold J. R., Nabelek P. I., Glasock M. D. (1987): Origin of rhythmic layering in the Calamity Peak satellite pluton of the Harney Peak Granite, South Dakota: The role of boron. Geochim. Cosmochim. Acta, 51, 487–496.

Seltmann R., Aksyuk A. A., Fedkin A. V., Zaraisky G. P. (1998): Geochemical evolution trends characterizing pegmatite-aplite and line rock formation related to Li-F granites in the Orlovka and Etyka tantalum deposits, Eastern Transbaikalia, Russia. Ber. DMG Bh. Europ. J. Mineral., 10, p. 271.

Seltmann R., Zaraisky G. P., Aksyuk A. M., Fedkin A. V., Shatov V. V. (1999): Amazonite in layered granites of the Orlovka and Etyka Ta deposits and its relation to magmatic-hydrothermal ore deposition. International Symposium "Physico-chemical aspects of endogenic geological processes" devoted to the 100-anniversary of D. S. Korzhinskii. Moscow, 136–138.

Shannon J. R., Walker B. M., Carten R. B., Geraghty E. P. (1982): Unidirectional solidification textures and their significance in determining relative ages of intrusions at the Henderson Mine, Colorado. Geology, 10, 293–297.

Skripov V. P., Skripov A. V. (1979): Spinodal decomposition (phase transition with consideration of unstable states). Uspekhi Fizicheskikh Nauk, 128, 193–231. (in Russian)

Tuttle O. F., Bowen N. L. (1958): Origin of granite in the light of experimental studies in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2-H_2O. Geol. Soc. Amer. Memoir, 74, 1–153.

Webber K. L., Falster A. U., Simmons W. B., Foord E. E. (1997): The role of diffusion-controlled oscillatory nucleation in the formation of line rock in pegmatite-aplite dykes. J. Petrology, 38, 1777–1791.

Webster J. D., Thomas R., Rhede D., Förster H-J., Seltmann R. (1997): Melt inclusions in quartz from an evolved peraluminous pegmatite: Geochemical evidence for strong tin enrichment in fluorine-rich and phosphorus-rich residual liquids. Geochim. Cosmochim. Acta, 61, 2589–2604.

Xiong Xiao-Lin, Zhao Zhen-Hua, Zhu Jin-Chu, Rao Bing (1999): Phase relations in albite granite-H_2O-HF system and their petrogenetic applications. Geochem. J., 33, 199–214.

Yaroshevsky A. A. (1970): On origin of rhythmic textures in the magmatic rocks. Geokhimiya, 5, 562–574. (in Russian)

Zaraisky G. P. (2000): Crystallization of K-feldspar from the fluorine-rich alkaline melt. Geochemistry of magmatic rocks, XIX All-Russia Meeting, 58–59. (in Russian)

Zaraisky G. P., Seltmann R., Shatov V. V., Aksyuk A. M., Shapovalov Yu. B., Chevychelov V. Yu. (1997): Petrography and geochemistry of Li-F granites and pegmatite-aplite banded rocks from the Orlovka and Etyka tantalum deposits in Eastern Transbaikalia, Russia. Mineral Deposits, Papunen (ed.). Balkema, 695–698.

Zharikov V. A. (1976): Bases of physicochemical petrology. MSU, Moscow, 1–270. (in Russian)