Brown and blue schorl from the Spiš-Gemer granite, Slovakia: composition and genetic relations

Hnědý a modrý skoryl ze Spišsko-gemerských granitů, Slovensko: chemické složení a genetické vztahy (Czech summary)

(5 text-figs.)

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Schorl is a widespread accessory mineral in Sn-bearing S-type rocks of the Spiš-Gemer granite suite (SGG), E Slovakia. Schorl content increases from Sn-, B-poor biotite-(muscovite) to highly evolved Sn, B-rich albite-muscovite leucogranite, locally with greisenized parts in granite cupolas. Optical, EMPA and OES data reveal two populations of tourmaline: (1) brown schorl with low X-site vacancy, and (2) X-site deficient blue schorl, enriched in Pb and Sn. A Fe/(Fe + Mg)$_{at}$ ratio varies between 0.75-0.97. The Mössbauer spectra determined Fe^{3+} < 10 % for both populations which indicate a low fO_2 conditions. Overgrowths of the blue variety on smoky cores and the trace-element chemistry indicate a two-stage evolution of SGG schorl: older brown schorl crystallized during magmatic stage with quartz, feldspars and micas, whereas younger blue schorl originated during late-magmatic to hydrothermal stage and it is a product of breakdown of brown schorl and biotite. Presence of schorl indicates B-rich protolite in the source rocks of SGG represented by illite- or muscovite-rich marine sediments.

Key words: schorl, granite, electron microprobe, Mössbauer spectroscopy, Spiš-Gemer granites, Slovakia

Introduction

Tourmaline-group minerals are widespread accessory phases in a very broad spectrum of igneous, metamorphic and sedimentary rocks due to their wide stability in P-T-X conditions. A sufficient boron content is a main factor of the mineral saturation. A complex crystal chemistry of the tourmalines requires an entry of various monovalent to tetravalent cations, including Na, K, Ca, Mg, Fe, Al, Cr, Ti, Si into three independent structural positions, often with significant X-site vacancies. This compositional variability is an usefull indicator of mineral and host-rock origin.

Schorl, a sodium-iron-rich member of the tourmaline group often occurs in relatively highly-fractionated, continental-collision-related, S-type leucogranite-pegmatite systems. West-Carpathian granites are generally very poor in accessory tourmaline, the Spiš-Gemer granite (SGG), eastern Slovakia is the single significant exception. Early descriptions of the SGG tourmaline gave general mineralogical informations about their occurrences in granites, tin-bearing greisens and vein-type mineralizations (Kamenický et al. 1953, Ončáková 1954, Kamenický - Kamenický 1955, Baran et al. 1971, 1978, Drnzík et al. 1973, Gubač 1977, Veselský et al. 1983, and others), recently tourmaline has been studied by electron microprobe (Faryad - Jakabská 1996).

Our study brings new compositional data of two basic color varietes of the mineral: brown and blue schorl in sense of a complex magmatic evolution of SGG as well as the first Mössbauer data of tourmaline from this region. Presented new results give a possibility to make new petrological conclusions on the tourmaline in SGG.

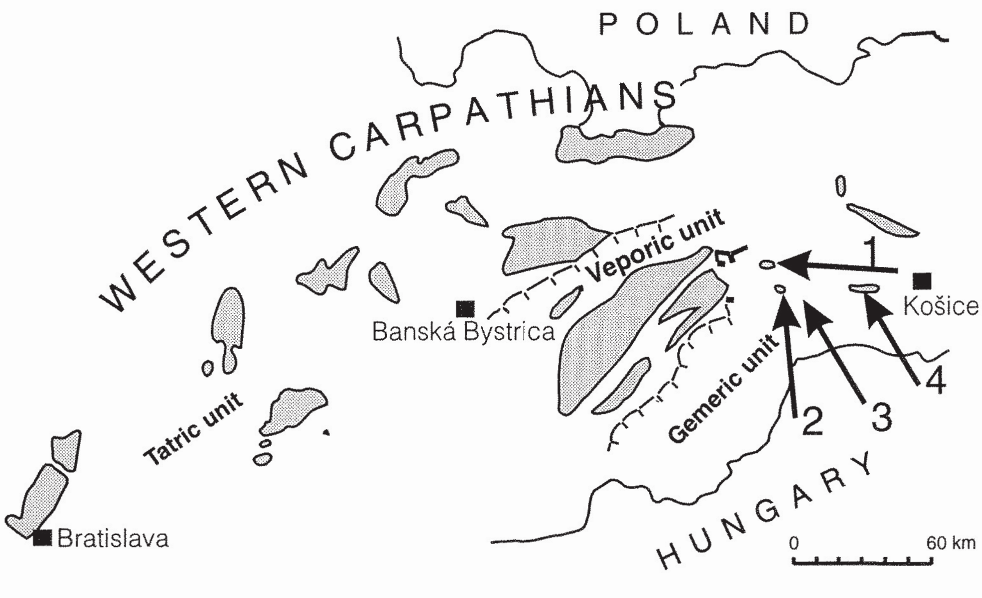


Fig. 1. Geological sketch map of the position Western Carpathian granites. The Spiš-Gemer granites (SGG) are situated in the Gemeric Alpine tectonic unit; the arrows show the position of the largest granite bodies: *1* - Hnilec, *2* - Betliar, *3* - Hummel, *4* - Zlatá Idka and Poproč

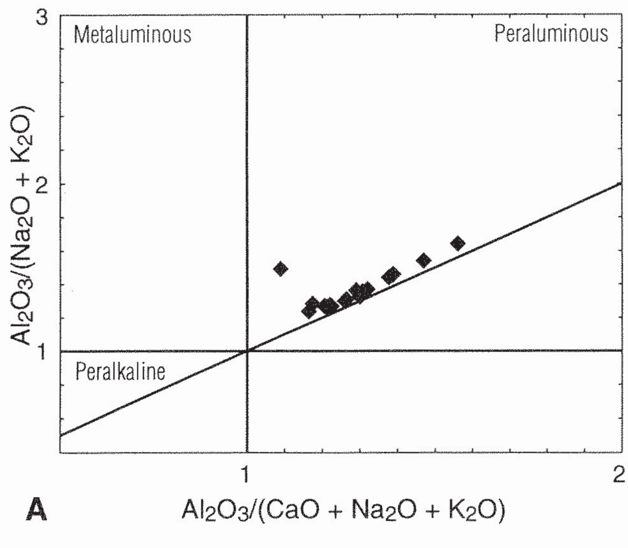
Host granites

The studied samples were taken from the all occurrences which are represented by small granite intrusions (Fig. 1). SGG intruded into folded Lower Palaeozoic metapelites and metapsammites as well as acidic metavolcanics of the Gelnica group or the Volovec Unit, both metamorphosed in greenschist facies (Grecula et al. 1995). The granite intrusions crop out in small 1 to 20 km^2 areas, however, the borehole and gravimetric data revealed large hidden massifs (Grecula, l.c.). The Spiš-Gemer granites (SGG) occur as a several discrete intrusions in the volcano-sedimentary Gelnica and Rakovec sequences, sometimes both united into the Volovec Unit (Maheľ 1986, Grecula et al. 1995), Fig. 1. The granite intrusions are represented mainly by fine- to medium-grained, locally coarse-grained and porphyric, biotite to biotite-muscovite and muscovite granites, locally accompanied by granite porphyries in the Betliar body (Kamenický - Kamenický 1955). On the basis of garnet study, the depth of magma generation has been estimated at minimally 21 km and 850 MPa, and the level of SGG solidification at 7 to 5 km, 200 to 150 MPa (Faryad - Dianiška 1989). Temperature of 750-780 °C has been calculated for the coexisting biotite-garnet phases in granites (Faryad - Dianiška 1989). Thin biotite+andalusite±cordierite±corundum contact-metamorphic aureole was originated at 450 to 570 °C and 100 to 200 MPa in host metapelites-metapsammites and acid metavolcanites (Faryad in Krist et al. 1992).

Albite-rich aplite granite and greisenized parts with Sn, (Nb, Ta), B, Li, F-mineralization occur in some granite cupolas, mainly in the Hnilec body and in hidden Dlhá Dolina intrusion (Malachovský in Grecula et al. 1995).

Geochemistry of SGG shows typical features of peraluminous, late- to post-orogenic leucogranite suite of S-type. The chemical composition of SGG shows acidic character with high SiO_2 content (mostly > 70 wt.%), relatively high alkalies especially K_2O (4 to 5 wt.%), low MgO (0.1 to 0.2 wt.%) and CaO (< 0.5, usually ~0.25 wt.%), Table 1. The A/NK vs. A/CNK diagram shows peraluminous character of SGG as well as relations among the investigated samples (Fig. 2A). The R_1-R_2 diagram indicates mainly the late-orogenic tendency (Fig. 2B).

Trace elements distribution with relatively high Rb (often above 350 ppm), Sn (≈ 19 ppm), Nb (≈ 11 ppm), B (≈ 400 ppm), and low Sr (≈ 25 ppm), Ba (≈ 120 ppm), Zr (≈ 85 ppm), and REE contents indicate highly evolved and mostly syn-collisional nature of SGG (Table 1, Fig. 2C).



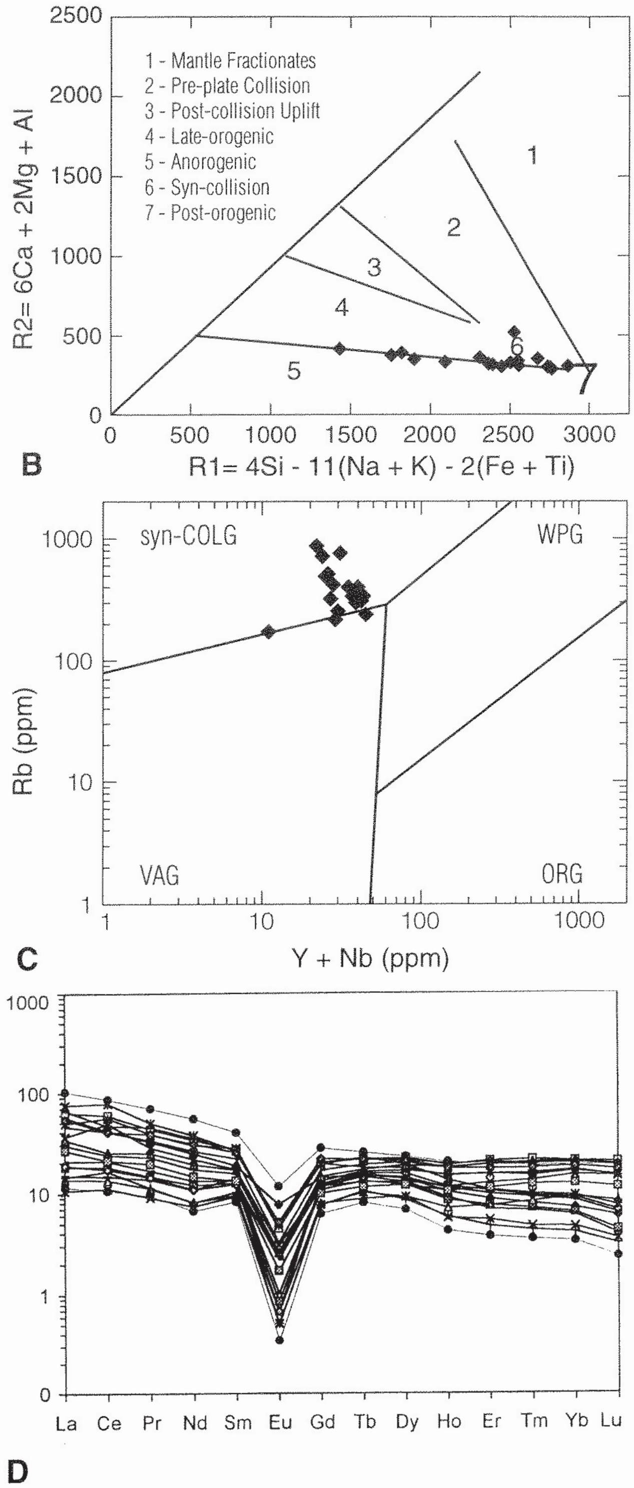


Fig. 2. The discrimination diagrams of SGG. A: A/NK vs. A/CNK (Maniar - Piccoli 1989); B: R_1-R_2 (Batchelor - Bowden 1985); C: Rb vs. Y + Nb (Pearce et al. 1984); D: REE chondrite-normalized patterns

Table 1. Chemical composition of SGG. A: Representative whole-rock chemical analyses (major and selected trace elements). Sample locations are in Fig. 1. B: Average, standard deviation, maximum and minimum values. Major elements and Rb, Sr, Ba Zr, Th, U, Zn, V, Ni determinations were done by XRF (Univ. Ottawa, Canada), B, Ga, Sn, by OES (Gological Institute of Slovak Acad. Sci. Bratislava), Ce, Y, Hf, Nb, Ta by ICP (Memorial University St. John's Canada)

granite sample	Hnilec GB-1	Betliar GB-16	Hummel GB-7	Zlatá Idka GB-13
SiO_2	71.21	73.69	71.01	74.73
TiO_2	0.04	0.10	0.12	0.13
Al_2O_3	16.14	13.69	15.27	13.16
Fe_2O_{3tot}	1.53	1.25	1.45	1.45
MnO	0.02	0.03	0.02	0.03
MgO	0.24	0.21	0.15	0.16
CaO	0.30	0.27	0.24	0.20
Na_2O	5.92	3.29	3.63	2.75
K_2O	1.25	4.92	5.60	5.10
P_2O_5	0.21	0.16	0.14	0.10
LOI	1.30	1.00	1.00	1.10
TOTAL	98.16	98.61	98.63	98.91
Rb	173	420	344	334
Sr	30	17	25	18
Ba	42	104	107	99
B	2040	280	148	72
Ga	33	24	24	23
Ce	6.8	13.3	16.2	25.8
Y	8.1	15.5	27.6	29.2
Zr	33	76	82	89
Hf	1.4	1.8	1.6	1.6
Th	15	29	15	14
U	3	3	7	11
Sn	25.7	24.5	9.6	18.2
Nb	6.7	11.9	12.7	12.5
Ta	2.4	2.4	2.2	2
Zn	78	37	21	34
V	3	3	5	3
Ni	5	5	4	5

Sample	average	st.dv.	max	min	n
SiO_2	72.76	1.68	75.93	67.91	18
TiO_2	0.18	0.11	0.73	0.04	18
Al_2O_3	14.52	0.94	17.26	13.07	18
Fe_2O_3	1.48	0.34	3.47	0.82	18
MnO	0.04	0.04	0.37	0.01	18
MgO	5.37	9.51	91.00	0.11	18
CaO	0.37	0.19	1.88	0.14	18
Na_2O	3.48	0.69	5.92	0.27	18
K_2O	4.37	1.02	5.87	1.25	18
P_2O_5	0.16	0.04	0.24	0.06	18
L.O.I.	1.21	0.27	1.70	0.90	13
Rb	360.67	90.78	758	173	18
Be	6.51	1.61	9.8	4.1	10
Zn	33.72	9.50	78	14	18
Sr	25.67	9.41	82	11	18
Ba	129.44	61.37	310	31	18
B	405.50	394.70	2040	49	10
Ga	27.20	2.80	33	23	10
Sn	19.25	6.13	28.6	9.6	10
Hf	2.06	0.59	4.74	1.21	18
Zr	85.67	31.19	214	33	18
Pb	31.86	31.94	185	0	14
Nb	11.22	2.52	18	4	18
Ta	2.52	0.91	5.46	1.19	18
V	10.43	7.27	41	3	14
Cr	9.00	6.46	22	1	13
Co	9.33	6.11	40	0	18
Ni	5.06	1.21	10	1	16
Th	15.06	3.74	29	8	18
U	7.72	4.19	29	3	18
Y	21.13	5.91	30.77	8.12	18
La	10.01	5.13	25.35	2.60	18
Ce	23.41	11.96	55.55	6.82	18
Pr	2.80	1.27	6.77	0.88	18
Nd	10.57	4.86	26.04	3.17	18
Sm	2.92	1.05	6.14	1.27	18
Eu	0.20	0.13	0.68	0.02	18
Gd	3.01	0.95	5.64	1.28	18
Tb	0.61	0.15	0.94	0.30	18
Dy	4.00	1.03	5.76	1.73	18
Ho	0.74	0.23	1.14	0.24	18
Er	2.16	0.78	3.41	0.62	18
Tm	0.33	0.12	0.54	0.09	18
Yb	2.15	0.88	3.38	0.55	18
Lu	0.30	0.14	0.51	0.06	18

REE chondrite-normalised patterns display a distinctive negative Eu-anomaly (Fig. 2D).

The $^{87}Sr/^{86}Sr$ ratios of rocks are very high: IR_{Sr} = 0.720 to 0.739 (Kovách et al. 1986), which fact also supported S-type character and a matured continental sedimentary or volcano-sedimentary magma sources of SGG. Similarly, a presence of Fe-rich annite: Fe/(Fe + Mg) = 0.70 to 0.96, almandine-spessartine garnet (Faryad - Dianiška 1989), ilmenite > magnetite and monazite-(Ce) > allanite-(Ce), xenotime-(Y), topaz and cassiterite indicate a relatively low fO_2, aluminous and evolved environment of the granite magma.

The whole-rock Rb-Sr analyses show the Permian age of SGG (Kovách et al. 1986, Cambel et al. 1989) and the earlier reported Mesozoic K-Ar data (Kantor 1957 and others) indicate Alpine uplift and tectono-metamorphic reworking of SGG.

Experimental methods

The electron microprobe analyses of tourmaline were done using a JEOL JCXA-733 Superprobe instrument at the Geological Survey of Slovak Republic, Bratislava, with an operating voltage of 15 kV and a sample current of 20 nA, measured on a Faraday cup. Beam diameter was ~3 μm and counting time was 25 s for the Kα lines of Si (SiO_2 standard), Ti (TiO_2), Al (albite), Cr (chromite), Fe (hematite), Mn (rhodonite), Mg (MgO), Ca (wollastonite), Na (albite) and K (orthoclase). The data were corrected by the ZAF procedure.

Trace elements in tourmaline were analyzed by optical emission spectroscopy (OES) using a Carl-Zeiss Jena PS-2 spectrometer at the Geological Institute, Slovak Academy of Sciences, Bratislava.

Room temperature spectra of tourmaline were obtained in transmission geometry using a conventional constant acceleration spectrometer at the Slovak Technical University, Bratislava. ^{57}Co in Rh matrix was used as a source of Mössbauer γ-radiation, collected, using powdered material in a conventional transmission Mössbauer spectrometer. The experimental data were least square fitted using the NORMOS computer program.

Results

Occurrence of tourmaline

Tourmaline was found in SGG as a euhedral to subhedral elongate rod-shape crystals, usually 0.1 to 2 mm long, locally as the only dark phase disseminated in bulk rock. Second type of tourmaline is represented by large, 0.5 to 10 cm lpng black crystals occurring in sun-shaped and globular aggregates with quartz or as discrete quartz-tourmaline veins which cut the granitic rocks (333ňčáková 1954, Grecula et al. 1995). We investigated only the first, disseminated type of tourmaline.

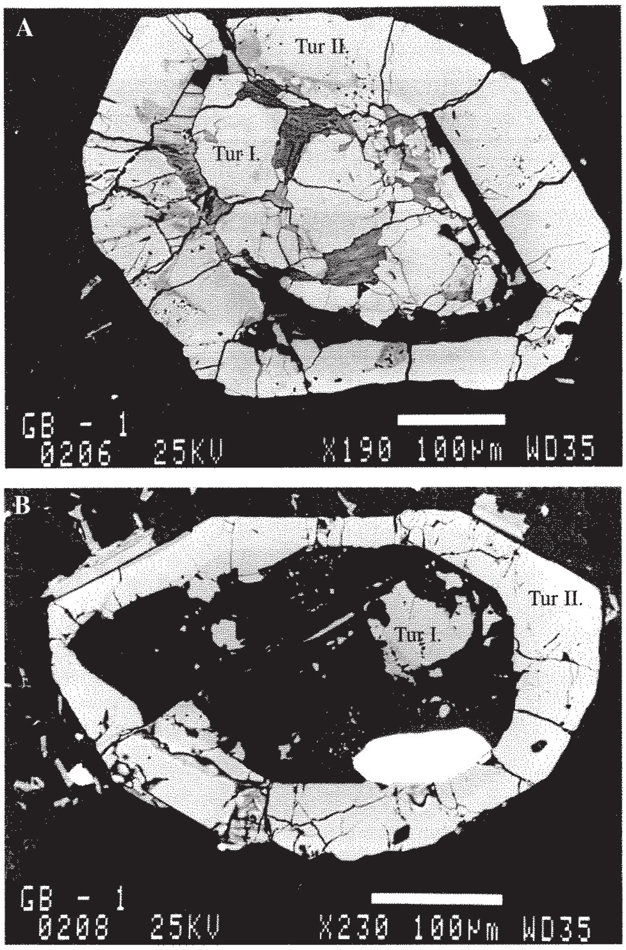


Fig. 3. BSE images of schorl from the Hnilec granite body. A: Remnants of the older population (brown) are in the centre of the crystal. The rim is a new-formed blue schorl. B: The old population of the schorl is almost completely replaced by albite and quartz. The light inclusion in schorl is zircon

Tourmaline associates with quartz, K-feldspar and albite, it is often interstitial or it corrodes alkali feldpars, its amount varies usually between 0.1 to 2 vol.% of rock. Althought the mineral is black in hand specimen, two color varietes of distinctly pleochroic tourmaline are evident under binocular lens or in thin sections: (1) brown variety with pale brown color in E and dark brown color in ω optical direction, and (2) blue variety with pale blue and dark blue color in E and ω direction, respectively. Both color varieties of tourmaline occur as discrete crystals or the brown variety forms a core with an overgrowth of blue one (Fig. 3A), locally the blue variety forms only rims on the formerly consumed brown tourmaline or biotite (Fig. 3B).

Chemical composition of tourmaline

On the basis of 48 electron microprobe analyses from five occurrences (the Hnilec, Betliar, Hummel, Poproč and Zlatá Idka granite bodies), both varietes of SGG tourmaline shows uniformly schorl composition with atomic Fe/(Fe + Mg) = 0.75 to 0.97, i.e., composition typical for magmatic tourmalines (Henry - Guidotti 1985, London - Maning 1995; Table 2, Fig. 4). There are no significant differences in Fe/Mg ratio between the brown and blue schorl in the Hnilec body, however, there are regional differences between the Hnilec body in north-west and the other granites in the south (Fig. 1:*4*). The brown schorl is slightly Ti- and Mn-enriched and Si-, Al-depleted in comparison to the blue schorl. The X-site vacancy is slightly to significantly higher in the blue variety, compared the

Table 2. Selected electron probe analyses of schorl from SGG (in wt. %). Boron and water was calculated on ideal stoichiometry (B = 3, OH = 4 apfu). * calculated on the basis of ideal stoichiometry

No Sample point	Hnilec GZ-1 brown core	Hnilec GZ-1 blue rim	Hnilec GZ-1 brown core	Hnilec GZ-1 blue rim	Hummel GZ-7 blue rim	Betliar GZ-16 brown rim
SiO_2	35.45	36.27	34.82	35.63	35.18	36.08
TiO_2	0.13	0.00	0.19	0.04	0.00	0.00
B_2O_3*	10.31	10.47	10.18	10.29	10.39	10.32
Al_2O_3	34.02	35.14	32.98	33.43	35.15	32.89
FeO	13.73	13.10	14.94	14.16	11.39	14.80
MnO	0.11	0.06	0.18	0.04	0.08	0.25
MgO	0.34	0.25	0.32	0.41	1.59	0.33
CaO	0.00	0.00	0.02	0.03	0.06	0.00
Na_2O	2.14	1.62	2.19	2.11	2.06	2.19
K_2O	0.03	0.03	0.05	0.00	0.01	0.02
H_2O*	3.56	3.61	3.48	3.55	3.58	3.56
TOTAL	99.82	100.55	99.35	99.68	99.50	100.44
Formulae based on 31 oxygens						
Si	5.974	6.020	5.945	6.021	5.882	6.075
Al_T	0.026	0.000	0.055	0.000	0.118	0.000
sum T	6.000	6.000	6.000	6.000	6.000	6.000
B	3.000	3.000	3.000	3.000	3.000	3.000
Al_Z	6.000	6.000	6.000	6.000	6.000	6.000
Al_Y	0.730	0.874	0.581	0.658	0.809	0.527
Ti	0.016	0.000	0.024	0.005	0.000	0.000
Fe	1.935	1.818	2.133	2.001	1.593	2.084
Mn	0.016	0.008	0.026	0.006	0.011	0.036
Mg	0.085	0.062	0.081	0.103	0.396	0.083
sum Y	2.782	2.782	2.846	2.794	2.810	2.804
vac Y	0.218	0.218	0.154	0.206	0.190	0.196
Ca	0.000	0.000	0.004	0.005	0.011	0.000
Na	0.699	0.521	0.725	0.691	0.668	0.715
K	0.006	0.006	0.011	0.000	0.002	0.004
sum X	0.706	0.528	0.740	0.697	0.681	0.719
vac X	0.294	0.472	0.260	0.303	0.319	0.281
OH	4.000	4.000	4.000	4.000	4.000	4.000
Fe/(Fe+Mg)	0.958	0.967	0.963	0.951	0.801	0.962

brown one with 27 to 47 atom.% and 19 to 29 atom.%, respectively. The Hnilec blue schorl reached the highest X-site vacancy and Al_Y atomic contents, some compositions are intermediate between schorl and the alkali-deficient member of the tourmaline group, foitite, $\square(Fe_2^{2+}Al)Al_6Si_6O_{18}(BO_3)_3(OH)_4$ (Table 2).

Table 3. Spectrochemical (OES) analyses of SGG schorl (in ppm)

sample	colour variety	Pb	Sn	Mo	V	Ni	Ga	Y
GB-4	blue tourmaline	> 500	150	2.8	3	11	141	8
GB-4	black tourmaline	30	115	2.3	4	9	140	6
GB-5	blue tourmaline	132	126	3.3	4	10	115	40
GB-5	black tourmaline	13	80	2.8	7	7	120	20
GB-16	mainly black	14	37	2.1	14	9	100	6

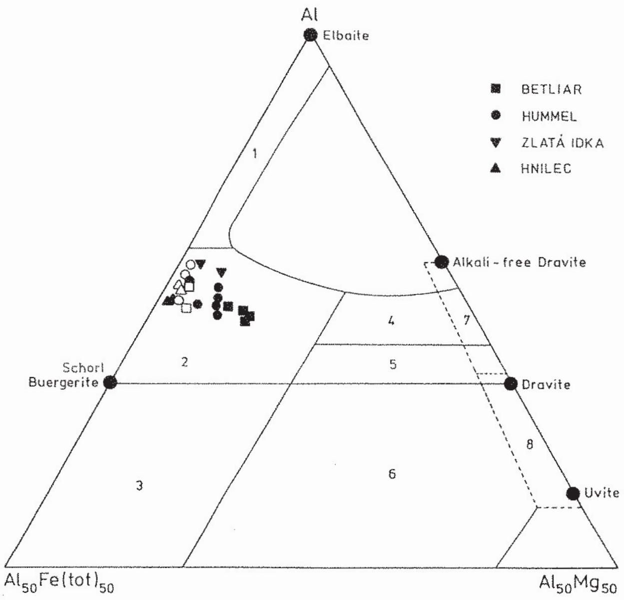


Fig. 4. Ternary Al-Fe-Mg diagram for tourmaline (Henry - Guidotti 1985) of SGG. Solid symbols represent cores (brown schorl), open symbols rims (usually blue schorl). Numbers: (1) Li-rich granitoid pegmatites and aplites, (2) Li-poor granitoids and their associated pegmatites and aplites, (3) Fe^{3+}-rich quartz-tourmaline rocks (hydrothermally altered granites) (4) Metapelites and metapsammites coexisting with an Al-saturating phase (5) Metapelites and metapsammites not coexisting with an Al-saturating phase (6) Fe^{3+}-rich quartz-tourmaline rocks, and metapelites (7) Low-Ca metaultramafics and Cr, V-rich metasediments (8) Metacarbonates and meta-pyroxenites

The OES of the brown and blue schorl population also reveals significant differences in some trace elements (Table 3). The blue variety is significantly richer in lead and also in tin contents in comparison to the brown one.

Mössbauer spectroscopy

We studied seven samples by Mössbauer spectroscopy and three samples for a comparison, two from the Rožná pegmatite, Czech Republic, and one from the Klenovský Vepor metapelite, Slovakia (Table 4). It was quite natural to fit spectra using four overlaping doublets. Our analyses have shown the effect of ionic substitution in the neighbouring cation sites. We have found that the Δ_4 doublet with the Mössbauer parameters indicates a Fe^{2+}-Fe^{3+} interaction (mixvalent state of iron $Fe^{2.5+}$), Table 4, Fig. 5. Thus, the amount of the Fe^{3+} is only estimated value but it is clear that this content is ca. < 10 % due to the well-known Fe-Fe charge interaction effects (Ferrow 1994). On the contrary, the comparative sample from the Klenovský Vepor metapelite shows 34.6 % of the ferric component (Table 4).

Discussion

Both the presence of accessory schorl and high boron content in SGG indicate that their protolith was different from the protolith of the rest of S-type granites in the Western Carpathians. Probably the melting of B-rich muscovite-bearing (meta)sediments caused the high concentration of boron in the magma. Such melting produced also the relatively high amount of melt, more than 40 vol.% in between 750 to 850 °C at 1 GPa (Guillot - LeFort 1995). Almost identical conditions for SGG crystallization were estimated by Petrík - Kohút (1997).

The schorl content increases progresively from more basic biotite granite to the most fractionated albite-rich leucogranite, often with greisenization in the granite cupolas. This fact along with increased Na, K, Rb, Cs, Li, Ta and F corroborates origin of SGG tourmaline as a product of primary magmatic evolution. The brown variety of schorl is texturally older than blue variety, the zonal tourmaline crystals with a brown core and blue rim was firstly observed in the Hnilec body by Ončáková (1954).

Table 4. Hyperfine interaction parameters and relative peaks areas of Mössbauer spectra of tourmaline in SGG, the Rožná pegmatite and the Klenovský Vepor metapelite for comparison

Code	Sample	Δ_1 [Fe^{2+}]			Δ_2 [Fe^{2+}]			Δ_3 [Fe^{2+}]			Δ_4 [$Fe^{2.n+}$]			Δ_5 [Fe^{3+}]		
		QS mm/s	IS mm/s	A_{rel} %	QS mm/s	IS mm/s	A_{rel} %	QS mm/s	IS mm/s	A_{rel} %	QS mm/s	IS mm/s	A_{rel} %	QS mm/s	IS mm/s	A_{rel} %
1313	GB-16 brown	2.45	0.98	29.6	2.16	0.98	31.9	1.65	1.00	14.3	1.15	1.00	14.3			
1314	GB-1 brown	2.49	0.99	30.4	2.19	0.99	33.4	1.82	1.00	19.2	1.13	1.00	17.0			
1315	GB-2 brown	2.45	0.98	29.6	2.16	0.98	31.9	1.83	0.98	20.8	1.09	0.99	17.7			
1337	GB-4 brown	2.48	0.99	30.4	2.19	0.99	31.6	1.87	1.00	21.0	1.14	1.01	17.0			
1338	GB-4 blue	2.46	0.99	32.6	2.17	0.99	32.5	1.79	0.99	19.8	1.11	0.99	15.1			
1335	GB-5 brown	2.47	0.99	32.7	2.18	0.99	33.0	1.79	0.99	19.5	1.17	1.01	14.8			
1336	GB-5 blue	2.46	0.99	33.3	2.17	0.99	31.4	1.81	1.00	20.5	1.18	0.99	14.8			
1341	Rožná - brown	2.47	0.98	40.4	2.19	0.98	23.0	1.82	0.97	25.5	1.23	0.86	11.1			
1339	Rožná - blue	2.42	0.95	59.4	2.34	1.02	26.1	2.00	1.09	14.5						
1340	Klen. Vepor UB-1	2.46	0.98	30.4	1.98	0.88	12.5				1.32	0.70	22.5	0.73	0.35	34.6

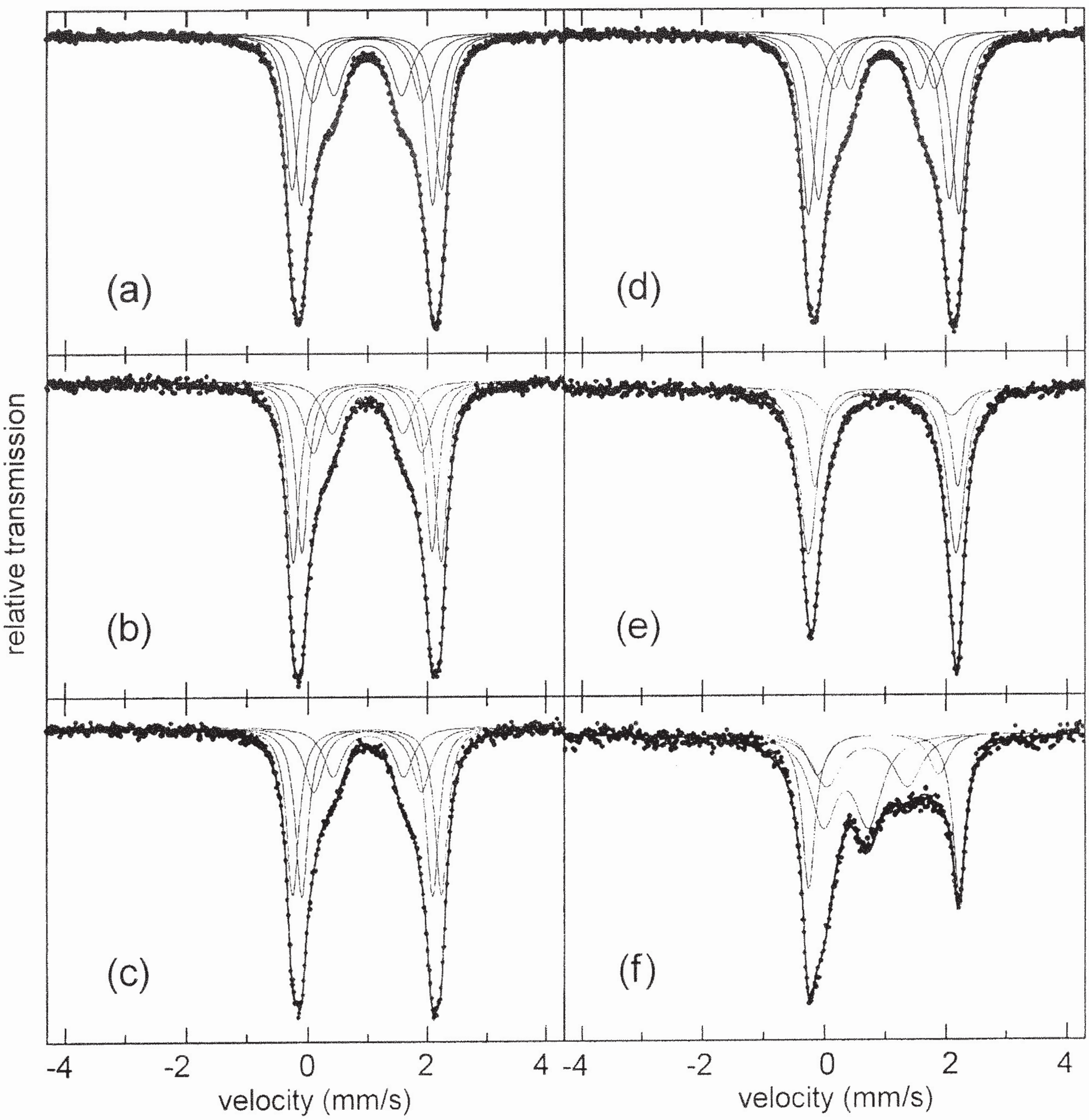


Fig. 5. Selected room temperature Mössbauer spectra of tourmaline from SGG, the Rožná pegmatite and the Klenovský Vepor metapelite for comparison
a - GB-5 brown schorl (Hnilec); b - GB-5 blue schorl (Hnilec); c - GB-1 mainly brown schorl (Hnilec); d - GB-16 mainly brown schorl (Betliar); e - UB-1 brown schorl (the Klenovský Vepor metapelite); f - Elbaite from the Rožná pegmatite

Electron microprobe and OES data also support the existence of two genetic populations of schorl. In contrast to the older brown variety, the younger blue schorl is significantly X-site deficient (≤ 47 %) and enriched in trace Pb and Sn. These results are in accordance with a late, hydrothermal origin of X-site deficient, foitite member of tourmaline group in granitic pegmatites (Selway et al. 1997, Aurisicchio - Pezzotta 1997). In addition, the highest Sn and Pb contents in tourmaline are reported from Sn-bearing granites and especially from their late differentiates: greisens and quartz-tourmaline veins; ~100 to 6000 ppm Sn and 30 to 1000 ppm Pb (Rub et al. 1970, Lyakhovich 1973).

Elevated contents of Sn in SGG tourmaline (73 to 292 ppm) were reported earlier by Baran et al. (1978), however these authors did not subdivide the mineral into brown and blue populations. Our analyses also show a small vacancy in the Y-structural position: 0.13 to 0.22 apfu (Y = Al, Ti, Fe, Mn, Mb, Li, Σ Y = 3 apfu). This fact can be explained by: (1) true vacancy in the Y-site, (2) presence of an undetermined element in the Y-site, particularly lithium, or (3) normalization of formula on OH = 4. Although SGG, especially their apical granite cupolas are positively enriched in Li, supported by a presence of Li-rich muscovite and zinnwaldite in the Hnilec and Dlhá Dolina intrusions, charge-balance calculations of EMPA compositions as well as negligible contents of Li in SGG tourmaline, determined by spectroscopy (8 to 27 ppm, Baran et al. 1978) exclude a significant admixture of Li (elbaite molecule) in the studied schorl.

There is a textural evidence of the breakdown of biotite and older brown schorl in SGG (Fig. 3). This breakdown reaction is known from the tourmaline-bearing the High Himalayan leucogranites as was shown experimentaly by Scailet et al. (1995). Indirectly, this fact supports also distribution of tourmaline in SGG when tourmaline is not very common in biotite-rich granite and its content increased from deeper part of body to the granite cupola (Rub et al. 1977, Grecula et al. 1995) what indicates increasing of tourmaline stability with the fractionation processes in SGG.

The Mössbauer spectroscopy shows a dominant presence of ferrous (Fe^{2+}) and only negligible, less than 10 % of possible ferric (Fe^{3+}) iron. This fact suggests reduction conditions during origin of SGG which is typical for the S-type granites.

Conclusions

Two generations of schorl were observed here: older brown and younger blue one. Magmatic origin of SGG brown schorl was proved (cf. Faryad - Jakabská 1996). On the contrary, the blue schorl is texturally evidently younger, X-site deficient and Pb, Sn enriched and it originated by the breakdown of brown schorl and/or biotite, probably during late-magmatic to hydrothermal stage. Mössbauer spectroscopy indicates low fO_2 regime for both varietes of schorl. Spatial changes of SGG schorl were observed; the highest Fe/(Fe + Mg) ratio was observed in the most fractionated Hnilec granite in the north-western part of the Gemeric Unit. Presence of schorl indicates B-rich protolith in the source rocks of SGG represented by illite- or muscovite-rich marine sediments.

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Hnědý a modrý skoryl ze Spišsko-gemerských granit, Slovensko: chemické složení a genetické vztahy

Skoryl patří mezi typické akcesorické minerály permských cínonosných Spišsko-gemerských granitů (SGG) S-typu ve Slovenském rudohoří. Na základě optického studia, analýz elektronovou mikrosondou a spektrální analýzy možno rozlišit dva genetické typy (generace) turmalínu: starší, patrně magmatický hnědý skoryl I, s nízkými vakancemi v pozici X, a mladší, pravděpodobně pozdně-magmatický až hydrotermální, sytě modrý (ve výbrusu až zelený) skoryl II, vyznačující se výraznějšími vakancemi v pozici X a zvýšenými obsahy Pb a Sn. Modrý skoryl přitom obrůstá a zatlačuje starší hnědý skoryl, nebo se tvoří i na úkor biotitu. Mössbauerovská spektroskopie ukázala u obou typů dominantní obsah Fe^{2+}, přičemž mixvalentní obsah Fe^{2+}+ Fe^{3+} je nižší než 10 %, což indikuje redukční podmínky prostředí, typické pro S-typ granitu. Přítomnost turmalínu v SGG současně poukazuje na protolit s primárně zvýšeným obsahem bóru, pravděpodobně illitem nebo muskovitem obohacené marinní sedimenty.