The role of boron and fluorine in evolved granitic rock systems (on the example of the Hnilec area, Western Carpathians)

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Abstract: The Hnilec S-type granites show a primary enrichment in the elements Sn, Rb, B, F, Nb, Ta and W which are hosted in mineral assemblage of cassiterite, tourmaline, fluorite, Ta- and Nb-phase etc. Such an evolved or specialized character of primary felsic melt was caused by a higher mobility of volatiles (B, F) due to the primary increased contents, which resulted in depolymerization of melt and consequently the decrease of density and viscosity. The B content in the granite body increases toward the granite roof-zone and reaches its maximum in the marginal granitic pegmatites and in the surrounding wall rocks. The greisenized granite parts are generally low in B. Although the F content also increases towards granitic cupolas and the highest F is in the altered parts (greisens), it is very low in the exocontact wall rocks compared to boron. Principally, there are not significant differences in boron and fluorine mobility but the observed assemblage are simply related to precipitation mechanisms, which are very different for the two elements. The main B carrier is tourmaline, which was formed by primary magmatic and secondary hydrothermal precipitation. The tourmaline found in the granites is mainly schorl, rarely foitite, whereas, tourmaline with higher dravite molecule is typical of the granitic exocontact. The schorl with higher dravite molecule also occurs in the cracks and rims of the primary schorl and formed from post-magmatic volatiles, which circulated between granites and granite host rocks possibly during mixing of magmatic and meteoric waters. The main concentrators of F are white mica, which trapped fluorine by OH exchanges, and fluorite. The outline of the greisen formation in the Hnilec region has been interpreted as a process above the emanation centre in the Hnilec granite cupola at locality Medvedí potok Valley. An emanation spot was a space with high volatile flux localized above the position of hydromagma which formed beneath a fine-grained granite carapace or between fine- and coarse-grained granites in the overpressurring regime. If the vapour pressure of the dissolved fluid exceeded the lithostatic pressure it caused the rupture of the overlying crystalline rocks and the flux of volatiles have altered rocks and became the source of special mineralization of the Hnilec and Gemer granites.

Key words: Western Carpathians, Gemeric Superunit, greisen, granite, tourmaline, muscovite, boron, fluorine.

Introduction

Boron and fluorine are widespread volatile elements of crustal granitic rocks, being found in sedimentary, volcanic, plutonic and metamorphic environments (Anowitz & Grew 1996). B_2O_3 concentrations may approach 1 wt. % in some evolved, peraluminous tourmaline-bearing granites (Pichavant & Manning 1984), fluorine is generally a minor component in granitic rock, but may be found highly concentrated in evolved residual melts. In certain topaz granites or rhyolites it reaches up to 3.2 wt. % F (Pichavant & Manning 1984; Icenhower & London 1995). The presence of these volatiles in the felsic melt significantly changes its rheological characteristics such as density or viscosity and consequently they influence the primary character of the melt (Dingwell et al. 1993). The decrease of liquidus and solidus temperature in the felsic melt is further promoted by the increase of water solubility (Manning 1981; Pichavant 1981; Pollard et al. 1987). Along with high P concentration high boron and fluorine results influence the depolymerization of felsic melt with following production of higher amounts of residual melts (Dingwell et al. 1985; Mysen et al. 1981).

Earlier, it was considered that in granitic melts F^- replaces O^{2-} forming Si–F bonds or it links with Na^+ and other network modifiers (Bailey 1977), but precision spectroscopic studies (Kohn et al. 1991; Schaller et al. 1992) have now shown that a significant short-range order exists between Na,K+Al and F, on the one hand, and Si–O, on the other hand. Along with removal of Al from bridging AlO_4-units, this explains the above mentioned depolymerization of silicate melts with increasing F content (Schaler et al. 1992). Moreover formation of $(Na,K)_3AlF_6$ units responds to the liquid immiscibility of F-rich granitic melts and the silicate component. This is also shown by experiments in granite-pegmatite melt enriched both in H_2O, B, P and F and consequently in Na_3AlF_6 and H_3BO_3 components in residual hydrosaline melt (Veksler & Thomas 2002). Silicate-melt inclusions in topaz-zinnwaldite-granites from Zinnwald indicate that F can reach up to several percentage (6 wt. %) in the differentiated melt (Thomas et al. 2005). The presence of fluorine in granitic melts might also increase the solubility of high-field-strength cations by making non-bridging O atoms available for complexing of these cations, what is metalogenetically significant.

The tin prospecting of the Hnilec Granite in the Gemeric Superunit, which is the uppermost Alpine West-Carpathian tectonic superunit, during the 1970's revealed the existence of granites with increased fluorine and boron concentrations enriched in rare metal elements as Sn, Nb, Ta and W. These granites were greisenized and became a source of hydrothermal mineralization manifested by the presence of cassiterite, molybdenite and wolframite occurring in the veins (Grecula & Drnzík 1995). Underground mining activity, exploration by drilling and geochemical prospecting has shown the presence of geological and chemical zonality within the Hnilec granite body. The analyses of volatile elements, which have been obtained during the prospecting works along granitic profiles, give the possibility of achieving a better understanding of boron and fluorine behaviour in granitic magmatic systems. The aim of this paper is to show the distribution of boron and fluorine within the granitic cupolas and the surrounding wall rock complexes on the basis B and F analyses gained during prospecting work additionally combined with the technique of microprobe mineral analyses. Tin distribution will also be discussed in the framework of B and F spatial variation.

Methods

The analysed material consisted of hand-specimen samples. Sampling was carried out by prospection regularly step by step in distances of 5 meters. The samples came from a prospecting gallery from the geochemical profiles and horizontal boreholes. Boron from crushed rock samples has been analysed by the AES-ICP (atomic emission spectrometry with inductively coupled plasma) and fluorine by the potentiometrical method (laboratory of the Geological Survey in Spišská Nová Ves). The whole rock analyses were performed in ACME Laboratory in Vancouver (Canada) by the ICP-MS analytical procedure which follows: **1** — sintering of a 0.2 g sample aliquot with sodium peroxide, **2** — dissolution of the sinter cake, separation and dissolution of the REE hydroxide-bearing precipitate, **3** — analysis by ICP-MS using the method of internal standardization to correct for matrix and drift effects. Natural rocks and pure quartz reagent (blank) were used as reference standards.

The mineral compositions present in apogranites (tourmaline, micas etc.) were determined by wave length electron microprobe Cameca SX 100 at the ŠGÚDŠ laboratory (accelerating voltage 15 kV, sample current 20 nA, beam diameter 5 μm) with calibrated natural standards.

Geological background — characterization of the Hnilec Granite

The Hnilec Granite is one of the granite bodies within the so called Spiš-Gemer granites or granites occuring in the Gemeric Superunit, which is the highest of the three major Alpine tectonic units of the Central Western Carpathians (Fig. 1). This thick-skinned sheet of Upper Cambrian–Silurian volcanogenic flysch (Gelnica Group) and the Devonian ophiolites (Rakovec Group) thrusted northward onto the Veporic Superunit during the Paleoalpine (Cretaceous) orogeny is usually correlated with the Upper Austroalpine units of the Eastern Alps (e.g. Maheľ 1974; Plašienka et al. 1997). During the Variscan Orogeny the Gemeric Superunit was metamorphosed in the greenschist and locally the amphibolite facies (Vozárová & Ivanička 1996; Faryad 1997; Soták et al. 2000), whereas the younger Alpine metamorphism reached greenschist facies conditions (e.g. Krist et al. 1992).

The western Hnilec Granite occurrence with hydrothermal Sn–W–(Nb–Ta) mineralization forms a granite body 2×1 km in size with strong zonal structures (Fig. 1). The occurrence and distribution of elements within the granitic rocks was studied along three geochemical profiles at the locality Medvedí potok Valley (Fig. 2). The lower part of this granite intrusion is composed of two-mica granite represented by a medium grained rock consisting of subhedral, sericitized plagioclase (31 vol. %), perthitic K-feldspar (24 vol. %), quartz (37 vol. %), muscovite (5 vol. %), and small amount of biotite (1 vol. %). Here the principal accessory minerals are tourmaline, zircon, apatite, monazite, xenotime, rutile and fluorite. The middle part of the Hnilec body consists of medium grained muscovite granite with similar rock-forming and accessory mineral proportions, the external part is composed of fine-grained granite with lower plagioclase (25 vol. %) and K-feldspar (13 vol. %) contents, and a higher amount of quartz (45 vol. %) and white mica (17 vol. %). Zircon, monazite, tourmaline, fluorite, Ta–Nb minerals (columbite groups, Nb–Ta-rutile) are the principal accessory mineral phases in this part. A fine-grained greisenized granite zone lies directly over the fine-grained granite and the major constituents are quartz (52 vol. %), white mica (22 vol. %), plagioclase (14 vol. %) and K-feldspar (12 vol. %). Accessory minerals include zircon, apatite, monazite, cassiterite, pyrite and rare tourmaline and fluorite. The greisen occurrences are found in the apical endocontact where they form bodies 100–200 m long and locally 30 m thick usually reaching 1–2 m. The greisens consist of quartz (60 vol. %) and white mica (37 vol. %), locally with plagioclase relics. Accessories are represented by tourmaline, increased amount of cassiterite, topaz, apatite, fluorite, molybdenite, arsenopyrite and pyrite. The external part of the altered granitic cupola is locally bordered by a layer of marginal pegmatite (stockscheider) (Fig. 2). The stockscheider zone is 0.5 up to several meters thick. Generally, the marginal pegmatite consists of large oriented K-feldspar crystals, with quartz, white mica, biotite and long prismatic tourmaline crystals. Accessory minerals are represented by fluorite and cassiterite. The greisenization caused a zonal arrangement of various types of metasomatites, appearing in the greisenized parts: **1** — the quartz zone (0.2–1.0 m), **2** — the zone of ore-bearing, quartz-micaceous greisens, **3** — the zone of the albitized fine-grained granite containing lenses of ore-greisens, **4** — the zone of microclinized medium grained granite. The disseminated Sn–W–(Nb–Ta) mineralization is concentrated mainly in the greisenized cupola as well as in the hydrothermal cassiterite-quartz veins (Drnzík 1982; Grecula & Drnzík 1995).

The geochemistry of the Hnilec granites shows typical features of the S-type peraluminous leucogranite suite (Table 1). The chemical composition of these granites is characterized by high SiO_2 contents (75.2 to 76.7 wt. %), relatively high alkalies, especially K_2O (3.8 to 4.9 wt. %), relatively low MgO
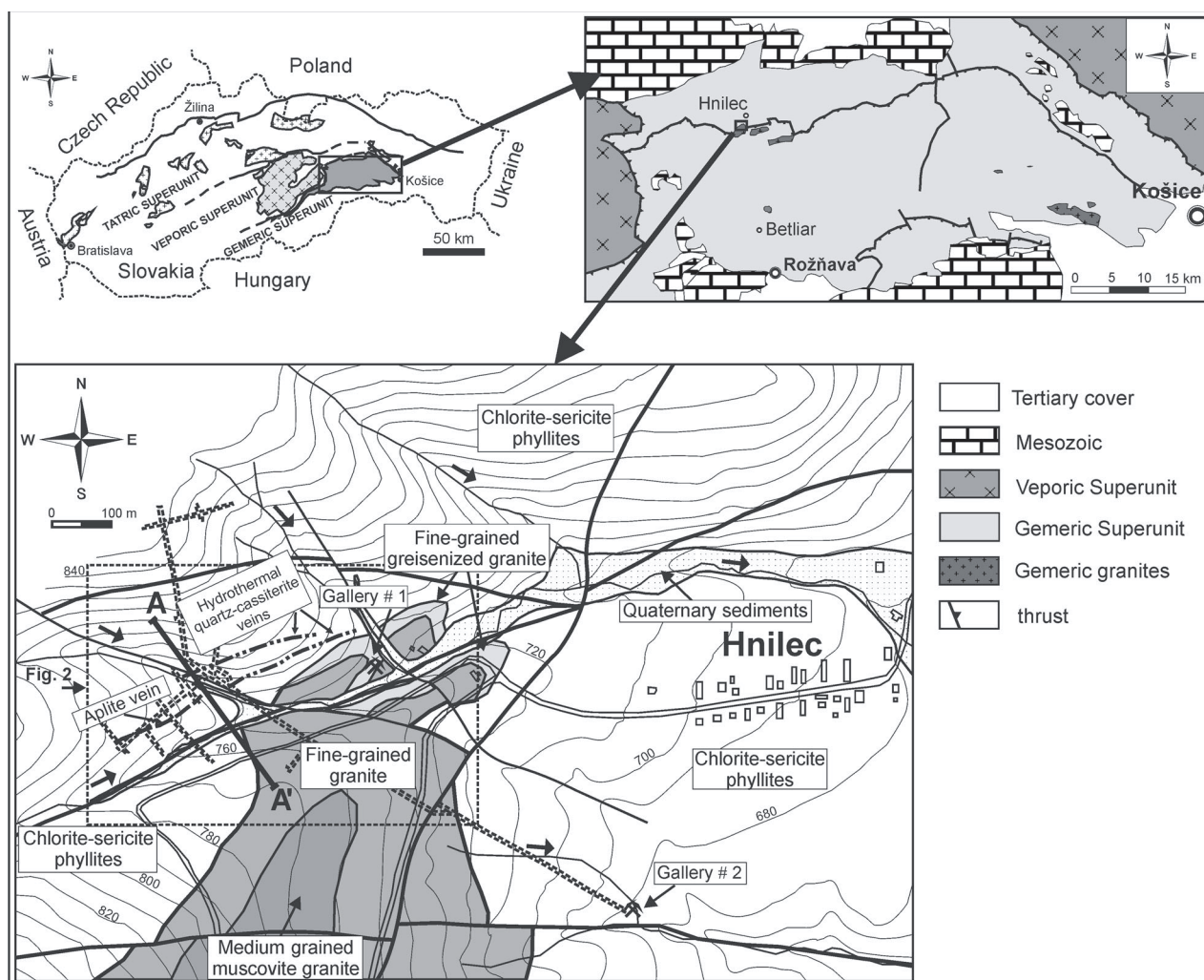
Fig. 1. Position of the Gemeric Superunit in the Western Carpathians mountain system and geological sketch map of the Gemer granite occurrences (according to Bajaník et al. 1984). Geological sketch map of the tin deposit in Hnilec-Medvedí potok (modified according to Drnzík 1982).

(0.06 to 0.28 wt. %) and CaO (0.36–0.54 wt. %). The REE normalized patterns of the granites have significant low negative Eu anomaly (Eu/Eu* $\approx$ 0.09), and the Rb contents range from 440 to 868 ppm depending on the differentiation level (Table 1). The S-type character of the Hnilec granites is also demonstrated by high initial $^{87}Sr/^{86}Sr$ ratio (0.71–0.72; Cambel et al. 1990), ASI index (1.1–1.2), total REE abundances as well as elevated P_2O_5 contents.

A Permian age for the Hnilec granites was determined from monazite (276 ± 13 Ma; Finger & Broska 1999) and single zircon grain dating (243 ± 18 Ma; Poller et al. 2002). The Permian age was also confirmed by associated ore mineralization in granite exocontact on molybdenite by Re-Os dating (262.2 ± 0.9 Ma; Kohút et al. 2004; Kohút & Stein 2005). Because the Hnilec granites represent a suite of S-type granitic bodies primarily enriched in the elements Sn, Rb, Nb, Ta and W reflecting a special mineral paragenesis, such as cassiterite and Ta- and Nb-phases, the name "specialized S-type granite suite" was accepted for these granites in the Spiš-Gemer region (Uher and Broska; 1996; Broska & Uher 2001).
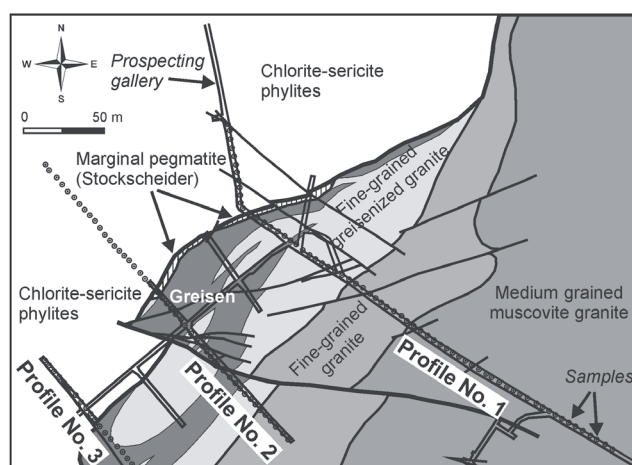

Fig. 2. Geological map of the prospecting gallery # 2 with marked the three profiles along the granite roof-zone marked. Sea level 680 m (modified according to Drnzík 1982).

Table 1: Representative whole-rock chemical analyses of granites from the Hnilec-Medvedí potok tin deposit (major elements in wt. % and trace elements in ppm). Analysed by ICP-MS in ACME Laboratory (Vancouver, Canada) and B, Sn by OES (Geological Institute of Slovak Acad. Sci., Bratislava).

Rock type Sample #	medium grained Ms granite GK-8	fine-grained granite GK-9	greisen GK-10
SiO_2	76.38	75.25	76.13
TiO_2	0.06	0.04	0.05
Al_2O_3	13.48	14.00	13.71
Fe_2O_3	1.12	1.25	1.68
MnO	0.02	0.05	0.04
MgO	0.28	0.06	0.25
CaO	0.54	0.36	0.28
Na_2O	3.32	3.82	3.04
K_2O	3.79	3.81	3.03
P_2O_5	0.19	0.25	0.20
L.O.I.	0.80	1.00	1.70
TOT/C	<0.01	<0.01	0.03
TOT/S	<0.01	<0.01	0.01
TOTAL	99.99	99.89	100.11
B	407	257	83
Ba	83	15	31
Ni	0.1	0.3	<0.1
Sc	3	3	3
Co	0.7	<0.5	0.7
Cs	18.6	28.4	60.3
Ga	24.3	29.3	36.3
Hf	2.2	1.9	1.9
Nb	16.6	22	18.1
Rb	500.2	867.5	806.6
Sn	27	105	852
Sr	9.9	26.9	10.1
Ta	5.3	8.2	6.1
Th	8.9	8.6	9.3
U	7.7	6.2	26.9
W	9.3	18.9	9.1
Zr	40.2	27.8	32.6
Mo	0.1	0.1	3.3
Cu	0.5	0.8	2.9
Pb	1.8	1.9	1.5
As	2.6	5.1	6.4
Sb	0.4	0.7	0.9
Bi	4.8	7.2	18.7
Y	13.1	23.3	11.6
La	2.5	1.6	2.3
Ce	7.5	4.8	6
Pr	0.92	0.71	0.69
Nd	3.4	2.5	3.1
Sm	1.6	1.5	1.2
Eu	0.05	0.05	0.06
Gd	1.71	1.38	1.34
Tb	0.37	0.33	0.41
Dy	2.25	2.06	2.16
Ho	0.37	0.25	0.33
Er	0.37	0.67	0.81
Tm	0.13	0.09	0.12
Yb	0.79	0.68	0.81
Lu	0.1	0.09	0.09

Boron and fluorine geochemistry of the Hnilec granitic cupola

The boron distribution in the geochemical profiles (Figs. 2, 3) shows certain regularities. An increased amount of boron is found in the fine- and medium grained Ms-granites (~200 ppm). In spite of the fact that boron is the principal volatile element in these rocks, relatively low B concentrations were transferred to the altered granite parts and/or to fine-grained greisenized granite (~15 ppm). On the other hand marginal pegmatite (stockscheider) from the contact with the wall rock contains very high B concentrations (~500 ppm), whereas ore greisens from the inner part are poorer in boron (~170 ppm). The highest B concentrations (~1000 ppm) were determined from the exocontact chlorite-sericite phylites (Drnzík 1982) (Fig. 3).

Fluorine distribution is different in comparison to boron. An elevated fluorine concentration was observed in the medium grained Ms-granites (~2500 ppm), but a relatively decreased fluorine content was found in the upper fine-grained granites (~1000 ppm) and in fine-grained greisenized granites (~1300 ppm). A similar concentration of fluorine is found in the ore greisens (~1500 ppm), a significant increase of fluorine has been observed in marginal pegmatites (stockscheider) — (~3000 ppm), although, on the other hand, lower fluorine content was found in the exocontact rocks (~1000 ppm; Drnzík 1982) (Fig. 3). The statistical parameters of dates from B, F distributions are presented in Table 2.

The specific boron and fluorine distributions reflect differences in the precipitation mechanisms of these elements, rather than in their mobility which is similar. Fluorine is transported as HF and alumino- and siliconhydroxylfluoride complexes (Tagirov & Schott 2001; Tagirov et al. 2002), whereas boron forms non-ionic bonds with oxygen, resulting in two types of oxyanions, trigonal (BO_3^{3-}) or tetrahedral (BO_4^{5-}). More important, the precipitation of fluorine compared to boron is dic-

Table 2: Average and ranges of granitic rock compositions from the Hnilec-Medvedí potok tin deposit (analyses are taken from Drnzík 1982). Averages have been counted from three profiles (see Fig. 2). Extreme values are omitted.

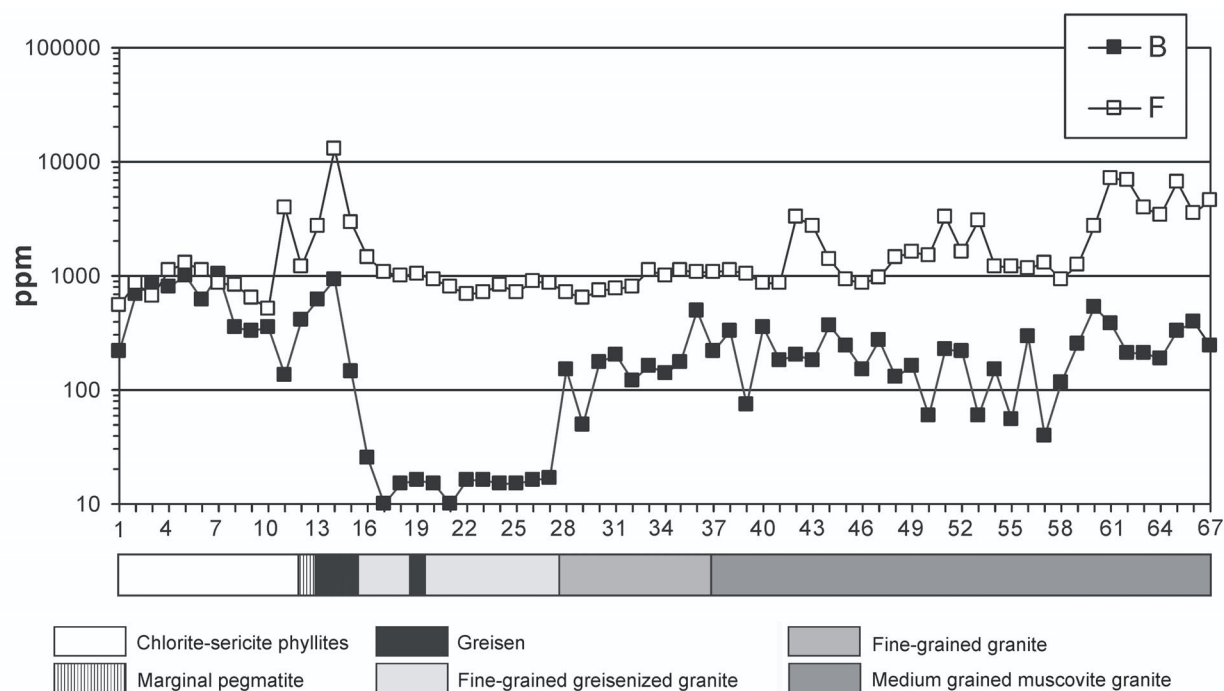|		B (ppm)	F (ppm)	Sn (ppm)
Chlorite-sericite phyllites	average	558	987	87
	st.dev.	394	759	80
	max.	1050	2600	361
n = 45	min.	120	260	12
Marginal pegmatite (stockscheider)	average	550	2773	376
	st.dev.	299	351	306
	max.	940	3100	800
n = 3	min.	245	2400	92
Greisen	average	172	1551	867
	st.dev.	132	1349	564
n = 24	max.	400	6200	2000
	min.	10	620	105
Fine-grained greisenized granite	average	16	1339	220
	st.dev.	5	817	214
	max.	30	3400	803
n = 11	min.	10	700	70
Fine-grained granite	average	208	1032	69
	st.dev.	127	236	14
	max.	360	1600	98
n = 16	min.	50	640	52
Medium grained Ms granite	average	216	2483	37
	st.dev.	115	1891	8
	max.	530	6700	54
n = 27	min.	40	860	29

Fig. 3. Boron and fluorine distribution (in ppm) along the profile # 1 in the prospecting gallery No. 2. (source data, Drnzík 1982). Anomalous values are ecluded from the statistical calculations (points 14, 15).

tated by different compositions of their host minerals (fluorite, micas vs. tourmaline). In the case of boron, large quantities of partition material are shifted to the aqueous fluid phase (during melt saturation, i.e. the first or second boiling), and it does not precipitate until the fluid phase reaches a high — Mg-Fe environment (country rock pelites). This explains why most of the tourmaline (and boron) is located around the contact. On the other hand, fluorine will not precipitate into abundant fluorite, because of Ca deficiency in the apical part of the cupolas, and its contents in the fluid are modified by OH–F exchanges with all mineral hydroxyl bearing phases such as micas.

B,F-bearing minerals in the Hnilec granites

Tourmaline is the main boron carrier in the Hnilec granites. In these granites and the corresponding greisens, it forms euhedral crystals without any rock-forming mineral inclusions (Fig. 4a,b). Tourmaline is there represented by schorl with high Fe/(Fe+Mg) = 0.95 to 0.97, locally with elevated F contents (0.64 and 1.17 wt. %). The amount of X-site vacancies varies in a relatively narrow ranges between 0.26–0.28 a.p.f.u. The high ferrous contents determined by Mössbauer spectrocopy (90 %; Broska et al. 1998) as well as the textural relationships of tourmaline to the other rock-forming minerals, indicate its primary origin. This tourmaline is identified as primary mineral phase — tourmaline I.

The tourmalines from the greisen part form single crystals (to 3 cm) or composite aggregates often exhibit zonal texture (Fig. 4c,d). This schorl probably primary in core (Fe/(Fe+Mg) = 0.99) is overgrown by secondary Mg-rich schorl (Fe/(Fe+Mg) = 0.62–0.73). The schorl with an increased dravite

proportion (Fe/(Fe+Mg) = 0.62 to 0.65) is also typical of the granite exocontact zone (Figs. 4e, 5; Table 3), where it forms large black crystals (0.5 mm to 10 cm) in rossete-like as well as massive globular aggregates with quartz, or discrete quartz-tourmaline crystals (Broska et al. 1998). This tourmaline represents a younger post-magmatic phase — tourmaline II. Postmagmatic tourmalines occurred also in the granite but mainly in its greisenized parts (Fig. 4c,d).

White mica and fluorite due to their abundances are the most significant fluorine concentrators, other F-mineral phases being apatite and topaz. Although white micas from the medium grained muscovite granite and greisens contain very low amounts of fluorine (0.01–0.4 wt.%), higher or moderate fluorine concentrations were determined in white muscovite from fine-grained granites (1.8–3.2 wt. %). Howewer, white mica in greisens also has a low content of F (0.50–0.70 wt. %). The compositions of white micas correspond to ferro-aluminoceladonite (Broska et al. 2002) and they occur as interstitial flakes (Fig. 4f,g,h, Table 4). Fluorite usually forms small crystals disseminated in granite, but also thin veinlets or aggregates along tectonic fissures in granitic rocks. The occurrence of fluorine veins is due to post-magmatic or hydrothermal fluid transfer.

Discussion and synthesis

Movement of postmagmatic fluids

Boron-bearing fluids easily escape along fractures to country rocks and form there widespread pervasive tourmaline mineralization. On the other hand, fluorine accumulates in al-

Table 3: Representative microprobe analyses of tourmaline (in wt. %).

Point	1	2	3	4	5	6	7	8
Rock type	medium grained muscovite granite		greisen			phyllite		
Sample	GK-8-2	GK-8-3	GK-11-1	GK-11-2	GK-11-3	HN-1-4	HN-2-2	HN-2-3
SiO_2	34.73	33.92	36.13	35.79	34.95	35.32	34.89	34.86
TiO_2	0.54	0.59	0.36	0.30	0.27	0.89	0.94	0.98
B_2O_3*	10.12	10.09	10.37	10.32	10.03	10.31	10.29	10.29
Al_2O_3	33.19	33.33	31.56	31.61	31.59	32.25	32.45	32.41
Cr_2O_3	0.03	0.00	0.00	0.00	0.00	0.00	0.05	0.04
FeO_{tot}	14.59	14.98	11.64	13.62	16.47	11.21	11.21	11.04
MnO	0.22	0.25	0.22	0.17	0.30	0.14	0.08	0.21
MgO	0.45	0.46	4.00	2.86	0.11	3.69	3.68	3.75
CaO	0.03	0.07	0.20	0.16	0.06	0.35	0.32	0.38
Na_2O	1.91	1.94	2.37	2.22	2.14	2.13	2.17	2.14
K_2O	0.03	0.04	0.04	0.04	0.06	0.05	0.04	0.05
H_2O*	2.98	3.03	3.10	3.05	3.13	3.27	3.26	3.31
F	1.07	0.95	1.01	1.08	0.70	0.60	0.61	0.50
Cl	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
O=F	−0.45	−0.40	−0.43	−0.45	−0.29	−0.25	−0.26	−0.21
O=Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.44	99.25	100.57	100.77	99.52	99.96	99.73	99.76
Atomic proportions based on the sum of T+Z+Y=15 cations ***B_2O_3 and H_2O calculated from ideal stoichiometry**								
Si^{4+}	5.965	5.844	6.057	6.027	6.055	5.953	5.893	5.887
$Al^{3+}T$	0.035	0.156	0.000	0.000	0.000	0.047	0.107	0.113
Total T	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
B^{3+}	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
$Al^{3+}Z$	5.996	6.000	6.000	6.000	6.000	6.000	5.993	5.995
$Cr^{3+}Z$	0.004	0.000	0.000	0.000	0.000	0.000	0.007	0.005
$Fe^{3+}Z$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Z	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Ti^{4+}	0.070	0.076	0.045	0.038	0.035	0.113	0.119	0.124
$Al^{3+}Y$	0.687	0.611	0.298	0.302	0.507	0.360	0.360	0.342
$Fe^{2+.3+}$	2.096	2.158	1.632	1.918	2.386	1.580	1.583	1.559
Mn^{2+}	0.032	0.036	0.031	0.024	0.044	0.020	0.011	0.030
Mg^{2+}	0.115	0.118	0.994	0.718	0.028	0.927	0.927	0.944
Total Y	3.000	2.999	3.000	3.000	3.000	3.000	3.000	2.999
Total Al	6.718	6.767	6.235	6.274	6.451	6.407	6.460	6.450
Ca^{2+}	0.006	0.013	0.036	0.029	0.011	0.063	0.058	0.069
Na^+	0.636	0.648	0.770	0.725	0.719	0.696	0.711	0.701
K^+	0.007	0.009	0.009	0.009	0.013	0.011	0.009	0.011
Total X	0.649	0.670	0.815	0.763	0.743	0.770	0.778	0.781
Vac. X	0.351	0.330	0.185	0.237	0.257	0.230	0.222	0.219
Total Cat.	18.648	18.670	18.815	18.762	18.743	18.770	18.777	18.780
OH^-	3.419	3.482	3.465	3.422	3.616	3.680	3.674	3.733
F	0.581	0.518	0.535	0.575	0.384	0.320	0.326	0.267
Cl	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000
Total W	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
O^{2-}	30.642	30.627	30.610	30.520	30.809	30.866	30.837	30.896
Fe/(Fe+Mg)	0.95	0.95	0.621	0.728	0.99	0.63	0.63	0.62

tered granites or greisenized near-roof parts, also in medium grained muscovite granite, but only very slightly in the country rocks. Similarly to the Gemeric Granite, the strong local tourmaline precipitation in aureole rocks is known around the B-rich Cornubian granites in SW England (Jackson et al. 1989; London & Manning 1995), and also from the Podlesí granite stock in the Krušné hory Mts (Breiter 2002). In contrast to it, fluorine aureole is observed around the rare metal Beauvoir Granite in the French Massif Central (Table 5). The strong F mobility is there documented by significant decrease of F along Li, Sn and W contents in the last 100 m below the granite roof (Cuney et al. 1992; Raimbault et al. 1995).

The behaviour of F-rich magmas is different compared to B-rich ones. The greater mechanical energy produced during crystallization of B-rich magmas, which is usually related to the higher content of water, provides a mechanism for breccia pipe and stockwork formation, while the more passive crystallization of F-rich magmas often results in the formation of disseminated mineralization (Pollard et al. 1987). A breccia pipe is known from the Hnilec area, although only in a restricted
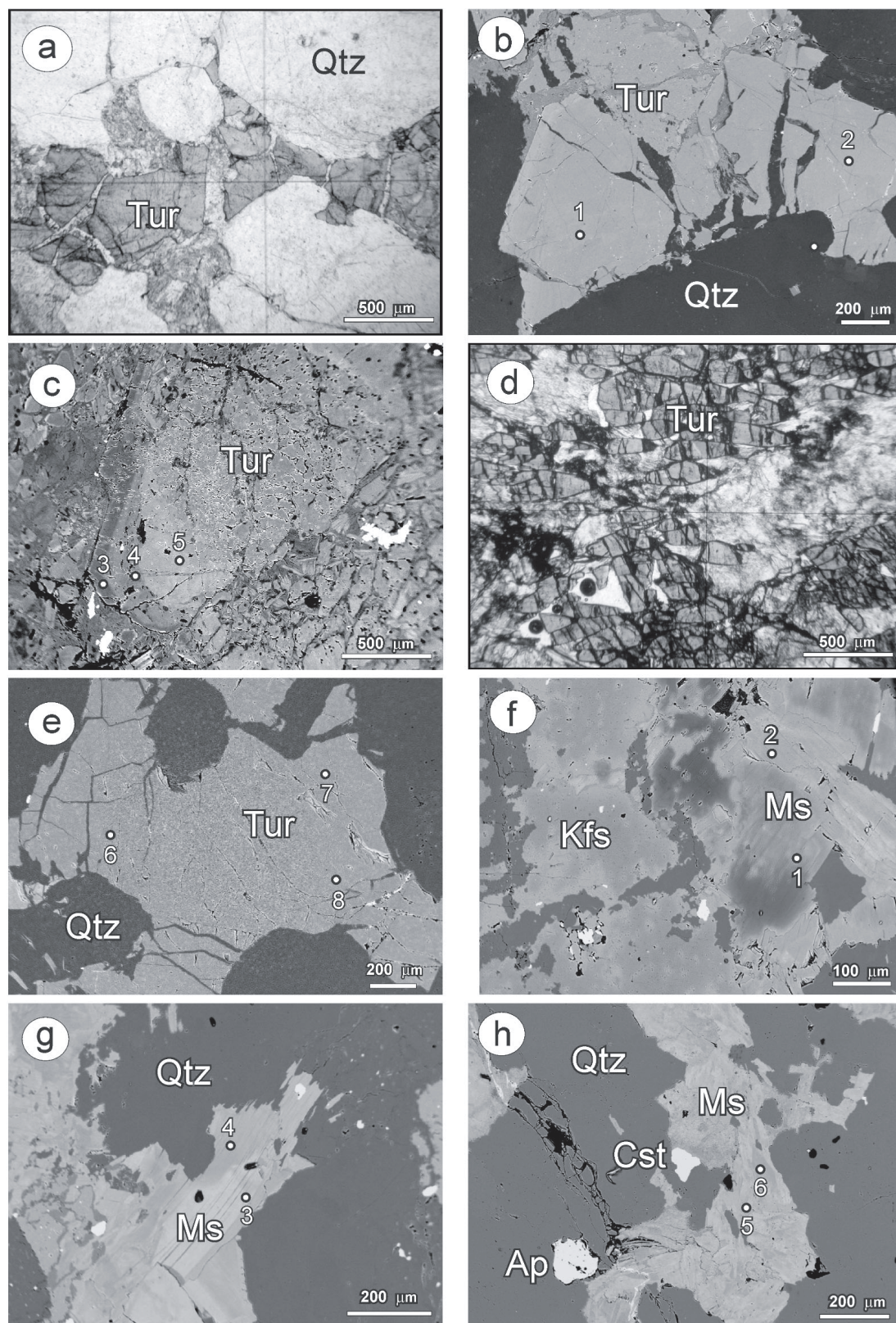
Fig. 4. Microphotographs from granites in the roof zone (a, b) and back-scattered electron (BSE) images of tourmaline and white mica at the Hnilec-Medvedí potok locality (c, d, e, f). **a, b** — interstitial schorl from the medium grained muscovite granite; **c, d** — schorl aggregates from greisen; **e** — schorl-quartz from exocontact phyllite; **f** — white mica from medium grained muscovite granite; **g** — white mica from fine-grained granite; **h** — white mica from greisen. **Tur** — tourmaline, **Ms** — muscovite, **Kfs** — K-feldspar, **Cst** — cassiterite, **Ap** — apatite.

Table 4: Representative microprobe analyses of white mica (in wt. %). Total FeO from microprobe analyses has been divided into FeO and Fe_2O_3 in ratio 50:50.

Point	1	2	3	4	5	6
Rock type	medium grained muscovite granite		fine-grained granite		greisen	
Sample	GK-8/6-1	GK-8/6-2	GK-9/1-16	GK-9/1-17	GK-10/7-9	GK-10/7-11
SiO_2	46.60	45.71	48.37	47.09	46.96	47.98
TiO_2	0.35	0.18	0.14	0.08	0.00	0.17
Al_2O_3	32.78	28.74	28.12	30.12	31.55	30.22
Cr_2O_3	0.00	0.00	0.05	0.15	0.01	0.00
FeO	1.95	4.24	3.27	2.89	3.31	2.84
Fe_2O_3	2.16	4.71	3.63	3.21	3.68	3.15
MnO	0.11	0.11	0.23	0.21	0.11	0.08
MgO	0.34	0.46	0.24	0.06	0.00	0.45
CaO	0.00	0.02	0.00	0.00	0.00	0.00
Na_2O	0.46	0.14	0.07	0.20	0.34	0.10
K_2O	9.62	10.09	10.92	10.80	10.38	10.94
H_2O *	4.49	4.37	3.47	3.33	4.19	4.23
F	0.00	0.00	1.87	2.26	0.50	0.43
Cl	0.01	0.03	0.01	0.01	0.00	0.00
O=F	0.00	0.00	−0.79	−0.95	−0.21	−0.18
O=Cl	0.00	−0.01	0.00	0.00	0.00	0.00
Total	98.87	98.79	99.23	99.46	100.82	100.41
Formulae based on 12 oxygens, H_2O based on the sum of OH+F+Cl=2 a.p.f.u.						
Si	3.146	3.168	3.302	3.215	3.156	3.230
Al T	0.854	0.832	0.698	0.785	0.844	0.770
Total T	4.000	4.000	4.000	4.000	4.000	4.000
Ti	0.018	0.009	0.007	0.004	0.000	0.009
Al M	1.755	1.515	1.564	1.639	1.655	1.628
Cr	0.000	0.000	0.003	0.008	0.001	0.000
Fe^{2+}	0.110	0.245	0.186	0.165	0.186	0.160
Fe^{3+}	0.110	0.245	0.186	0.165	0.186	0.160
Mn	0.006	0.006	0.013	0.012	0.006	0.005
Mg	0.034	0.048	0.024	0.006	0.000	0.045
Total M	2.033	2.069	1.985	1.999	2.034	2.006
Vac. M	0.967	0.931	1.015	1.001	0.966	0.994
Total Al	2.608	2.347	2.262	2.424	2.499	2.398
Ca	0.000	0.001	0.000	0.000	0.000	0.000
Na	0.060	0.019	0.009	0.026	0.044	0.013
K	0.829	0.892	0.951	0.941	0.890	0.940
Total I	0.889	0.912	0.960	0.967	0.934	0.953
Vac. I	0.111	0.088	0.040	0.033	0.066	0.047
Total Cat.	6.921	6.982	6.945	6.966	6.968	6.959
OH	1.999	1.996	1.595	1.511	1.894	1.908
F	0.000	0.000	0.404	0.488	0.106	0.092
Cl	0.001	0.004	0.001	0.001	0.000	0.000
Total X	2.000	2.000	2.000	2.000	2.000	2.000
Fe/(Fe+Mg)	0.762	0.838	0.884	0.964	1.000	0.779

extent. The common occurrence of B and F in a volatile system is not so widespread and is known in detail mainly from the Cornubian granites. The Hnilec granite system shows a lot of similarities with this evolution.

Mineralization derived from B and F-rich fluids

Boron-rich magmatic systems result in tourmaline precipitation. Tourmaline in such systems always occurs in the parental granites as well as in the country host rocks, which indicates a longer distance of boron migration from granites stopped by an Fe-Mg environment (London & Manning 1995). The hydrothermal tourmaline, schorl or schorl-dravite and dravite species, in the exocontact aureoles around granitic plutons usually shows a fine-scale chemical zoning within crystals and usually preserves the essential chemical characteristics of the
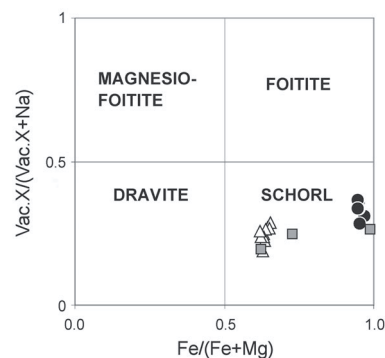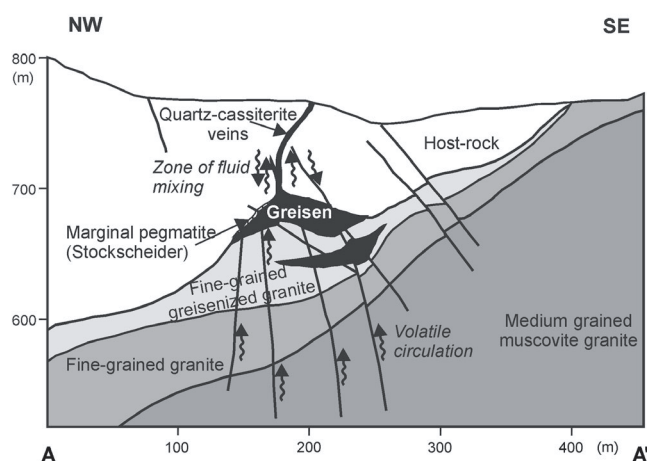

Fig. 5. Quadrilateral $Vac.^X/(Vac.^X+Na)$ vs. Fe/(Fe+Mg) diagram (atomic proportions) of tourmalines from Hnilec area (Medvedí potok Valley). **Black circles** — medium grained muscovite granite, **grey squares** — greisen, **triangles** — exocontact phyllite.
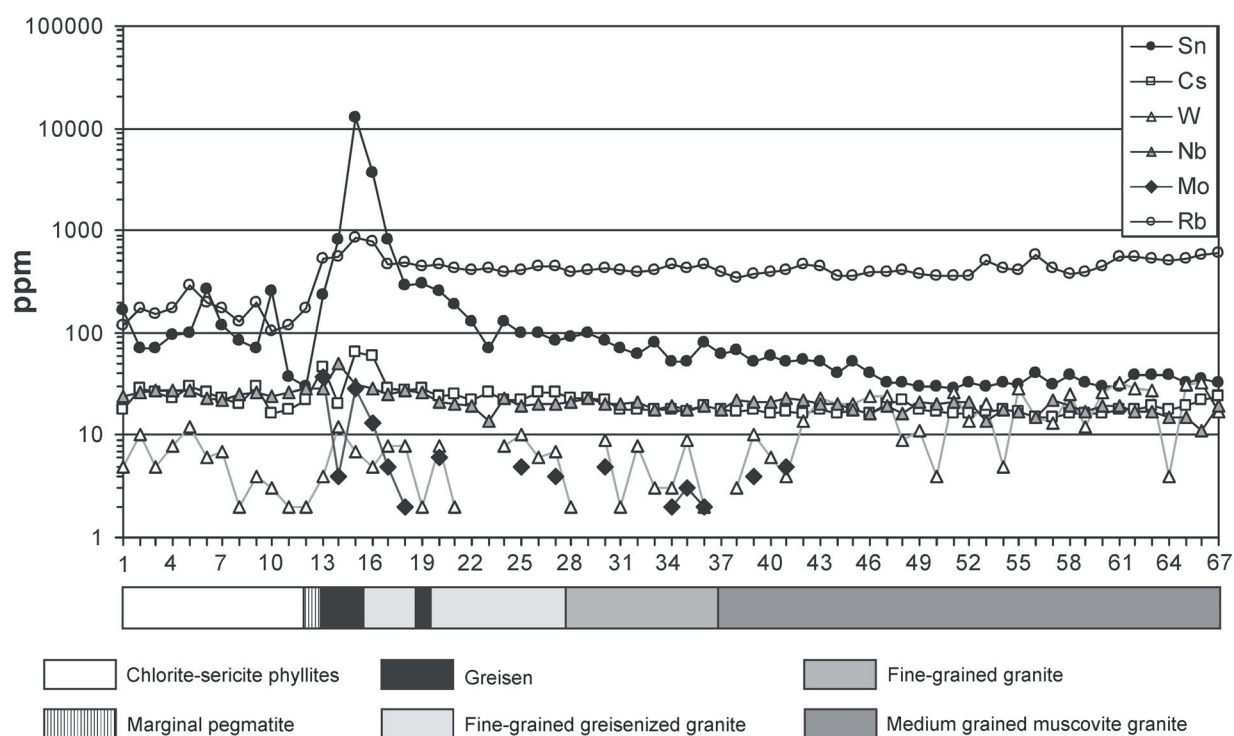
Table 5: Comparison of selected trace elements of highly evolved granites from world localities.

Localities	F (wt. %)	B (ppm)	Sn (ppm)	Rb (ppm)	Sr (ppm)	Source
Cornubian (SW England)	0.08–0.75	150–750	7–450	380–750	18–112	(Willis-Richards & Jackson 1989)
Beauvior (Massif Central, France)	1.33–2.39	<23	140–1405		70–448	(Cuney et al. 1992)
Podlesí (Czech Republic)	0.65–1.85	20–60	5–202	1106–3000	5–196	(Breiter 2002)
Cínovec (Czech Republic)	0.04–0.73	14–28	15–400	573–1807	<40	(Dolejš & Štemprok 2001)
Argamela (Central Portugal)	0.06–1.25	<71	77–806	241–2448	56	(Charoy & Noronha 1996)
East Kemptville (Canada)	1.2–4.6		87–2610	15–1056	21–29	(Halter & Williams-Jones 1996)
Phuket (SW Thailand)	0.03–1.44	15–1355	3–654	353–1272	2–130	(Pollard et al. 1995)

Fig. 6. General features of roof-zone granite evolution (apogranite) in the Hnilec area (adapted from Drnzík 1982). Profile A–A', see Fig. 1.

host rocks (Morgan & London 1987; London et al. 1996). In southwest England, such tourmaline in host rocks shows a higher Fe^{3+}/Fe^{2+} than in the granites, reflecting a higher oxidation state of the hosts (London & Manning 1995).

The tourmalines of Hnilec and generally in all Gemeric granitic rocks, including their altered parts are represented by schorl (Faryad & Jakabská 1997) and schorl-foitite (Broska et al. 1998). In the Hnilec area, the increased dravite component was found, except in granite exocontact, only in the rims and cracks of some primary tourmalines in granite roof zone (Fig. 4c). Such complex zonality could document a circulation of volatiles which are derived from granites. These fluids were contaminated by Mg, Fe-rich country rocks, mixed by meteoric waters, and partly returned back to granite cupolas, where they caused the formation of a mineral association, including the above mentioned tourmaline rims. A general scheme of the evolution of felsic granitic rocks in their apical parts with the effects of boron emanation on the surrounding rocks is presented in this sense (Figs. 3, 6).

Fig. 7. Sn distribution (in ppm) along the profile # 1 in the prospecting gallery No. 2. For comparison also other rare metals (Mo, W, Nb) and alkalies (Rb, Cs) distributions are presented (source data, Drnzík 1982).

The hydraulic rupture of roof-zone (apogranite) with strong alteration processes in the Hnilec area was also accompanied by the development of veinlet systems. The quartz veins are enriched in B, Sn, but also Ta, Nb, Mo, W in the form of cassiterite mineralization with low F content. Besides cassiterite, arsenopyrite, topaz, apatite, columbite and rare fluorite, these veins contain the higher dravite-schorl type of tourmaline (Fig. 6). According to the presented data boron can easily be transported for a long distance to the Fe-Mg-rich exocontact barrier, but fluorine seems to be stopped earlier by endocontact hydrated minerals such as micas. The different B and F geochemical behaviour resulted in the different mineral characters of the main B and F concentrators and their stability.

Tin, which generally accompanies the volatile-enriched granites, typically continually increases in the Gemeric granites from the internal parts of the granitic body towards the external altered parts with the maximum in the greisens and greisenized granites (Fig. 7). Tin distribution does not correspond to that of fluorine in granites but in greisen (compare Figs. 7, 3, Table 2). The deeper medium grained Ms-granites contain only around 40 ppm Sn, 200 ppm is a characteristic value for the upper situated fine-grained greisenized granite, whereas the highest content of Sn was determined in the apical greisens (~900 ppm). Exocontact aureoles usually have relatively lower contents of Sn (~90 ppm) (Fig. 7). Other rare metals, Mo and Nb are slightly enriched in greisen cupola, but on the other hand, the W content is not (Fig. 7; Drnzík 1982). To complete the picture of greisen evolution it is necessary to mention the increased Rb and Cs content in greisen because of eralier accumulated alkali feldspars in the granite cupola, later broke down to greisen (Fig. 7).

The Sn transportation in hydrothermal solutions is a function of a variety of parameters including temperature, pH, oxygen fugacity, bulk salinity and the presence of complexing ligands (Heinrich 1990; Halter & Williams-Jones1996). Sn has oxidation states of Sn^{2+} and Sn^{4+} in geologically relevant conditions, and as such its solubility, activity, diffusivity, and coordination in a silicate liquid may all vary as a function of fO_2. The following precipitation of cassiterite from magmatic fluids is connected with the decrease of pH of the fluid and fO_2 (Halter & Williams-Jones 1996). Sn is generally transported in the complexes with Cl^-, F^- or OH^- (Heinrich 1990). Jackson & Helgeson (1985) have also calculated that the rela-
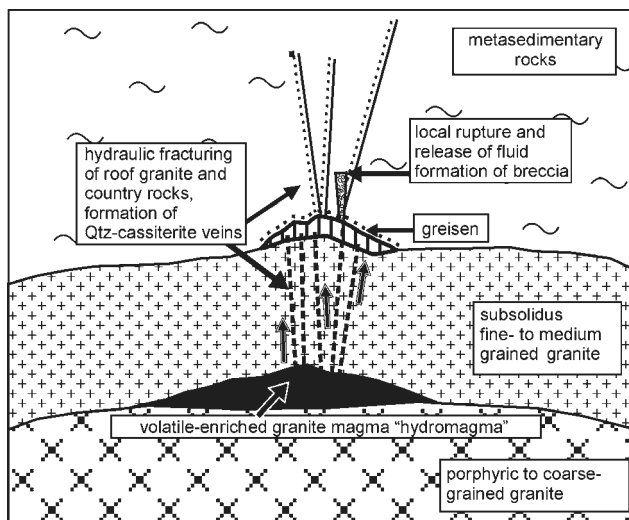

Fig. 8. A hypothetical cartoon of formation of the Hnilec granite cupola. The overpressuring hydromagma originated under the carapace of almost solidified fine-grained granites.
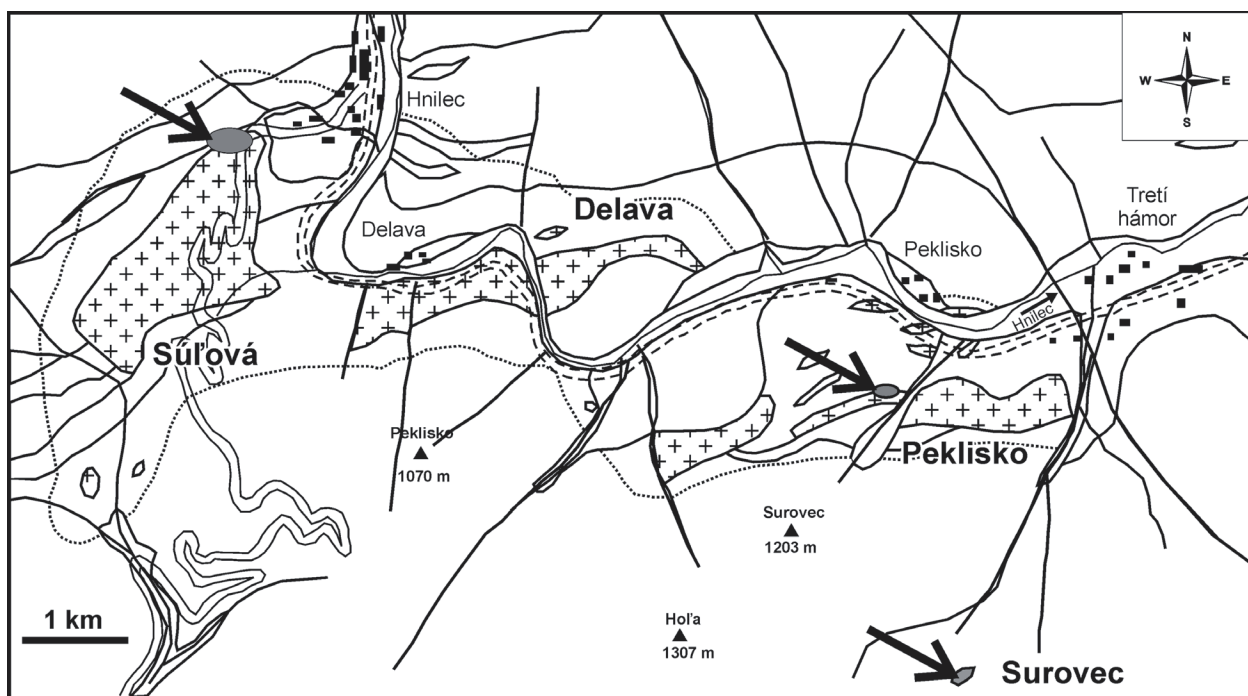

Fig. 9. Probable positions of emanation spots in the Hnilec area indicated by arrows (map background, Bajaník et al. 1984).

tive proportion of fluorine complexes are negligible compared to chloride complexing, even in F-bearing systems, but according to these authors, the most important tin species in solution is $SnCl^+$ (Wilson & Eugster 1990; Halter & Williams-Jones 1996), which is also supposed for the Hnilec area because Sn does not spatially correlate with F very much (Figs. 3, 7).

Hypothetical model of the evolution of the Hnilec granite cupola

The observed breccia pipes in the granite cupola are indirect evidence of an overpressuring regime in the granite cupola at the Hnilec locality. The hydrothermal breccia described in the prospecting gallery has been formed from angular fragments of rocks consisted from topaz granite blocks locally 40 cm in size cemented by vein mineralization containing cassiterite and quartz (Drnzík 1982). Unfortunately, the exact position of the topaz-bearing granites saved as fragments in breccias is still unknown in the Hnilec locality.

Basically the overpressuring volatile system could originate on the contact of the solidified fine-grained and underlaying coarse-grained to porphyric granite in sense that subsolid fine-grained granite became a carapace for the escape of volatiles (Jackson et al. 1989; Mark & Foster 2000). Beneath the crystallized granite carapace the upper parts of the magma column would have been enriched in volatile and lithophile elements and volatile rich granites or "hydrogranites" could form (Fig. 8). In the case when the vapour pressure of the dissolved fluid in the magma locally exceeds the lithostatic pressure, the rupture of the overlying crystalline rocks begins, and probably a catastrophic escape of volatiles occurs as it is supposed in the Cornubian ore (Jackson et al. 1989). The rupture of the roof granites and release of volatile-rich fluids, resulted in formation of tourmaline bearing hydrothermal veins and breccias occurs. The fracture propagation in the granite roof zone has created an open system for the degassed magmatic-hydrothermal fluids which triggered the greisenization of the fine-grained granite cupola as well as the start of formation of ore veins in the granite exocontact (Fig. 8). Volatile and metal-enriched residual fluids which accumulated beneath the roof represent probably a possible source of Sn, W and Mo. The greisenization and formation of the ore veins in the Hnilec area was restricted to several small places just above the emanation centres and in the Hnilec area it is mainly the valley of Medvedí potok near Suľová (Fig. 9).

Conclusion

Boron and fluorine in the Hnilec granites, significantly contributed to the depolymerization of the primary melts. They show cooperative effect on decreased liquidus and solidus temperatures and increases of melt quantity. Such a mechanism leads to the formation of a highly evolved and mobile granitic system, enriched in rare-metal elements. Increased contents of boron were determined from the deeper medium grained muscovite granite and fine-grained granite toward the granite cupolas. Boron concentrations are highest in the exo-

contact country rocks, where it forms a wide contact aureole around the granitic cupola. Increased boron volumes are also detected in the marginal pegmatite (stockscheider). Boron is mainly hosted in a tourmaline, which forms two genetic types: I. primary magmatic, II. secondary hydrothermal. In contrast, the highest contents of fluorine typically occur in greisens in the cupola. Low fluorine concentrations were determined in the country rocks which make the spatial distributions of B and F distinctly different. The boron and fluorine distribution within geochemical profiles indicates the higher geochemical mobility of boron compared to fluorine. Tin distribution does not correlate with F and B distribution the tin transportation in aqueous fluids probably occurs via the chloride complexes.

All data has been used to outline the greisen formation at the locality Medvedí potok Valley in Hnilec region, which represents one of several emanation centers within the Gemer granites. The emanation spot as a room with high volatile flux was localized above the hydromagmas pools which formed beneath the fine-grained granite carapace or between fine- and coarse-grained granites. These hypothetical places were overpressured and became sources of special mineralization of the Gemeric granites.

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