

Tourmaline and associated minerals in alkali-feldspar orthogneiss near Hluboká nad Vltavou, southern Bohemia



Turmalín a sdružené minerály v alkalicko-živcové ortorule u Hluboké nad Vltavou (Czech summary)

(5 text-figs.)

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Tourmaline in the Hluboká orthogneiss, a rock unit 7 by 2 km in outcrop size, is characterized by wet chemical analyses of four samples, microprobe analyses, unit-cell dimensions, density, and indices of refraction. The tourmaline compositions range from $sc_{49}dr_{36}ol_{15}$ to $sc_{78}dr_{11}ol_{11}$; the content of the olenite end-member ranges up to 26 %. The associated major and accessory minerals are also characterized by microprobe analyses. The data obtained are compatible with primary magmatic crystallization of tourmaline in the pre-Variscan parent rock. A comparison of tourmaline composition in five related orthogneiss and granite-metagranite bodies in the Moldanubian Zone of south-central and eastern Bohemia shows significant similarities, except the Radonice orthogneiss, carrying a notably more magnesian tourmaline.

Key words: tourmaline, schorl, composition, physical properties, Hluboká orthogneiss, Moldanubian Zone

Introduction

Tourmaline with a general formula: $XY_3Z_6(B_3Si_6O_{27})(OH,O)_3(OH,F)$ provides by its several different structural positions for a number of simple and combined substitutions by a variety of elements. Frequent substitution R^+/R^{2+} in the position X, or R^{2+}/R^{3+} in the position Y, are accompanied by a decrease in alkali elements and the hydroxyl group, resulting in numerous substitution series involving 11 end-members known at present. Tourmaline is thus a promising indicator of chemical activity of elements in parent rocks and it can potentially record information useful for thermometry and barometry. The previous petrological and geochemical study (Vrána et al. 1986, Slabý 1991) and study of apatite in Hluboká orthogneiss (Povondra - Vrána 1993) shows that this orthogneiss, 7 by 2 km in outcrop size, evolved from an original intrusive body of alkali-feldspar granite, similar in composition to tourmaline pegmatite. The Hluboká orthogneiss, emplaced in sillimanite-biotite paragneiss of the Monotonous Group of the Moldanubian Zone, has a probable intrusion age of the magmatic protolith 508 ± 7 Ma (Vrána - Kröner 1995).

The composition of tourmaline and of the associated minerals is used to characterize the plutonic and metamorphic history of the orthogneiss. Alternatives in the origin of tourmaline, i.e., primary magmatic crystallization, boron introduction in the course of the Variscan regional metamorphism, or recrystallization of a primary magmatic tourmaline, are discussed.

Samples and methods

The sites of sampling in the western part of the orthogneiss body and a brief information on geology and

petrology is given in Povondra and Vrána (1993). An additional sample No. 36, used in this study, was collected on elevation 800 m NE of the hill Velký Kameník.

Tourmaline concentrate was obtained by electromagnetic and heavy liquid separation, and by final hand picking. The four tourmaline average samples were analyzed using methods of wet analysis, modified for tourmaline analysis (Povondra 1981). Electron microprobe analyses, sited at random in crystal cores and rims, were obtained on the samples used for wet analysis. The physical properties of tourmaline are characterized by indices of refraction, measured density, and unit-cell dimensions.

The minerals associated with tourmaline are characterized by microprobe analyses in thin section (major minerals in sample 3), including K-feldspar, albite, biotite, and muscovite. Accessory minerals, mainly garnet and sphalerite, were analyzed by microprobe, using fractions from heavy mineral concentrates of the same samples used for tourmaline separation. Some accessory minerals, such as ilmenite-pyrophane and gahnite, were analyzed in polished sections of additional samples.

A set of major, minor, and trace element analyses on orthogneiss samples characterizes composition of Hluboká orthogneiss (Table 1). All the sample numbers bear a prefix HV, used in Povondra and Vrána (1993); in the present text the prefix is omitted.

Tourmaline

Field and petrographic study

Geological mapping at the scale 1:25 000 provided information on notably regular distribution of tourmaline

Table 1. Chemical composition of Hluboká orthogneiss

Major elements n = 3					Trace elements n = 12						
x		s	x		s	x		s	x		s
SiO ₂	73.50	(1.31)	Na ₂ O	3.90	(0.15)	Be	1.0	(0.0)	Y	15.3	(5.0)
TiO ₂	0.11	(0.05)	K ₂ O	4.26	(0.62)	V	16.1	(6.6)	Zr	29.3	(13.2)
Al ₂ O ₃	14.52	(0.46)	Li ₂ O	0.036	(0.013)	Cr	23.3	(5.6)	Nb	14.0	(4.6)
Fe ₂ O ₃	0.18	(0.04)	P ₂ O ₅	0.42	(0.15)	Ni	15.2	(7.2)	Sn	25.9	(14.7)
FeO	1.05	(0.27)	H ₂ O ⁺	0.55	(0.10)	Rb	414.3	(65.1)	Ba	77.5	(67.6)
MnO	0.025	(0.009)	F	0.21	(0.07)	Sr	35.2	(5.4)	Pb	14.3	(6.1)
MgO	0.15	(0.11)									
CaO	0.45	(0.11)									

Major elements: analyses of samples 3, 30, and 85; Chemical Laboratory, Czech Geological Survey, Prague

Trace elements: X-ray fluorescence analyses, [ppm], Geologický průzkum, Brno and Optical spectral analyses (Be, Sn)

Table 2. Chemical composition of tourmaline in Hluboká orthogneiss (wet analyses)

Sample	3	30	36	85
SiO ₂	34.89	34.86	34.95	34.87
B ₂ O ₃	10.11	9.80	9.90	10.10
Al ₂ O ₃	30.45	32.44	30.81	30.84
TiO ₂	1.21	1.12	0.92	0.91
Fe ₂ O ₃	4.61	3.58	3.43	3.84
FeO	10.25	11.45	12.96	12.31
MnO	0.10	0.11	0.16	0.12
MgO	2.41	1.81	1.25	1.66
Li ₂ O	0.005	0.003	0.015	0.022
CaO	0.15	0.23	0.12	0.22
Na ₂ O	2.10	1.76	1.96	2.06
K ₂ O	0.10	0.17	0.11	0.17
H ₂ O ⁺	2.03	2.10	2.05	1.77
F	0.41	0.41	0.44	n.d.
-O=2F	-0.173	-0.173	-0.185	-
Σ	98.665	99.670	98.890	98.892

Number of ions based on 31 (O,OH,F)

Si	6.052	5.996	6.087	6.138
B	3.025	2.908	2.975	3.057
Al	6.223	6.573	6.322	6.310
Ti	0.157	0.145	0.145	0.119
Fe ³⁺	0.602	0.464	0.450	0.502
Fe ²⁺	1.488	1.647	1.887	1.787
Mn	0.015	0.015	0.024	0.018
Mg	0.623	0.464	0.324	0.321
Li	0.003	0.006	0.010	0.016
Ca	0.028	0.042	0.022	0.041
Na	0.705	0.587	0.661	0.694
K	0.022	0.037	0.024	0.038
OH	2.348	2.409	2.382	2.051
F	0.225	0.223	0.243	0.231
O	1.427	1.368	1.375	1.718
Σ oct	3.111	3.314	3.162	3.073
Σ alk	0.755	0.666	0.707	0.773
F*	0.766	0.851	0.870	0.871

$$F^* = \text{Fe}_{\text{tot}} / (\text{Fe}_{\text{tot}} + \text{Mn} + \text{Mg})$$

ne in the orthogneiss body. It is present as a minor phase making approximately 1 to 3 vol. % in > 90 % of orthogneiss outcrops. Tourmaline forms mainly subhedral prisms 5 to 30 mm long, accompanied by a lesser amount of nearly anhedral grains. Lenticular aggregates of anhedral tourmaline several cm long, aligned in foliation and intergrown with feldspar and

quartz, also occur as a minor textural type. Tourmaline prisms show a tendency to planar and linear shape orientation, however, a strongly defined tourmaline lineation was not observed. The subhedral prisms are poikilitic and quartz inclusions make 30 to 60 % of the volume of tourmaline crystals. Information on compositional and optical zoning of tourmaline is included in the chemical section.

No tourmaline pegmatites or tourmaline-rich layers (e.g., tourmalinites) have been found in the orthogneiss. Minor streaks and patches of tourmaline crystallized from hydrothermal fluids occur in small and local quartz veins, which fill late brittle fractures. This late tourmaline post-dating metamorphism was not analyzed. Thin sections of the country rock sillimanite-biotite paragneiss are largely free of tourmaline or contain only an accessory amount.

Chemical study

Tourmaline separated from samples 3, 30, 36, and 85 was analyzed using wet analyses modified by Povondra (1981). The analyses and numbers of ions calculated to 31 (O,OH,F) are given in Table 2. The results show that tourmaline in the Hluboká orthogneiss corresponds to members of the schorl-dravite series. This trend is confirmed by 27 microprobe spot analyses, shown in Table 3 as arithmetic mean compositions (x) and their standard deviations (s).

A general formula for tourmaline is $\text{XY}_3\text{Z}_6(\text{B}_3\text{Si}_6\text{O}_{27})(\text{OH},\text{O})_3(\text{OH},\text{F})$. Distribution of elements in structural positions for the tourmalines analyzed is the following: the tetrahedral positions are fully occupied by 6 Si (apfu) and the boron content also corresponds to the theoretical number of 3 apfu. The position O₁ shows a strong predominance of hydroxyl ions over fluoride ions and their content is rather constant (0.223-0.243 apfu). The deficiency of OH ions in the position O₃ is a consequence of combined substitutions in the octahedral position Y₃.

In the positions occupied by cations a deficiency in position X is remarkable. The vacancy observed corresponds to 27 % of the position X. A larger variation

Table 3. Electron microprobe analyses of tourmaline in Hluboká orthogneiss, calculated as average compositions

Sample	3 n = 3		30 n = 3		36 n = 9		85 n = 5		10 n = 7	
	x	s	x	s	x	s	x	s	x	s
SiO ₂	34.24	(1.44)	34.29	(0.42)	35.16	(0.33)	34.94	(0.32)	35.90	(0.79)
Al ₂ O ₃	31.07	(1.37)	32.45	(0.81)	32.51	(0.72)	32.58	(0.46)	34.34	(0.39)
TiO ₂	1.27	(0.49)	0.67	(0.08)	0.66	(0.06)	0.82	(0.13)	0.74	(0.24)
FeO _{tot}	13.24	(1.45)	11.57	(0.61)	14.53	(0.48)	13.34	(0.47)	11.31	(0.57)
MnO	0.09	(0.05)	0.08	(0.01)	0.10	(0.03)	0.12	(0.02)	0.14	(0.05)
MgO	4.63	(0.62)	4.36	(0.47)	1.70	(0.11)	2.99	(0.23)	2.68	(0.19)
CaO	0.04	(0.07)	0.12	(0.01)	0.02	(0.04)	0.06	(0.03)	0.10	(0.05)
Na ₂ O	2.80	(0.21)	2.40	(0.08)	2.31	(0.12)	2.39	(0.07)	1.52	(0.13)
K ₂ O	0.08	(0.05)	0.03	(0.02)	0.06	(0.01)	0.04	(0.01)	0.02	(0.02)

Number of ions based on 24.5 (O)

Si	5.723	(0.173)	5.766	(0.023)	5.896	(0.066)	5.841	(0.035)	5.919	(0.101)
Al	6.165	(0.333)	6.432	(0.058)	6.434	(0.130)	6.421	(0.081)	6.674	(0.091)
Ti	0.159	(0.062)	0.085	(0.012)	0.089	(0.015)	0.102	(0.016)	0.091	(0.030)
Fe	1.851	(0.190)	1.629	(0.111)	2.041	(0.074)	1.865	(0.071)	1.559	(0.080)
Mn	0.012	(0.006)	0.012	(0.002)	0.011	(0.006)	0.016	(0.002)	0.020	(0.006)
Mg	1.153	(0.157)	1.091	(0.101)	0.438	(0.033)	0.695	(0.148)	0.625	(0.046)
Ca	0.001	(0.001)	0.021	(0.002)	0.004	(0.002)	0.010	(0.004)	0.019	(0.009)
Na	0.907	(0.058)	0.781	(0.035)	0.751	(0.041)	0.776	(0.024)	0.486	(0.045)
K	0.018	(0.011)	0.010	(0.002)	0.011	(0.005)	0.009	(0.003)	0.004	(0.003)
Σ oct	3.338	(0.251)	3.249	(0.042)	3.028	(0.071)	3.101	(0.072)	2.964	(0.128)
Σ alk	0.925	(0.068)	0.812	(0.037)	0.773	(0.039)	0.795	(0.023)	0.510	(0.050)
F*	0.613	(0.096)	0.596	(0.062)	0.819	(0.048)	0.725	(0.068)	0.709	(0.056)

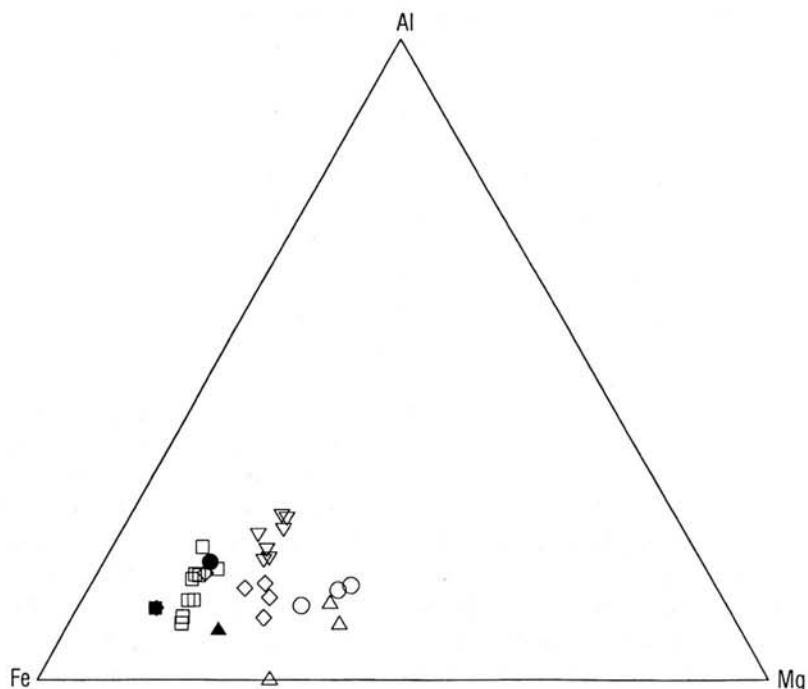
$$F^* = \text{Fe}_{\text{tot}} / (\text{Fe}_{\text{tot}} + \text{Mn} + \text{Mg})$$

is observed in the microprobe analyses (Table 3). Part of these vacancies is probably occupied by R²⁺ cations (Mg) from the position Y₃, showing in all samples a surplus of about 10 %, following the substitution scheme OMg Na₁H₁. The position Z is fully occupied by trivalent metals, i.e., Al and some Fe³⁺.

The position Y₃ is most important for a crystallochemical characterization of tourmalines. It is fully occupied in the samples analyzed (3 apfu). As show the values $F^* = \text{Fe}_{\text{tot}} / (\text{Fe}_{\text{tot}} + \text{Mn} + \text{Mg})$, the tourma-

lines correspond to iron-rich schorl exhibiting variation of the F* value from 0.60 to 0.87. The chemical composition is visualized by the relative ratios Fe_{tot} : Mg : Al, projected on the composition triangle schorl-dravite-olenite (Fig. 1). The compositions range from sc₄₉-dr₃₆-ol₁₅ to sc₇₈-dr₁₁-ol₁₁; the content of the olenite end-member ranges up to 26 %. Fig. 1 also shows that tourmaline compositions (microprobe analyses) in individual samples concentrate around projection points of the average compositions and

Fig. 1. Composition of tourmalines from the Hluboká orthogneiss in schorl (Fe), dravite (Mg), and olenite (Al) triangle
Solid symbols - "wet" chemical analyses, open symbols - electron microprobe analyses.
Triangles - sample 3, circles - sample 30, squares - sample 36, diamonds - sample 85, inverted triangles - sample 10



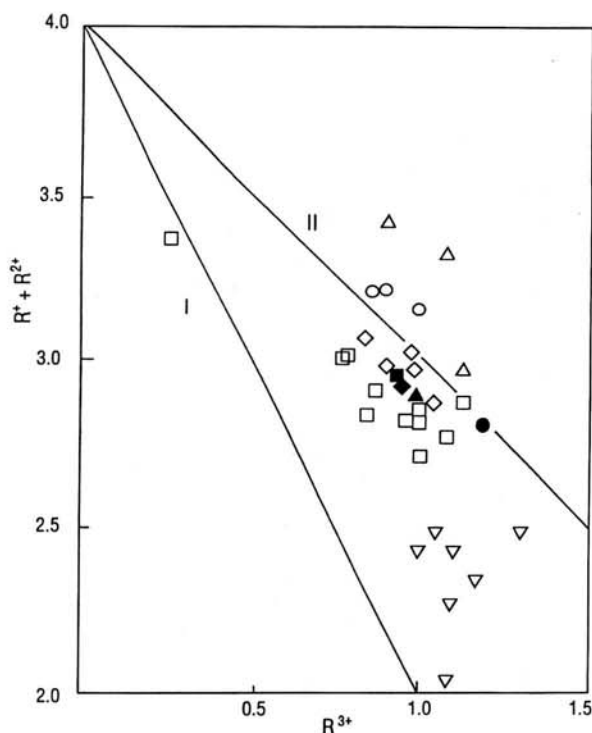


Fig. 2. Combined substitutions in tourmaline from the Hluboká orthogneiss. The line I = R^{3+} , vacancy, $R^{2+}_{-1}R^{+}_{-1}$, the line II = $O^{2-}R^{3+}R^{2+}_{-1}OH^{-}_{-1}$. Solid symbols - "wet" chemical analyses, open symbols - electron microprobe analyses. Triangles - sample 3, circles - sample 30, squares - sample 36, diamonds - sample 85, inverted triangles - sample 10

indicate limited ranges of miscibility. Wet analyses show higher total iron contents compared to the microprobe analyses. The schorl tourmaline analyzed is also notable by a relatively high Ti content (from 0.085 to 0.159 apfu), a feature characteristic of a majority of schorl-dravite phases analyzed from the Moldanubian Zone (Povondra 1981). The scatter in the average element abundances (values x and s) for individual samples is rather small. Compared to other schorl-dravite tourmalines, the tourmalines analyzed are low in Mn which shows a minimal variation. Lithium content is also rather low.

Trivalent cations (Al, Fe^{3+}) and Ti, which combined occupy approximately 30 % of Y_3 position, are notably high. These cations enter the position following two substitution mechanisms: (i) $XR^{3+}R^{2+}_{-1}Na^{+}_{-1}$ and (ii) $R^{3+}O^{2-}R^{2+}_{-1}OH^{-}_{-1}$, resulting in (i) alkali-deficient and (ii) proton-deficient tourmalines. Although the amount of H_2O in the microprobe analyses is unknown, we tried to correlate the two substitution mechanisms using the relation $R^{3+} + R^{2+}$ vs. R^{3+} in Fig. 2, where the line I is schorl-alkali-deficient tourmaline join and line II corresponds to substitution type (ii) resulting in proton-deficient tourmaline. The ferrous/ferric ratio determined by wet analyses was used for recalculation of the microprobe analyses. As seen in Fig. 2, the majority of analyses plots along the line for the reaction (ii). Tourmalines from the sample 10,

plotting near the reaction (i), are significantly alkali-deficient, as seen in Table 3.

Compositional zoning was measured in two profiles using electron microprobe. A cross section 1.3 mm long in sample 3 shows a clearly defined core with strongly increased Fe, slightly increased Ti and Na, accompanied by decrease in Al and a weak decrease in Mg, with respect to composition of the crystal rim (Fig. 3). This crystal, enclosing quartz and biotite, is moderately poikilitic. Another crystal examined (sample 51) was a strongly poikilitic cross section 10 mm in diameter, containing 60 vol. % of quartz inclusions. The variation in element abundances along the profile is rather irregular; the elevated Ti content in a poorly defined core and antithetic relations of Al and Fe are notable, but core and rim domains are not clearly defined. It appears that the strongly poikilitic texture is accompanied by lesser regularity in compositional variation across crystal.

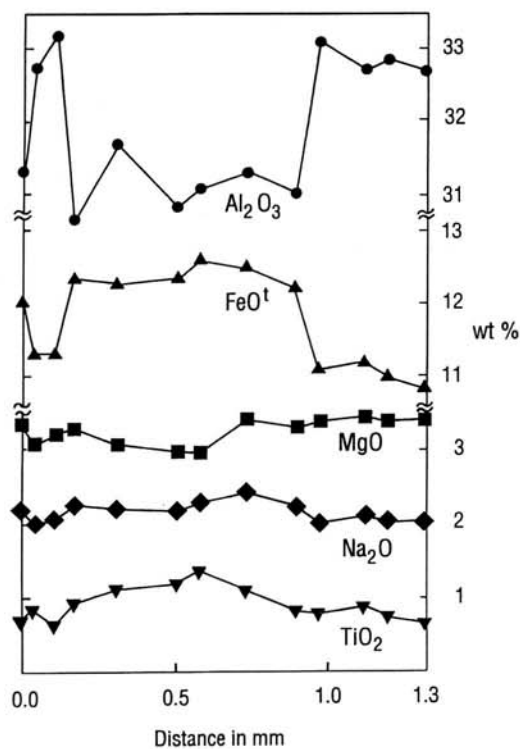


Fig. 3. Compositional zoning in a cross-section of tourmaline in sample 3

The Fe- and Ti-rich crystal cores have a deeper greenish brown colour compared to the rim. Composition of the outermost zone of bluish tourmaline, < 50 μm wide and observed in many thin sections, was not analyzed because it coincides with the non-planar crystal margin in polished sections.

The physical properties of the tourmalines measured, i.e., unit-cell parameters, density, and refraction indices (Table 4) correspond to values for dravite-schorl tourmalines from rocks in the Moldanubian Zone (Povondra - Čech 1985). The following methods

were used for the measurements: X-ray powder diffraction - Dron-2, $\text{CuK}\alpha_{1\text{r}\alpha}$ radiation, Ni-filter, sample speed $0.5^\circ/\text{min.}$, Si internal standard. Density was measured by double-weighing (air/xylene, Povondra 1989). Indices of refraction were measured by the immersion method using Na-light.

Table 4. Physical properties of tourmaline in Hluboká orthogneiss

Sample	3	30	36	85	
a	15.989(5)	15.959(13)	16.000(3)	16.000(3)	Å
c	7.164(4)	7.192(9)	7.161(5)	7.166(3)	Å
V	1586.1(1.2)	1586.3(2.0)	1587.6(1.0)	1588.7(0.8)	(Å) ³
ρ	3.237(5)	3.308	3.288(5)	3.267	g.cm ⁻³
n	1.630	1.632	1.632	1.632	
ω	1.658	1.659	1.660	1.660	
Pleochroism					
3	light greenish yellow - greenish brown				
30	light greenish yellow - greenish brown				
36	light brownish yellow - greenish brown				
85	light brownish yellow - greenish brown				

A comparison of tourmaline composition in related orthogneiss bodies

A comparison of the chemical composition of schorl samples from the Hluboká orthogneiss with tourmalines in related tourmaline orthogneisses in the Moldanubicum in south-central Bohemia (Blaník, Choustník, and Radonice orthogneiss) and eastern Bohemia (Přibyslavice peraluminous granite-metagranite) was undertaken. Location and geological situation of these orthogneiss bodies is shown in Vrána and

Kröner (1995). Twenty six microprobe and "wet" tourmaline analyses, used for calculation of averages for the individual orthogneiss bodies (Table 5), were available for the comparison. Composition of these phases and of their parent rocks is plotted in triangle Fe-Mg-Al (Fig. 4). For rock compositions, the Al value is calculated as the part of aluminium not bound in feldspars. As seen in Fig. 4, the Fe, Mg, and Al values for parent rocks are closely similar, but there is a considerable spread in tourmaline composition in the Hluboká orthogneiss, as was already indicated in Fig. 1. Tourmalines from several orthogneiss bodies used in the comparison are mainly scattered among the projection points for the Hluboká samples, except the Radonice orthogneiss tourmalines which are notably more magnesian than the other samples examined. This relation is in agreement with differences in whole rock composition. The Radonice orthogneiss [average of five analyses in Slabý (1991)] has $\text{MgO}/(\text{FeO}_{\text{tot}} + \text{MgO}) = 0.19$, while for the Hluboká orthogneiss (average of three analyses) the same ratio is 0.11.

Other rock-forming minerals and accessory minerals in Hluboká orthogneiss

Feldspars and micas in sample 3 are characterized by averages of microprobe analyses (Tables 6 and 7). K-feldspar compositions correspond to Or 91-95 An 05-09. Plagioclase is albite corresponding to Ab 94-96 An 03-05 Or 0.2-0.1. Perthite analyzed represents an Or-Ab mixture Or 59.9 Ab 39.8 An 00.3.

Table 5. Average composition of tourmaline in some Moldanubian orthogneisses, based on microprobe and wet analyses

Blaník orthogneiss n = 7			Choustník orthogneiss n = 6			Radonice orthogneiss n = 8			Přibyslavice granite-metagranite n = 5		
x		s	x		s	x		s	x		s
SiO ₂	37.16	(0.33)	35.82	(1.00)		35.38	(1.76)		34.94	(0.17)	
Al ₂ O ₃	31.56	(1.02)	31.07	(0.56)		32.30	(1.43)		31.49	(1.18)	
TiO ₂	1.19	(0.30)	0.39	(0.32)		0.82	(0.19)		0.94	(0.26)	
FeO _{tot}	11.15	(0.09)	1.25	(0.58)		6.99	(1.07)		13.28	(1.32)	
MnO	0.19	(0.22)	0.09	(0.03)		0.04	(0.02)		0.16	(0.06)	
MgO	3.37	(0.17)	3.01	(0.36)		6.29	(1.25)		2.39	(1.32)	
CaO	0.08	(0.02)	0.10	(0.05)		0.27	(0.23)		0.55	(0.21)	
Na ₂ O	2.12	(0.11)	1.97	(0.16)		2.39	(0.24)		2.17	(0.35)	
K ₂ O	0.08	(0.03)	0.09	(0.02)		0.05	(0.02)		0.14	(0.05)	

Number of ions based on 24.5 (O)

Si	6.120	(0.107)	6.128	(0.071)	5.976	(0.128)	5.987	(0.022)
Al	6.142	(0.143)	6.280	(0.171)	6.359	(0.194)	6.355	(0.239)
Ti	0.148	(0.038)	0.050	(0.041)	0.104	(0.031)	0.121	(0.034)
Fe	1.546	(0.032)	1.609	(0.070)	0.974	(0.156)	1.900	(0.206)
Mn	0.026	(0.030)	0.013	(0.005)	0.005	(0.004)	0.024	(0.009)
Mg	0.830	(0.035)	0.766	(0.081)	1.588	(0.314)	0.608	(0.333)
Ca	0.013	(0.004)	0.018	(0.009)	0.050	(0.048)	0.102	(0.038)
Na	0.677	(0.028)	0.653	(0.046)	0.782	(0.101)	0.721	(0.115)
K	0.017	(0.002)	0.020	(0.004)	0.010	(0.004)	0.028	(0.014)
Σ oct	2.692	(0.149)	2.717	(0.081)	3.047	(0.152)	3.030	(0.058)
Σ alk	0.698	(0.027)	0.673	(0.045)	0.792	(0.101)	0.749	(0.111)
F ⁺	0.644	(0.030)	0.674	(0.053)	0.379	(0.092)	0.750	(0.182)

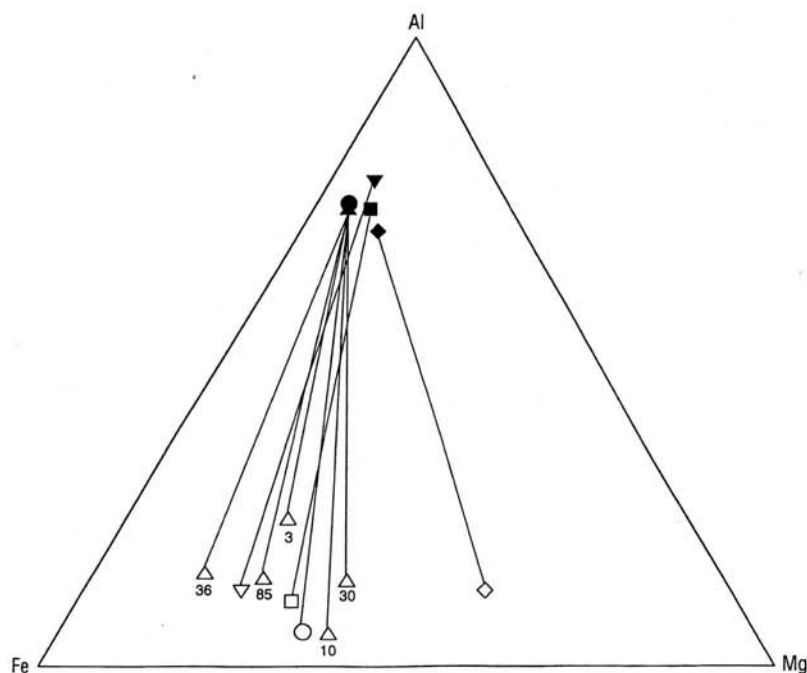


Fig. 4. Projection of whole rock orthogneiss composition and average tourmaline composition in triangle Fe, Mg, and Al. The average tourmaline compositions are calculated for individual samples from the Hluboká orthogneiss and for several samples for other orthogneiss bodies.

Solid symbols - whole rock compositions, *open symbols* - tourmaline compositions. *Triangles* - Hluboká orthogneiss, *circles* - Blanice orthogneiss, *squares* - Choustník orthogneiss, *diamonds* - Radonice orthogneiss, *inverted triangle* - Přibyslavice peraluminous granite-metagranite. See text for calculation of the whole rock Al value

Table 6. Electron microprobe analyses of feldspars in orthogneiss sample 3

	K-feldspar n = 8		Plagioclase n = 5		Perthite n = 1
	x	s	x	s	
SiO ₂	65.24	(0.56)	67.80	(0.62)	65.87
Al ₂ O ₃	18.37	(0.17)	20.98	(0.72)	19.29
CaO	0.00	-	0.92	(0.24)	0.06
Na ₂ O	0.80	(0.25)	11.03	(0.23)	4.46
K ₂ O	16.19	(0.43)	0.11	(0.07)	10.20

Number of ions based on 8 (O)

Si	2.998	(0.011)	2.945	(0.020)	2.980
Al	0.995	(0.014)	1.062	(0.024)	1.029
Ca	-	-	0.043	(0.011)	0.003
Na	0.071	(0.022)	0.929	(0.021)	0.391
K	0.949	(0.027)	0.006	(0.004)	0.589
Σ alk	1.020	(0.006)	0.935	(0.015)	0.983

Muscovite in sample 3 is a dioctahedral mica with a slightly increased Fe and Mg, and a relatively high deficiency in alkalis, near 15 %. Biotite corresponds to siderophyllite with annite 55, eastonite 25, phlogopite 20. The relatively high Ti contents are normal in micas of comparable composition. Again, alkali element deficiency (5 %) is noted. Since water and some large (inter-layered) cations are not determined, the significance of the vacancies indicated remains uncertain.

Garnet was analyzed in three samples (Table 8). It is a minor accessory phase as no garnet was observed in thin sections. The concentrate of orange red colour was obtained by separation from large samples. Average compositions are given in Table 8 and individual analyses are plotted in Fig. 5. The garnet is dominantly almandine with a relatively high spessartine and minor pyrope. It shows rather limited variation in composition.

Ilmenite-pyrophanite related mineral in sample 43 represents the single occurrence recorded. It forms

Table 7. Electron microprobe analyses of muscovite and biotite in orthogneiss sample 3

	Muscovite n = 5		Biotite n = 3	
	x	s	x	s
SiO ₂	48.71	(1.12)	36.54	(0.69)
Al ₂ O ₃	32.53	(1.26)	19.62	(0.60)
TiO ₂	0.72	(0.12)	3.01	(0.09)
FeO _{tot}	2.18	(0.19)	22.94	(0.03)
MnO	0.06	(0.01)	0.35	(0.01)
MgO	1.36	(0.34)	4.72	(0.16)
CaO	0.00	-	0.00	-
Na ₂ O	0.51	(0.06)	0.12	(0.02)
K ₂ O	9.43	(0.21)	9.58	(0.05)

Number of ions based on 22 (O)

Si	6.438	(0.123)	5.543	(0.015)
Al	1.496	(0.141)	2.458	(0.015)
Al	3.507	(0.092)	1.050	(0.065)
Ti	0.072	(0.012)	0.343	(0.005)
Fe	0.241	(0.021)	2.911	(0.044)
Mn	0.007	(0.001)	0.045	(0.002)
Mg	0.267	(0.066)	1.067	(0.052)
Ca	-	-	-	-
Na	0.131	(0.016)	0.034	(0.007)
K	1.590	(0.033)	1.855	(0.040)
Σ oct	4.087	(0.014)	5.416	(0.028)
Σ alk	1.721	(0.021)	1.888	(0.033)

subhedral tablets 0.2 mm long, aligned parallel the foliation of orthogneiss. Some parts of the grains shows deep red colour in transmitted light. Back-scattered electron images show that two phases, bound by an irregular interface, are present. Nineteen spot analyses split in two groups, i.e., Fe-dominant one with Fe/Mn = 4.189 (0.345) and a Mn-dominant with Fe/Mn = 0.732 (0.311) (Table 9). These relations show that two members of the ilmenite-pyrophanite solid solution coexist in single grains. Chromium, Al, Mg, and Ni contents are very low and the compositions are in part similar to those of ilmenite in some pegmatites. In all

Table 8. Electron microprobe analyses of garnet

	30 n = 6		36 n = 7		85 n = 5	
	x	s	x	s	x	s
SiO ₂	36.91	(0.47)	36.86	(0.61)	36.95	(0.29)
Al ₂ O ₃	21.90	(0.87)	22.16	(0.59)	21.76	(0.20)
TiO ₂	0.060	(0.019)	0.024	(0.024)	0.046	(0.045)
FeO	34.34	(0.81)	34.36	(0.42)	34.36	(1.14)
MnO	6.71	(0.66)	6.94	(0.13)	7.49	(1.25)
MgO	1.05	(0.12)	1.28	(0.08)	0.90	(0.11)
CaO	0.085	(0.040)	0.106	(0.048)	0.034	(0.021)

Number of ions based on 12 (O)

Si	2.979	(0.040)	2.957	(0.041)	2.978	(0.007)
Al	2.083	(0.077)	2.099	(0.057)	2.067	(0.007)
Ti	0.004	(0.001)	0.002	(0.002)	0.003	(0.003)
Fe	2.318	(0.066)	2.310	(0.021)	2.316	(0.078)
Mn	0.462	(0.045)	0.470	(0.007)	0.511	(0.084)
Mg	0.126	(0.014)	0.153	(0.010)	0.108	(0.015)
Ca	0.007	(0.004)	0.009	(0.005)	0.003	(0.002)
R ³⁺	2.087	(0.077)	2.087	(0.051)	2.071	(0.008)
R ²⁺	2.911	(0.038)	2.944	(0.012)	2.937	(0.017)

analyses the ratio $Ti/\sum R$ exceeds unity and reaches $x(s) = 1.220$ (0.103). An accurate identification of the phases is impossible without X-ray data on structure and information on oxidation state of Fe and Mn. As the number of Ti atoms is near to 2 apfu, it is possible that a part of cations was removed, resulting in vacant sites in the crystal structure. The stoichiometry does not correspond to pseudorutile.

A comparison of this ilmenite-pyrophanite related mineral with ilmenite and pseudorutile from pegmatites in the Moldanubian Zone of western Moravia (Novák - Jilemnická 1988) shows that material from the Hluboká orthogneiss has a higher Mn/Fe ratio. The deficiency in (Fe + Mn) is not quite comparable, as Novák and Jilemnická (1988) reported normal ilmenite and pseudorutile, the latter from some pegmatites in the Třebíč durbachite.

Sphalerite was identified in heavy mineral fractions of all four samples from which tourmaline was separated. Nine microprobe analyses (Table 9) correspond to average composition $Fe_{0.15}Zn_{0.85}S$, with a negligible content of the alabandine component. Associated pyrite contains Fe 46.7 wt. %, in accord with the formula.

Gahnite occurs as an accessory component in a foliation-parallel segregation sheet of quartz, carrying also minor muscovite and biotite (Table 9). The quartz segregation in orthogneiss is only 2 cm thick. Gahnite in another sample (No. 36) has unit-cell $a = 8.114(5)$ Å, indicating composition similar to that in Table 9. These compositions are similar to gahnite from Příbyslavice metagranite and from some Moldanubian pegmatites (Němec 1973).

Sillimanite of a fibrolitic variety is a relatively frequent accessory. Monomineralic aggregates in sample 10, analyzed with microprobe, gave major Al

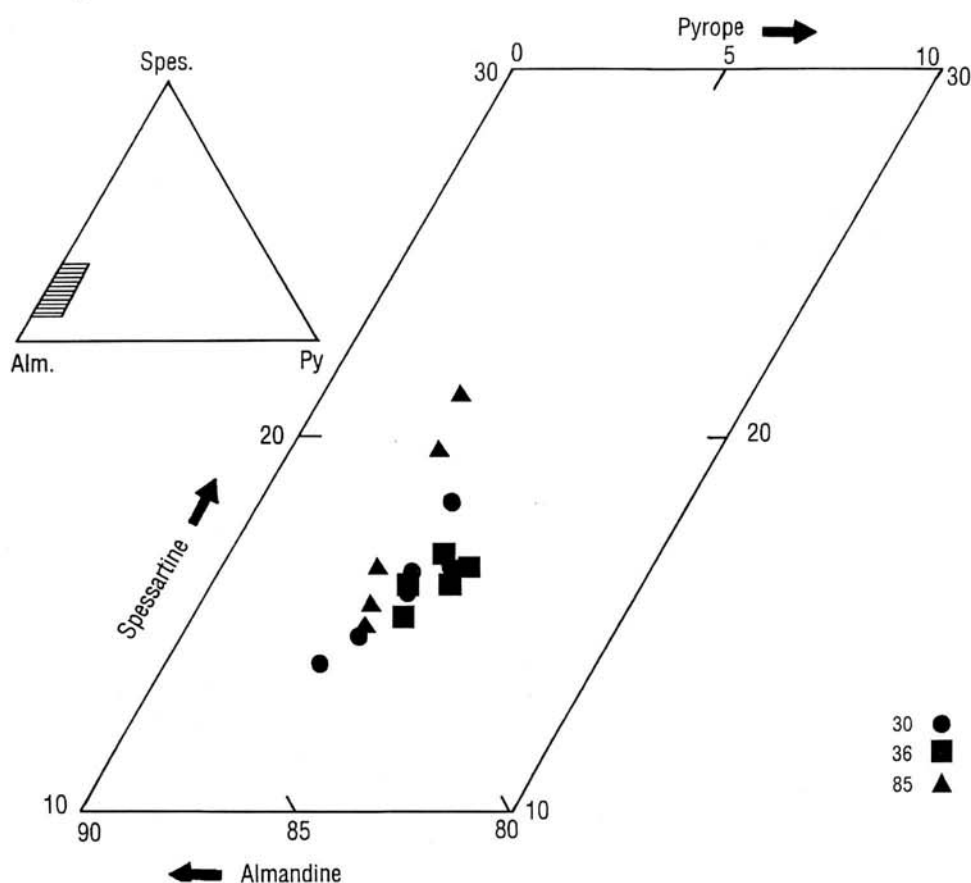


Fig. 5. Composition of garnet from the Hluboká orthogneiss in almandine, pyrope, and spessartine triangle. The symbols correspond to individual spot analyses

Table 9. Electron microprobe analyses of ilmenite-pyrophanite, gahnite, and sphalerite

10					43	85		
ilmenite n = 7		pyrophanite n = 12			gahnite n = 1	sphalerite n = 9		
x		s	x	s		x	s	
SiO ₂	-		-		0.08	Zn	57.39	(1.11)
TiO ₂	59.25	(0.53)	56.08	(1.49)	0.05	Fe	8.52	(0.32)
Cr ₂ O ₃	0.07	(0.03)	0.06	(0.04)	0.08	Mn	0.13	(0.04)
Al ₂ O ₃	0.12	(0.06)	0.16	(0.12)	55.23			
Fe ₂ O ₃ *	-		-		1.37	Zn	0.878	(0.017)
FeO	31.60	(3.09)	16.94	(1.68)	12.76	Fe	0.150	(0.014)
MnO	8.69	(2.69)	26.48	(3.23)	0.21	Mn	0.002	(0.001)
MgO	0.05	(0.03)	0.09	(0.18)	0.48			
ZnO	n.d.		n.d.		29.46			
Number of ions based on 6 (O)					4 (O)			
Si	-		-		0.002			
Ti	2.158	(0.020)	2.171	(0.286)	0.001			
Cr	0.003	(0.001)	0.002	(0.002)	0.002			
Al	0.007	(0.004)	0.009	(0.007)	1.961			
Fe ²⁺	1.285	(0.127)	0.701	(0.067)	0.321			
Fe ³⁺	-		-		0.031			
Mn	0.356	(0.106)	1.103	(0.141)	0.005			
Mg	0.004	(0.003)	0.006	(0.013)	0.022			
Zn	-		-		0.655			

and Si corresponding to Al₂SiO₅ and Fe₂O₃ 0.23 to 0.26 wt. %.

Other accessory phases including ordinary brown monazite, rare green monazite (relatively rich in U and Th, compensated by Ca ranging from CaO 3.4 to 4.1 wt. %), and a single occurrence of dumortierite, are characterized only by semi-quantitative analyses and X-ray data.

Discussion and conclusions

There is a significant volume of information on composition of tourmaline from world-wide localities. The mineral is of interest as a petrogenetic indicator in magmatic, metamorphic, and diagenetic processes; it was also widely studied in stratiform deposits of Ag, Pb, Zn, Sn, and W.

Henry and Guidotti (1985) used 400 tourmaline analyses for examination of relations between tourmaline composition and host rock composition. Tourmaline from Hluboká orthogneiss plots in Al-Fe¹-Mg triangle (Henry - Guidotti 1985), inside (samples 36, 85, and 10) and in close proximity (samples 30 and 3) of the field 2, corresponding to tourmalines from Li-poor granitoids and associated pegmatites and aplites. This indicates that composition of tourmaline from the Hluboká orthogneiss is compatible with its primary magmatic crystallization in the course of Ordovician (Vrána - Kröner 1995) solidification of the alkali-feldspar granite, which was later, during the Variscan events, transformed to orthogneiss.

The homogeneous and uniform distribution of tourmaline in the orthogneiss body and rather limited variation in trace element abundances in the orthogneiss (Table 1) also support a primary magmatic origin for tourmaline. Indications of localized fluid conduits

and a more pronounced variation in whole rock element concentrations could be expected in case that tourmaline should be introduced during the superimposed metamorphism. Microscopic study of orthogneiss indicates that in the course of the Variscan superimposed deformation and recrystallization under amphibolite facies conditions, which transformed the original granite to orthogneiss, quartz, feldspars, and probably micas behaved as soft phases and they largely underwent dynamic recrystallization. Tourmaline behaved as a hard and relatively refractory phase which probably experienced some passive re-orientation during deformation. The information available is interpreted as indicating persistence of the original magmatic tourmaline. A similar behaviour is indicated for apatite (Povondra - Vrána 1993) and zircon (Vrána - Kröner 1995).

Garnet of dominant almandine composition with a significant content of spessartine shows uniform element distribution in individual crystals. The spread of projection points in Fig. 5 reflects mainly compositional variation in large samples (approximately 20 kg) from which garnet was separated. This garnet is similar to primary accessory almandine-spessartine garnets described in the literature from a number of leucogranites, alkali-feldspar granites, and related aplites and pegmatites. Spessartine contents in the range 30 to 60 mol. % are frequent, though in some cases the lower limit is near 15 mol. %. Miller and Stoddard (1981) proposed the following reaction for crystallization of such magmatic garnets:

biotite + (Mn, Al, Fe) in residual melt → garnet + muscovite

This reaction describes relations in late members of a suite of granitic rocks reaching a high Mn/(Fe + Mg) ratio in the process of differentiation. Siebel

(1993) documented in the Leuchtenberg granite differentiation series the range of $Mn/(Fe + Mg) = 0.01$ to 0.20 .

In the Hluboká orthogneiss, Fe, Mg, and Mn are dominantly partitioned in tourmaline and biotite. A comparison of Fe, Mg, and Mn cation wt. % (re-calculated to 100 %) shows that tourmaline contains Mn 0.6 %, biotite 1.3 %, and whole rock orthogneiss 1.7 %. Garnet containing Mn 16 cation % on average, and present in very minor quantity, thus compensates for the low Mn content in tourmaline and biotite. A comparison with chemistry of apatite and its content in the same samples (Povondra and Vrána 1991) shows that apatite, containing MnO 2.1 to 2.8 wt. % (of 100 % of analyses), serves as the main repository of manganese. The role of garnet, because of its very small quantity, is secondary only in this respect.

The Hluboká orthogneiss has a low $Mn/(Fe + Mg)$ ratio of 0.02 and does not compare with relatively Mn-enriched garnet-muscovite granites. The compositional criteria for magmatic spessartine-rich garnets, developed for garnet-muscovite granites with a high $Mn/(Fe + Mg)$ ratio (Hall 1965, Miller and Stoddard 1981, Siebel 1993), are not applicable to Hluboká orthogneiss, which has a different mineralogical composition and partitioning relations. Yet, the accessory garnet in the orthogneiss is similar to some relatively low-spessartine magmatic garnets in several garnet-muscovite granites, it has a similar low pyrope content, and can be probably interpreted as a minor primary magmatic phase.

Four samples of tourmaline characterized by wet analyses (Table 2) suggest that the orthogneiss and its tourmalines tend to relatively limited variation. It is therefore interesting that the tourmaline from sample 10 (Table 3), characterized by microprobe analyses, is different from the first group of samples, though qualitative petrography of the orthogneiss sample 10 did not suggest some distinctive features. It may be important to note that the case of sample 10 indicates an internal variability in the orthogneiss body which is not revealed by variation in trace element data (Table 1). A set of five random samples (Tables 2 and 3) does not probably represent sufficient sampling to cover some (cryptic) variation in the orthogneiss body 7 by 2 km in size.

A comparison of tourmaline compositions from several separate bodies of tourmaline-bearing muscovite-biotite orthogneisses in the Moldanubian Zone in south-central Bohemia (Blaník, Choustník, and Radonice orthogneiss) and eastern Bohemia (Přibyslavice peraluminous granite-metagranite) in Table 5 and Fig. 4 reveals previously unsuspected differences. Tourmaline from the Radonice orthogneiss has a significantly higher Mg/Fe ratio in comparison to samples from the other orthogneiss bodies. This leads to a geologically significant conclusion. The data obtained suggest for the Radonice orthogneiss deriva-

tion from a separate magma batch, with a higher Mg/Fe ratio.

A qualitative comparison of mineralogical, petrological, and chemical information also shows significant differences between the Přibyslavice tourmaline-bearing granite-metagranite and Hluboká orthogneiss. The Přibyslavice body (Povondra et al. 1987) shows internal petrographic and chemical variation, including portions with a strongly developed pegmatite stage rich in garnet, phosphates, Zn-staurolite, rare Sn minerals (cassiterite, nigerite), and rare Li-tourmalines. Comparable mineralizations appear to be unknown in the Hluboká orthogneiss, which is compositionally rather uniform, including limited variation in abundance of several minor and trace elements (Table 1).

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References

- Hall, A. (1965): The origin of accessory garnet in the Donegal granite. - *Mineral. Mag.*, 35, 628-633. London.
- Henry, D. J. - Guidotti, C. V. (1985): Tourmaline as a petrogenetic indicator mineral: an example from the staurolite-grade metapelites of NW Maine. - *Amer. Mineralogist*, 70, 1-15. Washington.
- Miller, C. F. - Stoddard, E. F. (1981): The role of manganese in the paragenesis of magmatic garnet: an example from the Old Woman-Piute Range, California. - *J. Geol.*, 89, 233-246. Chicago.
- Němec, D. (1973): Das vorkommen der Zn-Spinelle in der Böhmischen Masse. - *Tschermaks mineral. petrogr. Mitt.*, 19, 95-109. Wien.
- Novák, M. - Jilemnická, L. (1988): Ilmenite from pegmatites of western Moravia. - *Čas. Mineral. Geol.*, 33, 4, 411-417. Praha.
- Povondra, P. (1981): The crystal chemistry of tourmalines of the schorl-dravite series. - *Acta Univ. Carol., Geol.*, 3, 223-264. Praha.
- (1989): Hustota turmalínu, její stanovení a význam. - *Acta Univ. Carol., Geol.*, 4, 439-446. Praha.
- Povondra, P. - Čech, F. (1985): Lattice parameters of tourmalines of the dravite-schorl series and their relation to chemical composition. - *Acta Univ. Carol. Geol.*, 8, 235-245. Praha.
- Povondra, P. - Pivec, E. - Čech, F. - Lang, M. - Novák, F. - Prachař, I. - Ulrych, J. (1987): Přibyslavice peraluminous granite. - *Acta Univ. Carol., Geol.*, 3, 183-283. Praha.
- Povondra, P. - Vrána, S. (1993): Crystal chemistry of apatite in tourmaline-bearing alkali-feldspar orthogneiss near Hluboká nad Vltavou, southern Bohemia. - *J. Czech Geol. Soc.*, 38, 3-4, 165-170. Praha.
- Siebel, W. (1993): Der Leuchtenberger Granit und seine assoziierten magmatischen Gesteine: Zeitliche und stoffliche Entwicklungsprozesse im Verlauf der Entstehung des Nordoberpfalz-Plutons. - Thesis. Univ. Heidelberg.

Slabý, J. (1991): Petrology and geochemistry of orthogneisses in the Moldanubian Zone of southern Bohemia (In Czech). - MS Postgradual thesis. Czech Geol. Surv. Praha.

Vrána, S. - Kröner, A. (1995): Pb-Pb zircon age for tourmaline alkali-feldspar orthogneiss from Hluboká nad Vltavou in southern Bohemia. - J. Czech Geol. Soc., 40, 1-2, 127-131. Praha.

Turmalín a sdružené minerály v alkalicko-živcové ortorule u Hluboké nad Vltavou

Turmalín v hlubocké ortorule, tvořící těleso 7 x 2 km velké, je charakterizován pomocí chemických analýz a analýz z elektronové mikrosondy. Pro podrobně analyzované čtyři vzorky jsou uvedeny základní fyzikální vlastnosti, t.j. hustota, rozměry základní cely a indexy lomu světla. Zjištěný rozsah složení turmalínu odpovídá $sc_{49} - dr_{36} - ol_{15}$ až $sc_{78} - dr_{11} - ol_{11}$ a obsah koncového členu olenitu dosahuje až 26 %. Složení sdružených hlavních a akcesorických minerálů je také charakterizováno pomocí analýz pořízených elektronovou mikrosondou. Získané údaje lze interpretovat jako projev primární magmatické krystalizace turmalínu v původním předvariském alkalicko-živcovém granitu. Chemické složení turmalínů z hlubocké ortoruly je srovnáno s turmalíny ze tří dalších těles ortorul - radonické, choustnické a blanické ortoruly a s turmalíny z přibyslavického granitu-metagranitu. Srovnání ukazuje na značné analogie chemismu turmalínu v těchto tělesech, s výjimkou radonické ortoruly, která obsahuje hořčíkem bohatý turmalín s převahou dravitové složky. To odpovídá značně vyššímu poměru $Mg/(Mg + Fe)$ v horninovém chemismu radonické ortoruly ve srovnání s hlubockou ortorulou a indikuje vznik výchozí horniny radonické ortoruly ze samostatné porce magmatu.