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Phosphorus and rubidium in alkali feldspars: case studies and possible genetic interpretation

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Abstract. Potassium feldspar (Kfs) and albite (Ab) are major hosts of phosphorus in peraluminous highly fractionated granitic systems. Kfs is also an important carrier of Rb. The absolute contents of P and Rb, their homogeneous, zoned, or disturbed distribution within individual Kfs and Ab crystals, the ratio of P contents in the whole rock (WR) vs. Kfs and the ratio of P contents in Kfs vs. albite can serve as useful indicators of the grade of parental magma fractionation and late- and/or post-magmatic crystal–fluid reaction. The P and Rb distributions in feldspars were studied in detail in four peraluminous granitic systems widely differing in intensity of influence of late- to post-magmatic fluids: dominantly magmatic Podlesí granite system (Bohemia), Beauvoir granite (France) influenced by late magmatic fluids, hydrothermaly altered Křížový Kámen granite (Bohemia – Bavaria) and a quartz-Kfs-amblygonite pegmatite-like dyke at Vernéřov (Bohemia). Rubidium is firmly bound in the Kfs lattice and preserves well its magmatic signature during post-magmatic processes. In contrast, phosphorus can be easily released from the feldspar lattice and P content serves as a sensitive indicator of the late- and/or post-magmatic fluid-related reactions.

Key words: alkali feldspar granite, pegmatite, chemical composition, alkali feldspar group, magmatism, fractional crystallization, phosphorus, rubidium

Introduction

Alkali feldspars are major hosts of phosphorus and rubidium in peraluminous highly fractionated granitic systems. The absolute contents of P and Rb, their homogeneous, zoned, or disturbed distribution within individual Afs crystals, the ratio of P contents in the whole rock (WR) vs. Kfs and the ratio of P contents in Kfs vs. albite can serve as useful indicators of the grade of parental magma fractionation and late- and/or post-magmatic crystal-fluid reaction.

High P content in crystal lattice of Kfs was first described from the pegmatite at Hagendorf, Bavaria (Mücke 1966). Later, high P content in both Kfs and albite was identified as an important feature of peraluminous granites by London (1992). P_2O_5 content in granitic Kfs may reach 1–2 wt%, while P content in coexisting albite is usually lower (London 1992, Frýda and Breiter 1995). London et al. (1993) calibrated the distribution coefficient for geologically relevant conditions $D_P^{Afs/melt} = 2.05*ASI-1.75$ and $D_P^{Kfs/Ab} = 1.2$. During late magmatic and/or post-magmatic reactions with fluid, phosphorus is much more easily released from the lattice of albite than from Kfs, and the disequilibrium in P content between Kfs and Ab may indicate some kind of fluid-involved post-magmatic alteration (Breiter 1999).

High Rb content in Kfs was reported especially from the pollucite-type pegmatite. Magmatic microcline contains up to 2–4 wt% Rb_2O, triclinic feldspars formed in subsolidus conditions may exceed the limit of 50 mol% in Rb-feldspar rubicline (Teertstra et al. 1997, 1998). The reported Rb contents in granitic Kfs are much lower (Parsons 1994, Deer et al. 2001).

The Podlesí granite stock (Czech Republic) and the Beauvoir granite stock (France) represent two well-described P- and Rb-rich, strongly fractionated granitic systems with similar chemistry of parental melts but different late-magmatic and fluid evolution. This, taken together, allows to estimate the influence of magmatic and post-magmatic processes on the concentration and distribution of both elements. In addition, some complementary data from P-rich granites and pegmatites from Bavaria and western Bohemia are also presented.

Brief characteristic of the studied granitic systems

Podlesí

The Podlesí granite system is located in the western part of the Krušné hory Mts. within the Saxothuringian Zone of the Bohemian Massif, Czech Republic. It is the youngest intrusion within the multistage late Variscan peraluminous tin-specialized Eibenstock-Nejdek granite pluton, intruding the Lower Paleozoic phyllites and Variscan biotite granite. The Podlesí granite stock is generally formed by a tongue-like intrusion of albite-protolithionite-topaz granite (stock granite), at the upper contact rimmed by marginal pegmatite (stockscheider) (Fig. 1). The stock granite is intercalated with flat dykes of the albite-zinnwaldite-topaz granite (dyke granite) at a depth of 40–100 m with locally well-developed magmatic layering. The stock granite is strongly fractionated, rich in P (c. 0.5% P_2O_5), F (0.5–1.2%), Rb (c. 1000 ppm), Li (500–1000 ppm), and Cs (100–150 ppm) (Tab. 1). The dyke granite represents extremely fractionated residual

Table 1. Average of chemical compositions of granite types from Podlesí (borehole PTP-1, wt%).

Unit	upper stock granite	UST dyke granite	homogen dyke granite	deeper stock granite
n	7	1	8	20
SiO_2	73.5–74.4	67.3	68.8–72.5	72.5–74.0
TiO_2	0.03–0.08	0.02	0.02–0.05	0.03–0.05
Al_2O_3	13.8–14.1	17.5	14.8–15.9	13.8–14.5
Fe_2O_3	0.1–0.5	0.15	0.1–0.3	0.1–0.3
FeO	0.5–0.9	0.6	0.8–1.1	0.7–1.0
MnO	0.020–0.025	0.052	0.04–0.18	0.02–0.03
MgO	0.04–0.07	0.02	0.02–0.04	0.03–0.06
CaO	0.40–0.55	0.29	0.16–0.64	0.35–0.50
Li_2O	0.17–0.21	0.32	0.20–0.40	0.13–0.20
Na_2O	3.9–4.1	3.2	3.8–4.7	3.5–3.8
K_2O	4.1–4.6	7.6	3.5–4.6	4.2–4.5
P_2O_5	0.41–0.46	0.82	0.62–0.87*	0.44–0.50
F	0.90–1.15	1.57	1.5–2.4	0.9–1.2
Rb	0.11–0.13	0.30	0.17–0.19	0.11–0.14

* in outcropping part of the dyke up to 1.5% of P_2O_5

melt even more enriched in P (c. 1% P_2O_5), F (1–1.5%), and Rb (up to 3000 ppm). Prominent manifestation of K-feldspar-dominated unidirectional solidification textures (UST sensu Shanon et al. 1982) were found within both the stock and dyke granite types. The system was studied along a vertical section by up to 350 m deep drillholes PTP-1 and PTP-2 (Lhotský et al. 1988) and PTP-3 and PTP-4a (Breiter 2002).

Beauvoir

The Beauvoir granite stock is a small body (<0.2 km^2) at the southern edge of the late Variscan Echassieres granite pluton in the northern part of the French Massif Central, about 50 km NNW of Clermont-Ferrand, France. Geochemically it is a highly specialized, strongly peraluminous, rare metal-bearing granite enriched in P, F, Li, Rb, Nb, Ta, Sn, and W, and depleted in Si, Fe, Ti, Mg, Sr, REE etc. The Beauvoir granite is the latest intrusion in a peraluminous granitic complex composed of three successively emplaced units: the hidden more-or-less hypothetical La Bosse granite, the Colettes two-mica granite, and the Beauvoir topaz-lepidolite-albite granite (Cuney and Autran 1987, Cuney et al. 1992). The 900 m deep drillhole GPF1 allowed to study the vertical evolution of the Beauvoir granite in an interval more than 700 m thick. Three granitic units, designated B1 to B3, were distinguished by Rossi et al. (1987) and Raimbault and Azencot (1987). Later, a detailed geochemical study subdivided the Beauvoir granite into two substantial units: B and B' (Raimbault et al. 1995). Unit B builds the upper part of the stock and represents geochemically more evolved, more fluid-enriched part of the Beauvoir initial magma. Unit B', smaller in volume, represents relatively less evolved and later emplaced portion of the Beauvoir magma. Separation of melts of units B and B' took place in the early stage of the granite system evolution. Later, both melts fractionated in fact independently. Upper unit B can be divided into three sub-units from the uppermost, ultimately fractionated unit B1 (depth 98–423 m) through unit B2 (depth c. 423–571 m) to unit B3 (depth 765–790 m). Within the lower unit B', a relatively more fractionated unit B'2 (depth c. 571–746 m) and less fractionated unit B'3 (depth c. 850–870 m) can be distinguished. An idealized cross-section of the Beauvoir granite stock is shown in Fig. 2, characteristic chemical analyses of individual genetic granite units are presented in Tab. 2.

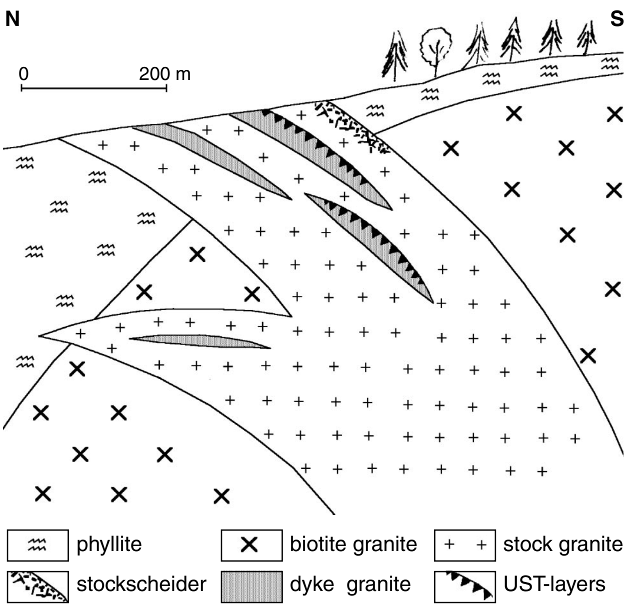

Fig. 1. Schematic geological cross-section of the Podlesí stock.

Table 2.Chemical compositions of granite types from Beauvoir (borehole GPF-1, wt%).

No.	3059	3061	3063	3067	3069
Unit	B1f	B1	B2	B'2	B'3
Depth (m)	109	232	522	660	858
SiO_2	67.8	69.2	69.7	71.1	72.4
TiO_2	udl	0.11	0.10	0.01	0.03
Al_2O_3	17.60	17.7	17.40	15.90	15.7
Fe_2O_{3tot}	0.19	0.20	0.24	0.46	0.74
MnO	0.035	0.04	0.11	0.09	0.095
MgO	udl	0.14	0.03	0.16	udl
CaO	0.85	0.27	0.25	0.41	0.29
Li_2O	1.22	1.54	0.99	0.58	0.49
Na_2O	4.33	4.83	4.73	4.11	4.41
K_2O	3.7	3.38	3.62	4.02	3.74
P_2O_5	1.12	1.35	1.52	0.97	0.82
F	1.6	2.6	1.99	1.52	1.2
Rb	0.41	0.42	0.25	0.20	0.18

Symbols of units and chemical analyses acc. to Raimbault et al. (1995)

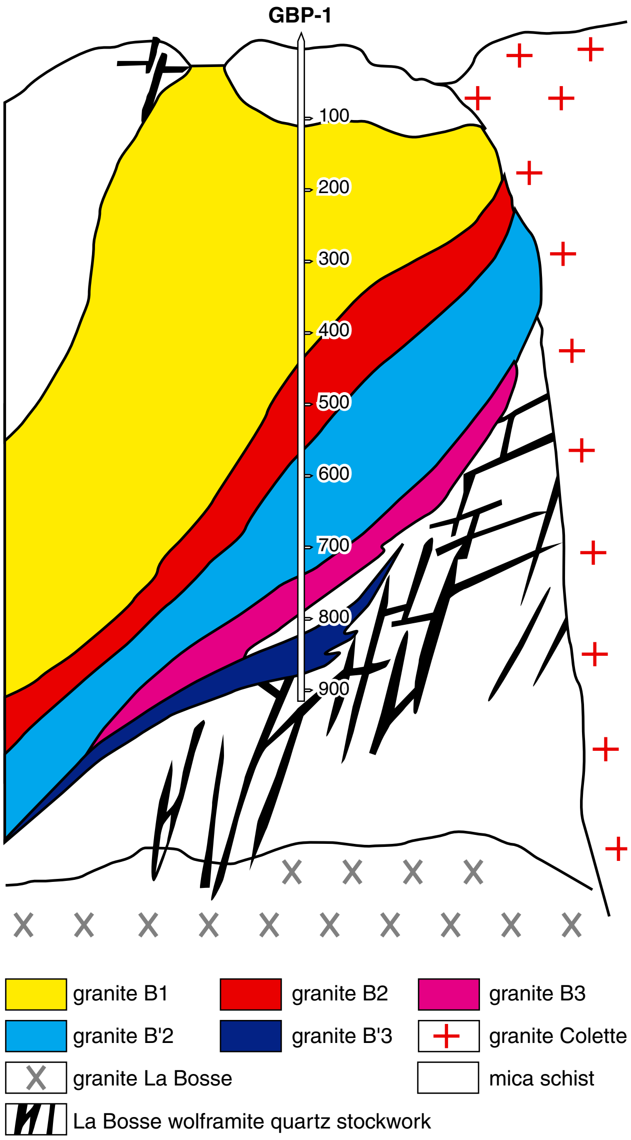

Fig. 2. Simplified geological cross-section of the Beauvoir granite (acc. to Raimbault et al. 1995).

Křížový Kámen – Waidhaus

The area of northern Oberpfalz (Bavaria, Germany) close to the German-Czech border is a well-known province of phosphorus-rich pegmatites such as, for example, Hagendorf (Forster et al. 1967, Keck 1990). Several small stocks of the Křížový Kámen-type granite were recently found in this area directly on the Czech-German border (Breiter and Siebel 1995), very probably representing a source of the famous P-rich pegmatites.

The Křížový Kámen granite is late Variscan (297 ± 2 Ma, Siebel et al. 1999), phosphorus-rich (0.8% P_2O_5) fine- to medium-grained albite-zinnwaldite-topaz granite. It builds several small stocks arranged in a NNW–SSE-trending zone between slightly older Flossenburg and Barnau two-mica granite massifs. Deeper parts of eroded stocks are exposed in the northern part of this zone. The southern part of the zone was less affected by uplift and erosion. Cupola-shaped apices of hidden granite stocks are developed as large pegmatite bodies containing important accumulations of phosphates (in Hagendorf). Muscovite marginal pegmatite is developed elsewhere (e.g. Waidhaus). The P-rich granite was post-magmatically altered in several stocks; zinnwaldite to F-poor muscovite, P-rich feldspars to P-poor feldspars, and locally (in Silbergrube at Weidhaus), a wide spectrum of secondary phosphates overgrow the surface of, and filled the microcracks in grains of primary rock-forming minerals (Breiter and Siebel 1995, Novák et al. 1996). So, this granite system provides ideal conditions for the study of phosphorus behaviour during post-magmatic hydrothermal alteration.

Vernéřov near Aš

A swarm of W-E-orientated pegmatite-like dykes were emplaced into Ordovician phyllites at Vernéřov near Aš, in the westernmost edge of Bohemia. The dykes are characterized by mineral assemblage of microcline-quartz-amblygonite with minor muscovite, crandallite, cassiterite, stannite-kosterite and many subordinate phosphates (Čech 1962). Kfs from this locality was studied as an example of coexistence of Kfs with major amblygonite.

Results

Cathodoluminescent images of the zoning of feldspars

Cathodoluminescent study of feldspars was undertaken to distinguish homogeneous and zoned crystals and to choose the most suitable crystals for microprobe analyses.

Podlesí

Stock granite: K-feldspar is zoned. The zone with a very bright blue to white CL forms the central part of the grain, the outer rim displays brownish CL. EMP analyses revealed no differences in chemistry. Albite inclusions are characterized by blue CL. The contacts between the K-feldspar host and albite inclusion are diffuse, and indicate possibly some dissolution of primary albite by later crystallizing K-feldspar.

Plagioclase is generally dark blue in CL but some domains show no CL and appear therefore black (Fig. 3a, b). Both types are mostly represented by pure albite, no difference were found in major element chemistry. Apatite inclusions are frequent in both types of albite. The albite domains without CL contain mainly apatite with yellow luminescence, while apatite with bright yellow-white CL is enclosed in the blue albite. The latter is enriched in MnO (1.34 wt%) and FeO (0.77 wt%) if compared to yellow apatite (0.19 wt% FeO, <0.1 wt% MnO).

Dyke granite: K-feldspars exhibit well-developed zoned fabric. Some grains have a perthitic core with

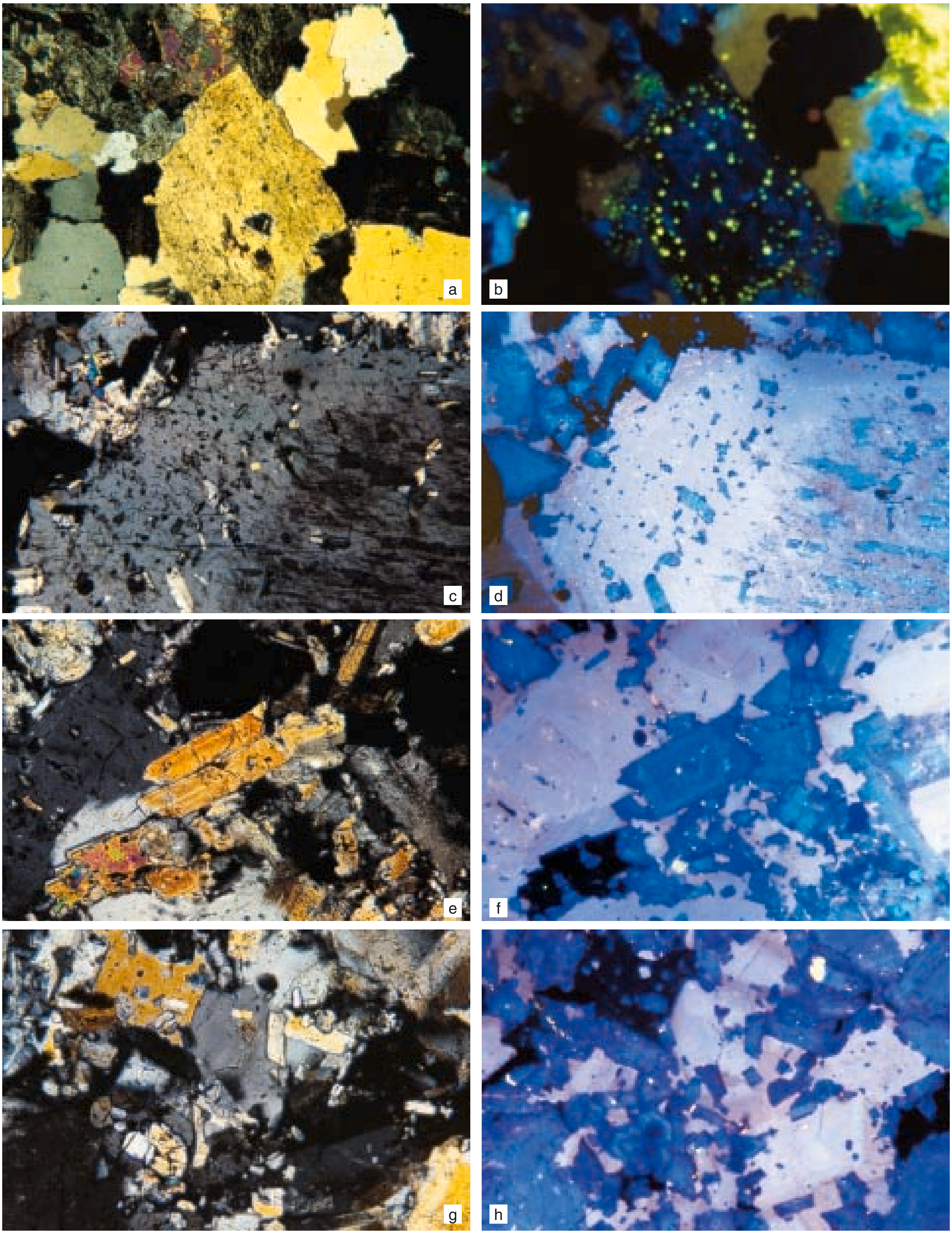

Fig. 3. Microphotograph and CL images from Podlesí: a – albite with apatitized zones, stock granite, borehole PTP-1, depth 300 m, crossed polars, b – as above, CL image, small yellow grains inside albite and large yellow grain in the right corner is apatite, c – fragment of a zoned Kfs crystal with perthitic core and albite inclusions in the outer zone, dyke granite, borehole PTP-1, depth 82.3 m, crossed polars, d – as above, CL image, albite is dark blue, Kfs is light blue to creamy, e – Kfs and albite crystals, dyke granite, old quarry, crossed polars, f – as above, CL image, blue zoned albite, creamy-yellowish zoned Kfs, g – Kfs, albite and zinnwaldite crystals, dyke granite, old quarry, crossed polars, h – as above, CL image, dark blue albite, creamy-yellowish zoned Kfs, black zinnwaldite. Area of images a-d is 3.2 × 2.3 mm, area of images e-h is 1.2 × 0.85 mm.

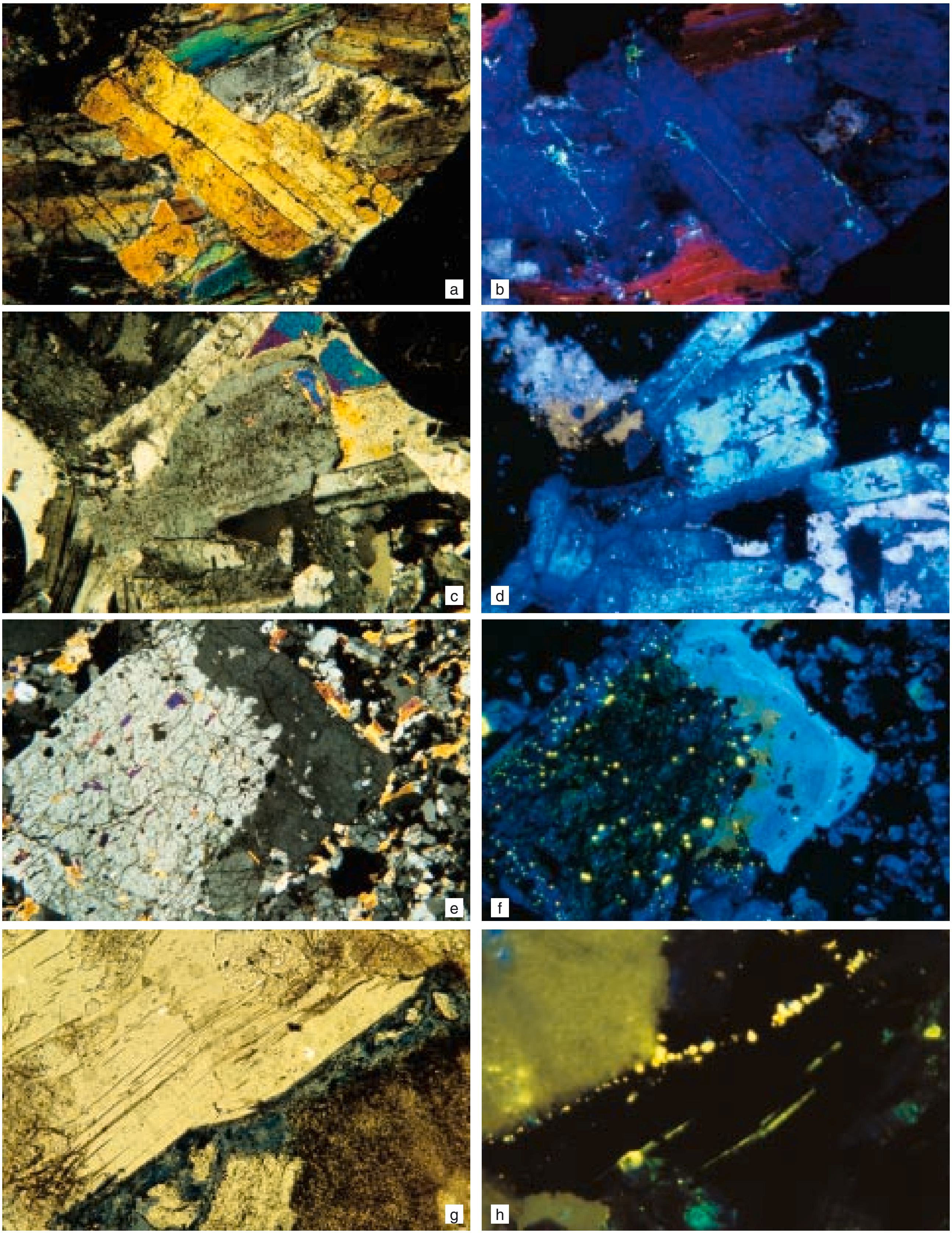

Fig. 4. Microphotograph and CL images from Beauvoir and Křížový Kámen granites: a – Beauvoir, borehole GBP-1, depth 107 m, granite of unit B1, crossed polars, b – as above, CL image, dark blue altered albite, red lepidolite, yellow apatite veinlets, c – Beauvoir, borehole GBP-1, depth 657 m, granite of unit B'2, crossed polars, d – as above, CL image, light blue fresh albite cores, dark blue altered albite rims, yellow apatite, e – Křížový Kámen, albite phenocryst with Kfs rim, crossed polars, f – as above, CL image, very dark blue albite with yellow apatite grains, blue zoned Kfs rim, g – Silbergrube at Waidhaus, hydrothermally altered granite with muscovitized zinnwaldite, altered Kfs and a veinlet of blue secondary Fe-phosphates, without polars, h – as above, CL image, small yellow grains of apatite inside the veinlet of Fe-phosphates, apatite also forms thin veinlets inside a muscovite flake, large yellowish apatitized Kfs in the left upper corner. Area of images a-f is 3.2 × 2.3 mm, area of images g-h is 1.2 × 0.85 mm.

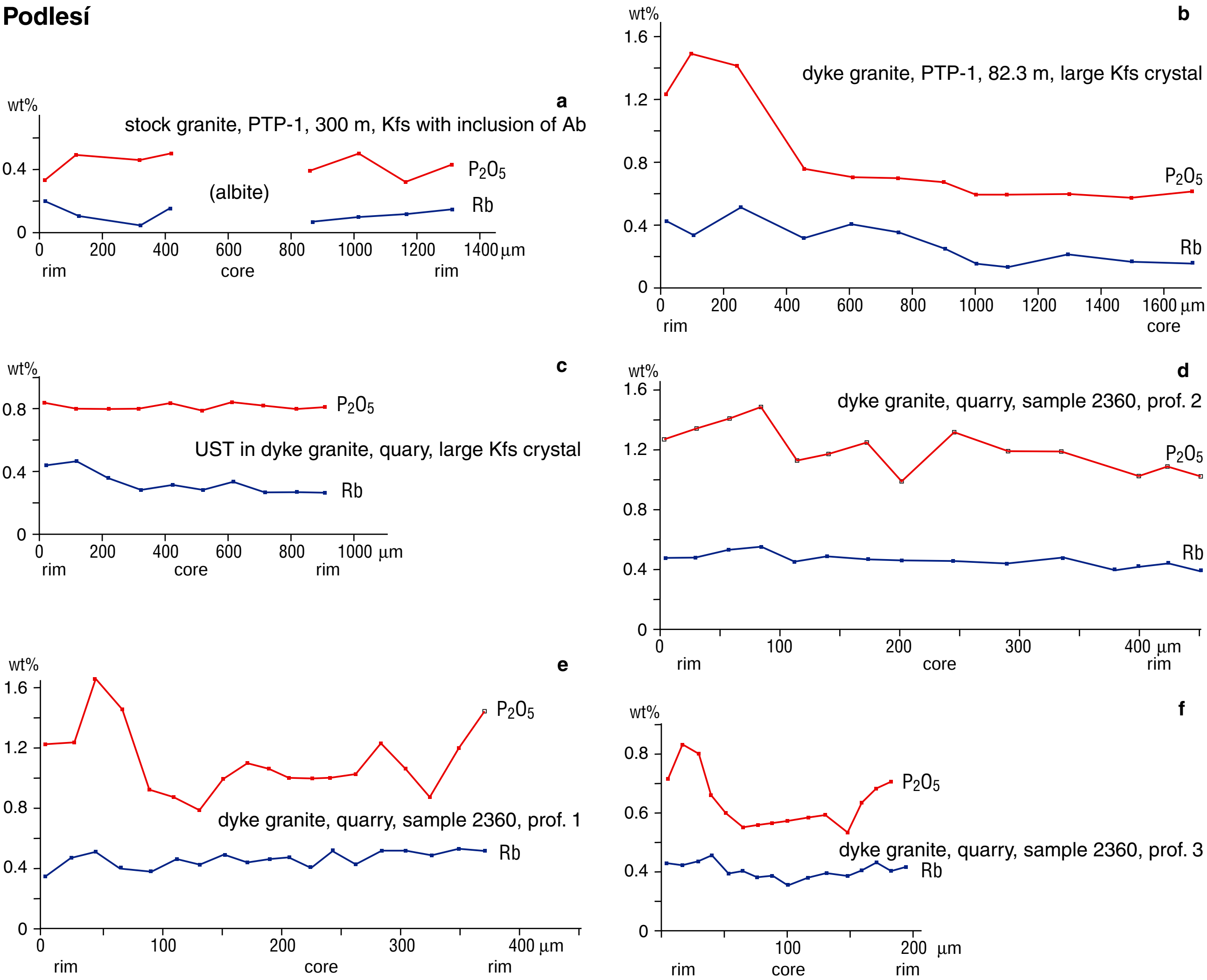

Fig. 5. P and Rb contents in Kfs crystals from Podlesí.

violet-blue CL (Fig. 3c, d). The central zone is rimmed by a zone with well-developed multiple oscillatory zoning with inclusions of small albite crystals. The zoning is marked by variable intensity of creamy CL, albite inclusions are blue. Such a style of zoning indicates that fractional crystallization plays an important role during the formation of this part of the grain. K-feldspar with brownish CL forms the outermost zone of the crystal (Fig. 3e–h). Only indistinct oscillatory zoning was rarely documented in this zone. Such style of fabric with three zones with different CL (violet-blue, blue and brown) suggests that the growth of the crystal occurred under three different p-T or chemical conditions, with an important role of fractional crystallization in the middle zone. Inclusions of plagioclase found in all three zones indicate contemporaneous crystallization of both feldspars. Because admixtures of bright yellow apatite were documented in all three zones as well, it seems probable that the magma was enriched in P during the whole history of their crystallization.

Plagioclases exhibit poorly developed zoning, defined only by a darker blue core, brighter internal zone and again darker rim (Fig. 3e, f).

Beauvoir

Within unit B, lath-shape albite exhibits homogeneous dull blue luminescence (Fig. 4a, b). Lepidolite displays red CL. Yellow apatite forms small admixtures in albite and K-feldspar or fills the twinning plains or cracks in K-feldspar.

In unit B', albite is zoned in CL with blue core and dull blue rim (Fig. 4c, d). Both zones are composed of albite, however albite in rims is slightly depleted in P_2O_5 (0.4–0.49 wt%) compared to the core (0.98–1.57 wt%). Three types of K-feldspar were documented using CL. The first type exhibited no CL, it appears black in the upper right corner. The second type of K-feldspar with bright light blue CL and abundant albite inclusions is exposed in the lower right and upper left corners. This type is characterized by elevated P_2O_5 content (0.82 wt%). The last K-f type with brownish CL rims the second blue type in the upper left corner of the photographs.

Křížový Kámen

Nearly all granites of the Křížový Kámen type are altered by fluids to a different degree. Granite from the type

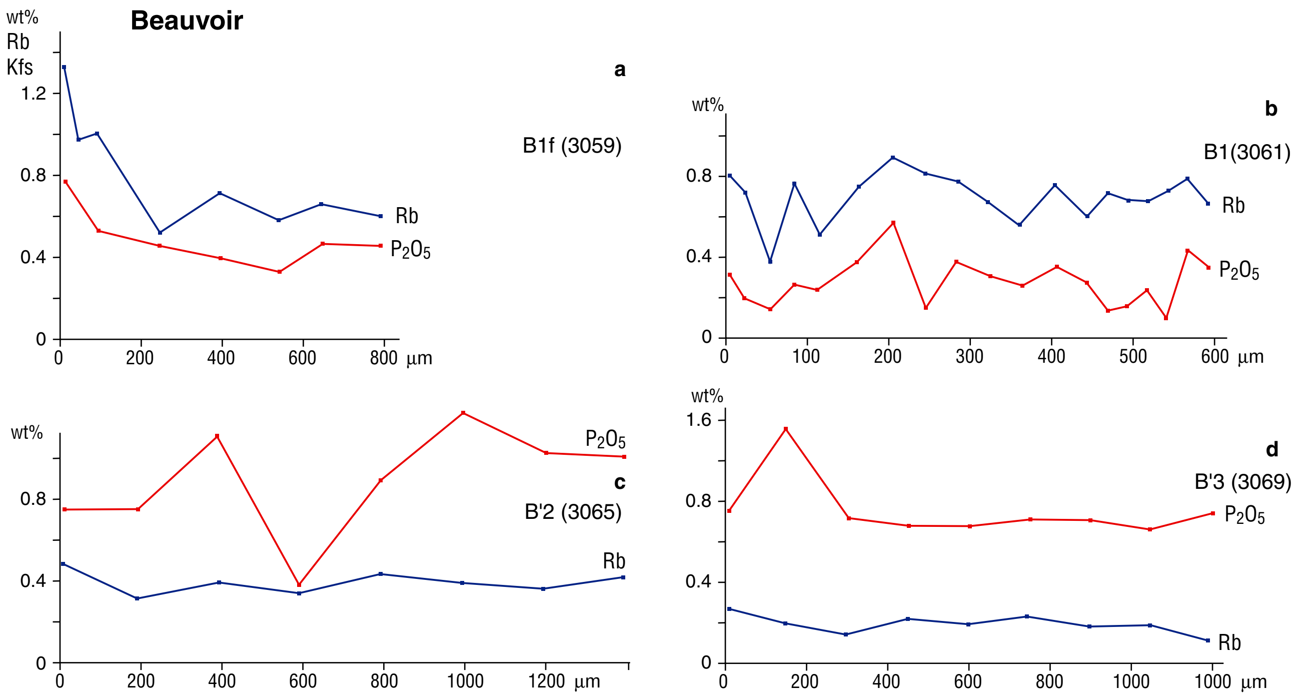

Fig. 6. P and Rb contents in Kfs crystals from Beauvoir.

locality directly on the Czech-German border (medieval border stone) underwent probably only late-magmatic reactions. Fig. 4e, f impressively document different resistivity of Kfs and albite to this process. The core of the crystal with no CL is albite with low content of phosphorus and numerous admixed apatites. In contrast, the Kfs rims with blue CL retain the primary higher P content and contain no apatite admixture.

K-feldspar from relatively low-temperature hydrothermally altered granite from the Silbergrube Quarry at Waidhaus shows weak creamy-brownish CL, albite is dark blue or without CL (Fig. 4g, h).

Vernéřov

K-feldspar from the pegmatite dyke is generally light brownish with fragments of blue-zoned patterns. The blue zones are not concordant with the actual shape of individual grains. CL is completely missing in surroundings of joints and thin phosphate veinlets cutting the Kfs grains.

Distribution of phosphorus in Kfs and albite

Podlesí

All studied alkali feldspars from Podlesí are rich in phosphorus (Frýda and Breiter 1995, Breiter et al. 1998, Breiter 2002). Kfs from the stock granite is often slightly perthitic and contains c. 0.3–0.6 wt% P_2O_5 (Tabs 3, 4). Phosphorus contents vary notably between the individual grains of each sample. Distribution of P within individual crystals is generally homogeneous, with no indication of zoning (Fig. 5a). Kfs from the stockscheider is perthitic, only slightly enriched and disturbed in phosphorus (0.3–0.6 wt% P_2O_5) and with no zoning.

Table 3. Microprobe analyses (wt%) and structural formulae (per 8 oxygen atoms) of feldspars from Podlesí.

No.	2203 upper stock	2203 upper stock	2687 deeper stock	2687 deeper stock	2669 dyke	2669 dyke	2360 dyke	2360 dyke
mineral	Kfs	albite	Kfs	albite	Kfs	albite	Kfs	albite
SiO_2	64.46	68.08	64.31	68.84	62.14	67.98	62.33	66.67
Al_2O_3	18.96	19.85	19.07	19.97	19.12	20.12	19.69	20.55
P_2O_5	0.51	0.31	0.55	0.16	1.55	0.68	2.52	1.27
CaO	0.07	0.16	0	0.05	0	0.12	0.09	0.05
Na_2O	0.42	11.52	0.96	11.59	0.55	11.05	0.58	11.1
K_2O	16.37	0.19	15.82	0.21	16.59	0.19	15.76	0.23
Total	100.76	100.08	100.69	100.82	99.92	100.14	100.9	99.76
Si	2.96	2.97	2.95	2.98	2.88	2.96	2.84	2.91
Al	1.02	1.02	1.03	1.02	1.05	1.03	1.06	1.06
P	0.02	0.01	0.02	0.01	0.06	0.02	0.1	0.05
Ca	0	0.01	0	0	0	0	0	0
Na	0.04	0.97	0.08	0.97	0.05	0.93	0.05	0.94
K	0.96	0.01	0.92	0.01	0.98	0.01	0.92	0.01

Table 4. Comparison of the contents of phosphorus and rubidium in whole rock, Kfs, albite and mica in Podlesí (wt%).

Unit	P_2O_5WR	P_2O_5 Kfs	P_2O_5Ab	RbWR	RbKfs	Rbmica
upper stock granite	0.41–0.46	0.3–0.6	0.2–0.4	0.12	0.2–0.3	0.97
UST dyke granite	0.8–0.9	0.7–0.8	0.2–0.9*	0.30–0.32	0.30–0.45	1.12
homogen dyke granite	0.8–1.6	0.8–2.0	0.3–0.8	0.18–0.25	0.40–0.60	1.11
deeper stock granite	0.45–0.55	0.4–0.6	0.1–0.6	0.11–0.14	0.10–0.20	0.72

* 0.6–0.9% of P_2O_5 in Ab inherited in UST-Kfs, 0.20–0.25% of P_2O_5 in Ab in matrix

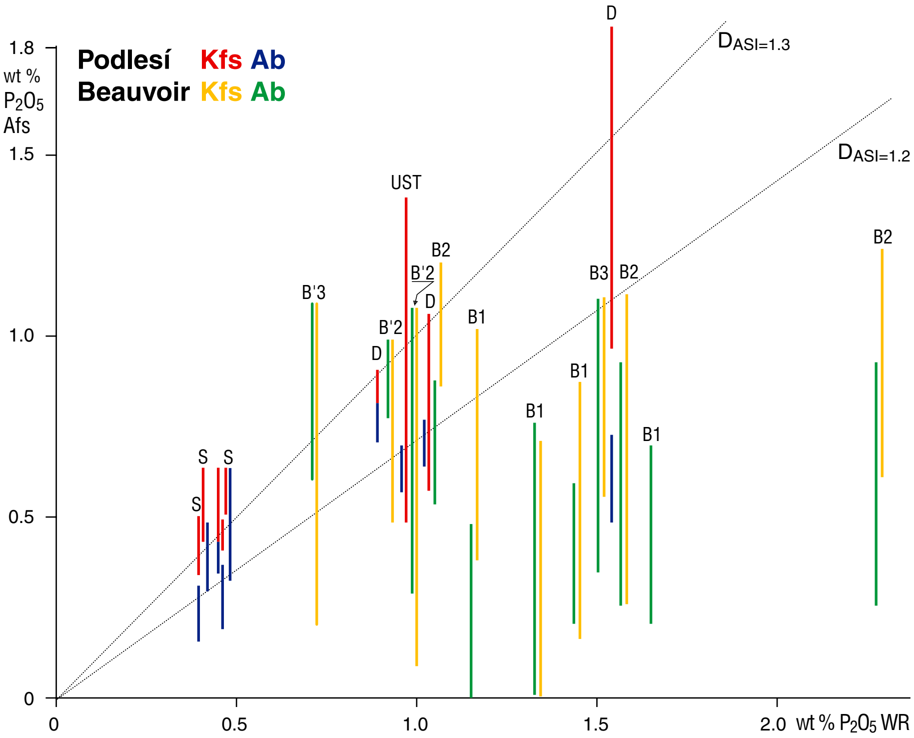

Fig. 7. Comparison of the P^{WR} with P^{Kfs} and P^{Ab} contents in the studied granite systems. The lines marked $D_{ASI=1.2}$ and $D_{ASI=1.3}$ show a correlation between P^{WR} and P^{Kfs} expected on the basis of London's equation (London et al. 1993) in peraluminous granitic melt with ASI = 1.2, resp. ASI = 1.3. Abbreviations: S – Podlesí stock granite, D – Podlesí dyke granite, UST – Podlesí dyke granite, UST domain. B1, B2, B3, B'2 and B'3 – units of the Beauvoir granite system acc. to Raimbault et al. (1995).

Table 5. Microprobe analyses of feldspars from Beauvoir (wt%) and structural formulae (per 8 oxygen atoms).

No.	3059	3059	3064	3064	3067	3067	3069	3069
rock	B1f	B1f	B2	B2	B'2	B'2	B'3	B'3
depth	107m	107m	570m	570m	657m	657m	858m	858m
mineral	Kfs	albite	Kfs	albite	Kfs	albite	Kfs	albite
SiO_2	64.45	68.26	64.66	68.38	63.39	68.55	64.24	67.97
Al_2O_3	18.54	20.12	18.94	19.48	18.68	20.94	18.92	20.45
P_2O_5	0.50	0.52	0.80	0.40	0.78	1.01	0.85	0.76
CaO	0.00	0.10	0.00	0.04	0.00	0.16	0.00	0.10
Na_2O	1.10	11.52	0.91	11.30	0.33	11.75	0.65	12.38
K_2O	15.02	0.16	15.77	0.21	16.57	0.17	16.14	0.13
Total	99.08	100.69	100.56	99.82	99.46	102.45	100.80	101.80
Si	2.98	2.96	2.96	2.99	2.95	2.92	2.93	2.90
Al	1.01	1.03	1.02	1.00	1.02	1.05	1.04	1.05
P	0.02	0.02	0.03	0.01	0.03	0.04	0.05	0.05
Ca	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Na	0.10	0.97	0.08	0.96	0.03	0.97	0.05	1.05
K	0.89	0.01	0.92	0.01	0.98	0.01	0.95	0.00

Symbols of units acc. to Raimbault et al. (1995)

Table 6. Comparison of the contents of phosphorus and rubidium in whole rock, Kfs, albite and mica in Beauvoir (wt%).

No.	Unit	P_2O_5WR	P_2O_5 Kfs	P_2O_5Ab	RbWR	RbKfs	Rbmica
3059	B1f	1.45	0.3–0.8	0.4–0.6	0.420	0.65–0.80	1.68
3061	B1	1.35	0.4–0.8	0.3–0.6	0.410	0.35–0.50	1.56
3063	B2	1.75	0.6–1.0	0.3–0.9	0.253	0.00–0.20	1.10
3067	B'2	0.95	0.6–1.0	0.3–0.8	0.200	0.00–0.15	1.00
3069	B'3	0.82	1.0	0.4–0.5	0.180	0.00–0.20	0.97

Symbols of units and WR chemical analyses acc. to Raimbault et al. (1995), contents of Rb in mica acc. to Monier et al. (1987)

Three types of Kfs occur within the dyke granite:

1. The relatively larger "rock-forming" Kfs is distinctly zoned (Fig. 5b). Crystal cores are similar to those of Kfs described from the stock granite (occasionally perthitic). The rims are never perthitic (but may contain small automorphic albite inclusions) and show distinct P-enrichment of up to 2 wt% P_2O_5. P-rich rims and P-poorer cores are often divided by a zone rich in albite inclusions. This is an indication of interruption in crystallization of the melt.
2. Small Kfs crystals in the matrix are either homogeneous (Fig. 5c, d), or zoned (Fig. 5e, f). In either case, they are chemically similar to the rims of larger crystals.
3. The big comb-like orthoclase crystals from the UST layer are never perthitic but enriched in crystallographically oriented albite inclusions. P content is zoned, being elevated in the outer zone but not as high as in the disseminated "rock-forming" Kfs crystals.

Phosphorus content in albites of all rock types is lower and more uniform, usually between 0.05 and 0.7 wt% P_2O_5 in the stock granite. Albite from the dyke granite contains 0.2–1.0 wt% P_2O_5. This albite is zoned but the zoning is less pronounced than in the case of Kfs. In perthites, the admixed albite is usually slightly depleted in phosphorus compared to the surrounding Kfs.

Beauvoir

The studied samples confirmed a fundamental difference between units B and B' (Tabs 5, 6). P contents in both Kfs and albite from unit B are highly variable and, compared to P^{WR}, relatively low (Fig. 6a, b). These feldspars are associated with amblygonite and are generally strongly altered.

Within unit B', Kfs is relatively fresh and its P content is in good agreement with that expected from the P^{WR} – about 0.7–1.0 wt% P_2O_5 (Fig. 6c, d). Albite from unit B' is optically fresh but its P content is disturbed in a broad interval of 0 to 1 wt%. No regular zoning was found within the Beauvoir Afs.

Křížový Kámen granite

P content in Kfs in relatively fresh samples (P^{WR} = 0.4–0.6 wt% P_2O_5) lies between 0.4–0.8% P_2O_5, P content in albite between 0.1–0.4% P_2O_5. Hydrothermally altered (muscovitized) samples show wide differences between P^{Kfs} (0.5–0.6 wt% P_2O_5) and P^{Ab} (0.1 wt% P_2O_5) and fundamental discrepancy between the above-mentioned P^{Afs} and P^{WR} = 0.72 wt% P_2O_5.

Vernéřov pegmatite

Large grains of Kfs associated with amblygonite contain 0.6–0.8 % P_2O_5, which is distributed homogeneously with no primary zoning or signs of secondary redistribution.

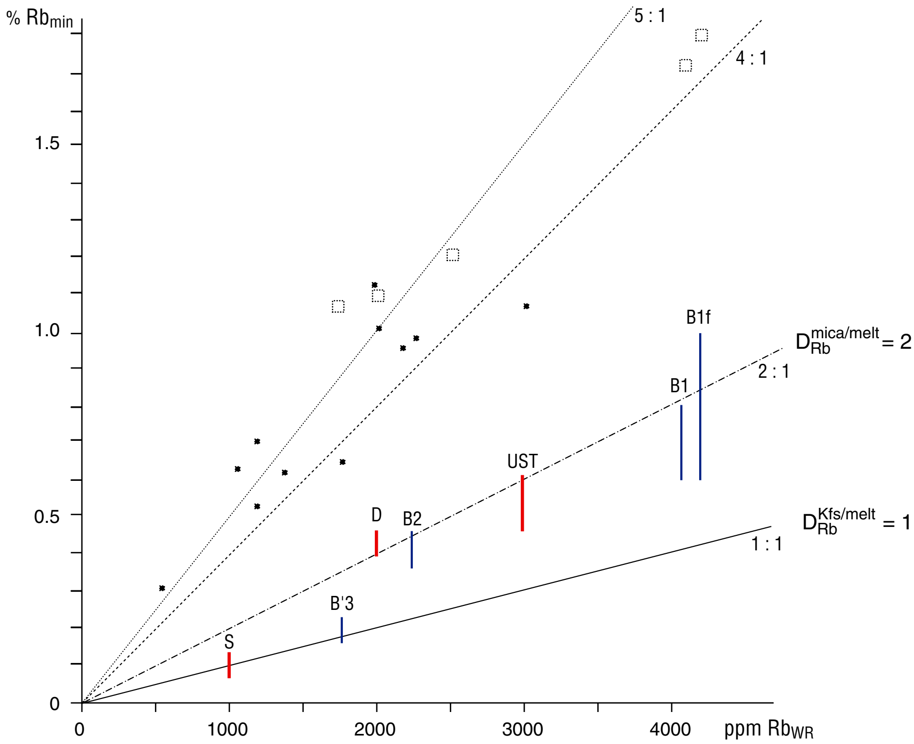

Fig. 8. Comparison of the Rb^{WR}, Rb^{Kfs} and Rb^{mica} contents in the Podlesí and Beauvoir granite systems. Experimental $D_{Rb}^{Kfs/melt}$ = 1 (London et al. 1993) and $D_{Rb}^{mica/melt}$ = 2 (Icenhower and London 1996) are shown. Abbreviations: filled squares – mica from Podlesí, empty squares – mica from Beauvoir, red columns – Kfs from Podlesí, blue columns – Kfs from Beauvoir, S – Podlesí stock granite, D – Podlesí dyke granite, UST – Podlesí dyke granite, UST domain. B1, B2, B3, B'2 and B'3 – units of the Beauvoir granite system acc. to Raimbault et al. (1995).

Distribution of Rb in Kfs

Podlesí

In Podlesí, Rb content in Kfs is generally distinctly lower and more uniform than the content of P. In the stock granite, the contents of 0.15–0.25 wt% Rb were found. Rb content in cores of larger Kfs from the dyke granite is c. 0.3–0.4 wt%. Some Rb enrichment of up to 0.4–0.6 wt% Rb was found in rims of larger Kfs crystals (Fig. 5b) and small late Kfs grains from the dyke granite. Large Kfs crystals from UST in layered parts of the dyke granite contain about 0.4 wt% Rb.

Beauvoir

The Beauvoir system shows a higher enrichment in Rb as a whole, and the Kfs from Beauvoir also shows a more intensive Rb enrichment than that from Podlesí. In unit B1, extremely irregular distribution of Rb was found, varying between 0.6–0.8 wt% Rb (Fig. 6b), locally up to 1.4 wt% Rb (Fig. 6a). Rb distribution in unit B2 is much more regular, c. 0.3–0.5 wt% Rb. Regular distribution of Rb in about 0.2 wt% was found also in unit B' (Fig. 6c, d).

Rb contents in albites from the two studied localities are usually lower than 0.1 wt%.

Křížový Kámen

Kfs from the relatively fresh Křížový Kámen granite contains about 0.2 wt% Rb (at Rb^{WR} of 900–1000 ppm). Kfs from the hydrothermally altered granite associated with secondary phosphates contains 0.28–0.38 (max. 0.49) wt% Rb (at Rb^{WR} of 950 ppm).

Vernéřov

The Vernéřov dyke contains Kfs in association with amblygonite. Its Rb content is relatively low: 0.16–0.18 (max. 0.22) wt% Rb.

Discussion

Mineral assemblages with P-rich Afs

Alkali feldspar is the main host of phosphorus in Ca-poor peraluminous granites up to P^{WR} of c. 0.5 wt%. Contribution of apatite in these rocks is, due to the lack of calcium, negligible. When the P^{WR} is distinctly higher, the rock usually contains also another P carrier, mostly amblygonite. The other carriers, namely Fe-Mn phosphates, are much less abundant. According to our opinion, three different peraluminous P-rich parageneses can be distinguished:

1. Extreme P-rich Afs with only accessory phosphates (example: dyke granite, Podlesí),
2. P-rich Afs with common phosphates (particularly amblygonite) (example: unit B, Beauvoir),
3. P-poor Afs with major amblygonite (example: P-rich pegmatite, Vernéřov).

Assuming that the present P^{WR} roughly equals the P^{melt}, the London's equation $D_P^{Afs/melt} = 2.05*ASI-1.75$ (London et al. 1993) is valid only for P-rich parageneses sub 1., in which the late magmatic and/or postmagmatic reactions with fluid were suppressed. Here (Fig. 7: all Podlesí samples and B'-unit samples from Beauvoir), the measured P contents in Kfs and albite are well comparable with those predicted on experimental basis (London et al. 1993). In parageneses sub 2. and 3., where intensive melt-fluid and/or crystal-fluid reactions took place, P was incorporated preferentially into the lattice of amblygonite. This process was probably primarily magmatic in conditions of pegmatite crystallization at Vernéřov. In the case of unit B at Beauvoir (B-samples in Fig. 7), the relatively low P content in feldspars should be better explained by late reaction of feldspar crystals with water-rich residual melt. In this condition, phosphorus was leached and incorporated into newly formed amblygonite (cf. the extremely irregular P distribution in Kfs associated with young amblygonite from unit B1, Fig. 6b).

Behaviour of P in Afs during hydrothermal alteration

During hydrothermal alteration of some parts of the Křížový Kámen granite pluton, the primary mineral assemblage of P-rich Afs + zinnwaldite was changed into P-poor Afs + muscovite ± Fe, Mn-phosphates. P_2O_5 contents in Kfs in relatively fresh samples fall between 0.4–0.8% P_2O_5, and lack correlation with whole-rock contents. More strongly altered samples show wide differences between phosphorus content in Kfs and albites and a wide scatter in the WR-phosphorus content. Possible explanation is that the primary P content of melt in the whole pluton was nearly the same for all samples – ca. 0.6–0.7% P_2O_5. If unaltered samples retained all phosphorus, phosphorus contents in Kfs and albites would be consistent with those predicted experimentally (London et al. 1994). In altered samples, phosphorus was liberated preferentially from albites, while its content in Kfs decreased only insignificantly. When the fluid removed free phosphorus, the whole-rock P contents decreased to ca. 0.4% P_2O_5. Whenever the free phosphorus reacted with Fe and Mn released from destroyed zinnwaldite, the newly crystallized secondary phosphates retained phosphorus in the rock and the whole-rock phosphorus budget did not change. Similar mobility of phosphorus during hydrothermal alteration of plagioclase described recently Broska et al. (2002) from Hnilec granite, Slovakia: products of alteration are pure albite and apatite.

Distribution of Rb between Kfs, mica and melt

We assume that Rb content in Kfs, due to its stable bond in the Kfs-lattice, can be used for the estimation of Rb content in the parental melt. The value of $D_{Rb}^{Kfs/melt}$ should equal about 1 (Icenhower and London 1996).

Major host of Rb in peraluminous granites are micas, in highly evolved pegmatites also polucite. The studied granites contain Li-rich trioctahedral micas but the experimental value of $D_{Rb}^{Li\text{-}mica/melt}$ is not known. We thus used the value of $D_{Rb}^{biotite/melt}$ ~2 (Icenhower and London 1995) for the estimation of Rb content in crystallized parental melt (Fig. 8). When $D_{Rb}^{Kfs/melt} \div 1$ and $D_{Rb}^{biotite/melt}$ ~2, then the value of $D_{Rb}^{mica/Kfs}$ should equal roughly 2.

There is no limit of Rb saturation of in Kfs while Rb-feldspar rubicline exists (Teertstra et al. 1998), but low distribution coefficient ($D_{Rb}^{Kfs/melt}$ ~1) does not allow higher Rb concentration in magmatic feldspar. The natural triclinic rubicline is a product of subsolidus or hydrothermal processes (Teertstra et al. 1997). In contrast to that, the synthetized Rb-feldspar was only monoclinic (Gasperin 1971).

The behaviour of Rb at Podlesí and Beauvoir is similar. With the assumption that granite systems do not lose substantial amount of Rb, the actual Rb^{WR} should roughly equal to the Rb^{melt}. Feldspars from the less evolved units meet the expected $D_{Rb}^{Kfs/melt} = 1$ but more evolved units do not. The $D_{Rb}^{Kfs/WR}$ value of the dyke granite from Podlesí and unit B from Beauvoir equals ~2. The analysed micas also showed much higher Rb contents in all rocks than expected from their WRcontents – $D_{Rb}^{mica/WR} = 4–6$, higher in less evolved units than in more evolved. Two conclusions should be drawn from these data:

1. the $D_{Rb}^{mica/Kfs}$ decreased during the fractionation of P, F, Li-rich systems from about 5 to about 2,
2. both the $D_{Rb}^{Kfs/WR}$ and $D_{Rb}^{mica/WR}$ are distinctly higher in both studied systems than those predicted experimentally. This means that both $D_{Rb}^{Kfs/melt}$ and $D_{Rb}^{mica/melt}$ are distinctly higher in near-solidus (probably non-equilibrium) conditions of P, F, Li-rich melt than in the haplogranitic melts. Another explanation is that the parental melt was significantly richer in Rb, and major part of Rb was later exsolved into aqueous fluid and released from the system.

An extensive aureole of Rb enrichment from regional clark of 250 ppm up to 400 ppm was detected within the phyllites enveloping the Podlesí stock (Breiter, unpublished data). Thomas (in Breiter et al. 1997) reported high Rb values (0.6–0.7 wt% Rb_2O) in crystallizing melt inferred from the composition of melt inclusions in quartz from Podlesí. Both these arguments support the second interpretation as a more probable one: Rb-enriched aqueous fluids released preferentially from the granite body caused intensive external metasomatism, while the granite remained intact.

History of Kfs from Podlesí

The Podlesí Kfs can be divided into three genetic groups:
1. the oldest crystals transported in magma and crystallized at relatively higher temperature: unzoned perthitic grains in the stock granite, perthitic cores of larger crystals in the dyke granite,
2. early *in situ* crystallized: large perthitic triclinic columns in stockscheider,
3. late *in situ* crystallized: large monoclinic columns with albite inclusions in UST layer in the dyke granite, rims of inherited Kfs in the dyke granite, small late Kfs grains in the dyke granite.

At Podlesí, P^{Kfs} and Rb^{Kfs} correlate well with P^{WR} and Rb^{WR} (Fig. 5). The values of $D_P^{Kfs/WR}$ in all rock types and $D_{Rb}^{Kfs/WR}$ in the stock granite roughly correspond to the values experimentally defined by London et al. (1993) and Icenhower and London (1996) for geologically relevant conditions: $D_P^{Kfs/melt}$ ~1 (with ASI = 1.2) and $D_{Rb}^{Kfs/melt}$ ~1. Simultaneously, rims of most of the Kfs crystals are enriched in P compared to their cores (Fig. 5). This fact evidences their crystallization from fractionated melt without any later redistribution. The distribution of Rb in Kfs crystals is generally homogeneous with no disturbances observed. This all supports the interpretation of the Podlesí granite system as being a result of crystallization from fractionated peraluminous P, F, Rb, Li-rich melt with no or only minor influence of late- and/or post-magmatic fluids. Nevertheless, the Kfs from the dyke granite most prominently enriched in Rb and the exocontact aureole enriched in Rb and F indicate some late admixture of Rb, F-rich fluid. This very late fluid did not significantly influence the already existing P-rich feldspars.

History of the Kfs from Beauvoir

At Beauvoir, Rb^{Kfs} shows a good positive correlation with Rb^{WR} (Fig. 8), but there is no correlation between the P^{Kfs} and P^{WR}. In the less fractionated unit B'3, the $D_P^{Kfs/WR}$ = 1 and $D_{Rb}^{Kfs/WR}$ = 1, roughly corresponding with experimental results. Within the more evolved unit B, both D values differ significantly: D_P decreases and D_{Rb} increases up to 2. Unit B underwent intensive crystal-fluid reactions according to Raimbault et al. (1995). This is also evidenced by high porosity up to 2 vol% in unit B1 (Chlupáčová, unpublished data). Our data proved that Rb incorporated in the Kfs lattice was stable during all fluid-related reactions, while P was effectively leached and later incorporated in different phosphates. In unit B', the content of fluid was low (Raimbault et al. 1995) and the fluid-related reactions were suppressed (porosity is lower than 0.5 vol%) and both P and Rb are conserved in their magmatic position.

Conclusions

Phosphorus and rubidium are good tools for a better understanding of late- to post-magmatic evolution of highly evolved peraluminous melt. Rubidium is firmly bound in the Kfs lattice and preserves well its magmatic signature during post-magmatic processes. In contrast, phosphorus can be easily released from the feldspar lattice and serve as a sensitive indicator of the late- and/or post-magmatic fluid-related reactions.

Compared to the Podlesí and Beauvoir granite systems, the Kfs from Podlesí is relatively rich in phosphorus and poor in rubidium. The Podlesí feldspars are often zoned with increasing P content from core to rim. The Beauvoir feldspars are not zoned and the feldspars from unit B are chemically often strongly disturbed. Based on all existing data, the Podlesí granite system is thus preserved in nearly original magmatic stage. In the case of the Beauvoir system, our data are in good correlation with the interpretation by Raimbault et al. (1995) that unit B was strongly and unit B' only moderately modified by aqueous fluids.

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Appendix

Studied samples

Podlesí: About 20 samples from the outcrops, the quarry and borehole PTP-1 were studied between 1996 and 2000 using the microprobe of the CGS. The whole database contains more than 1000 individual point analyses of both granite types – stock granite and dyke granite. Recently, several hundreds of new analyses were realized to describe the distribution of P in feldspars from layered and UST textures.

Beauvoir: A series of 11 samples from borehole GBP-1 covering all granite units was kindly supplied by L. Raimbault and more than 500 microprobe analyses were done in 1999 and 2000 in CGS Praha.

Křížový Kámen: About 10 samples of fresh and altered P-rich granite from Silbergube at Waidhaus and other samples from the deeply eroded non-altered granites of the Křížový Kámen type were studied between 1996 and 2000 using the microprobe of the CGS.

Vernéřov near Aš: 5 samples of P-rich pegmatite were studied using the microprobe of the CGS.

Analytical conditions

CL: The samples were analysed using cathodoluminescence equipment with hot cathode HC2-LM, Simon Neuser, Bochum, accelerating voltage 14 kV, beam density 10 m A/mm^2. Photographic documentation was taken on positive film Kodak EPH P1600X.

Microprobe: Feldspars were analysed using a CAMSCAN 4-90DV electron microscope equipped with LINK eXL and Microspec WDX-3PC X-ray analysers. Accelerating voltage of 10 kV, beam current of 3nA and counting time of 100 s were used for the EDX analyses of Si, Ti, Al, Ca, Na, K, P, with the detection limits of 0.1 wt%. WDX system was used for analyses of Rb (TAP, 20 kV, 50 nA). The detection limit for Rb was 0.01 wt%.

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