Tourmaline of dravite-uvite series in graphitic rocks of the Velké Vrbno Group (Silesicum, Czech Republic)

Turmalíny dravit-uvitové řady z grafitických hornin velkovrbenské skupiny (silesikum, Česká republika) (Czech summary)

(8 text-figs.)

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Graphite gneisses of the Velké Vrbno Group, metamorphosed in lower amphibolite facies (garnet to staurolite zone), from the Petříkov and Malé Vrbno graphite deposits contain accessory tourmaline (dravite I). Dravite I columns contain fine graphite inclusions (euhedral graphite flakes up to 0.003-0.01 mm) in the core of the crystals. The second type of tourmaline (dravite II) occurs in massive pyrrhotite ore from dolomitic marbles of the Petříkov graphite deposit. Both types of tourmaline range in composition from $dravite_{95}$ $uvite_5$ to $dravite_{61}$ $uvite_{38}$ with minor, but constant, schorl component (0.5-3 mol.%). Rims of dravite I crystals are enriched in uvite component relative to the core. The contents of V (0.00-0.40 wt.% V_2O_3), and Cr (0.05-0.14 wt.% Cr_2O_3) are very low in tourmaline.
The tourmaline and graphite in the host rocks were formed during progressive regional metamorphism (T about 500-540 °C, P about 0.5 to 0.7 GPa). The tourmaline's chemical compositions fall into a field between low- and medium-grade metamorphosed metapelites and marbles. The primary boron content in these metasediments can be explained by an increased salinity within a regressive shelf-sea.

Key words: dravite, uvite, graphitic rocks, pyrrhotite ore, Velké Vrbno Group, Silesicum

Introduction

Recently, Kříbek (1989) noted high boron concentration and occurrences of tourmaline in graphitic rocks of the Velké Vrbno Group. Two occurrences (Malé Vrbno and Petříkov graphite deposits) with increased concentrations of tourmaline in the graphitic metasedimentary rocks were found in the Velké Vrbno Group, Silesicum, during a study of graphitic rocks (Losos 1992, Losos - Hladíková 1995, Fojt et al. 1994). Tourmaline with uvite-dravite composition was described from granitic pegmatite in the Barbora graphite mine at Petříkov (Fojt et al. 1994).

Very similar tourmaline occurs in the graphite deposit at Amstall in the Austria part of the Moldanubian zone (Richter et al. 1991). This deposit is located in the variegated series of metasedimentary rocks (graphitic paragneisses, graphitic marbles, graphitic quarzites and amphibolites), metamorphosed at amphibolite to upper amphibolite metamorphic grade. Dravite with graphite inclusions in the core of crystals is common and tourmaline contents may be up to 10 vol.% of graphitic gneiss. The V content of tourmaline from Amstall is low 0.1-0.4 wt.% of V_2O_3. Accessory dravite characterized by elevated V contents, up to 7.67 wt.% V_2O_3, occurs in graphite quarzite from Bítovánky near Třebíč (Houzar - Šrein 1993, Houzar - Selway 1997). However, the host rock sequence is apparently different from that in Velké Vrbno and Amstall as the graphitic rocks are not associated with metacarbonates.

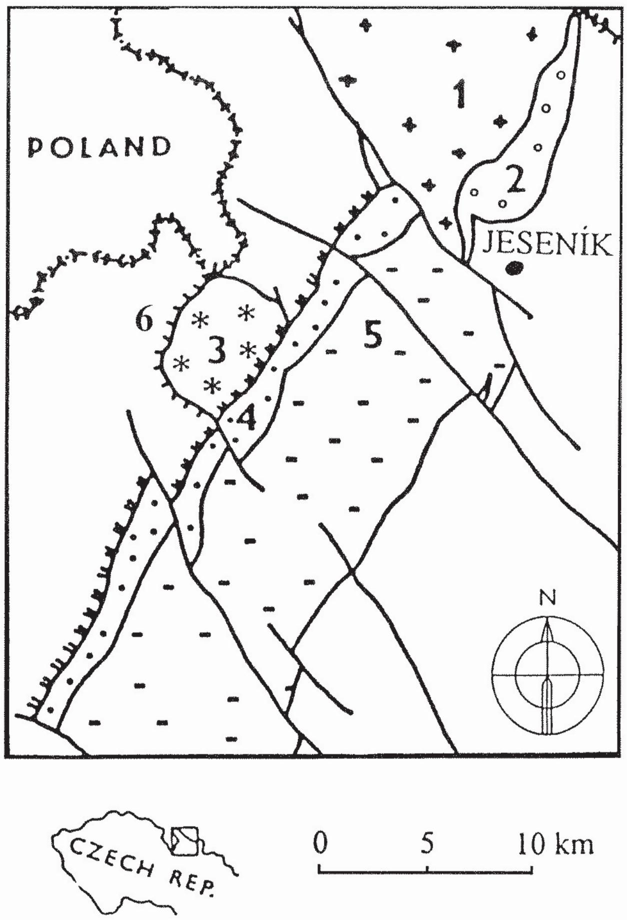

Fig. 1. Schematic map of studied area
1 - Žulová granite massif; *2* - country rocks of the Žulová massif; *3* - Velké Vrbno Group; *4* - Branná Group; *5* - Keprník Group; *6* - Staré Město Crystalline Complex

Geology

The Velké Vrbno Group (Dome) of the Silesicum is lithologically and tectonically complicated series of metasedimentary and metavolcanic rocks generally with a brachy-

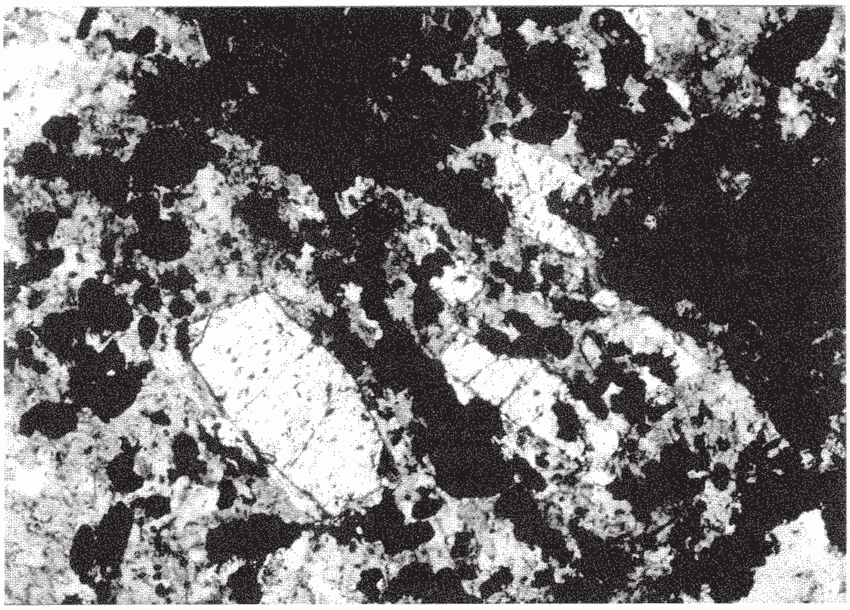

Fig. 2. Pyrite-graphite gneiss from Petříkov with dravite I. The euhedral columnar crystals, up to 0.5 mm long, have prismatic form with a trigonal pyramids. Thin section, crossed polars

anticlinal structure (Fig. 1). The Dome is disturbed by longitudinal and transverse faults and a local syncline is developed in the southeast (so called Šleglov block, Květoň 1951).

The middle lithostratigraphic part of the Velké Vrbno Group contains a horizon of graphite-bearing rocks (pyrite-graphitic paragneisses, graphitic marbles, graphitic quarzites and massive graphite layer). Graphite seems to occur predominantly within the limestones; dolomitic marbles occur mostly in the hangingwall of the graphite layer. The graphite layer is immediately underlain by biotite paragneisses and garnet mica schists. The graphitic rock series is accompanied by metalydites, amphibolites, orthogneisses and pegmatites (Voda 1971).

Isotopic thermometry in graphite-carbonate pairs (from graphite marbles intercalating graphite gneisses of Velké Vrbno Group) indicate the peak metamorphic event at 460-610 °C (Losos - Hladíková 1995). According to Wada - Suzuki (1983) thermometer, the maximum of the $\Delta\delta\ ^{13}C_{cc\text{-}gr}$ values corresponds to temperatures of 500-540 °C which represent lower amphibolite facies (garnet to staurolite zone). The estimated pressures are about 0.5 to 0.7 GPa based on the sphalerite geobarometer (Fojt et al. 1994) for massive pyrrhotite-pyrite ores in the neigbourhood of the tourmaline-bearing graphitic rocks at Petříkov.

The $\delta\ ^{13}C$ values of graphites from non-carbonate rocks (i.e., tourmaline-bearing graphitic gneisses) of the Velké Vrbno Group range from -23.1 to -25.0 ‰ which corresponds to organic matter of marine sediments (Losos - Hladíková 1995). The sulphides of graphitic rocks obviously originated in anoxic environments of closed or semiclosed, shallow water lagoons. The $\delta\ ^{34}S$ values of most sulphides from graphitic gneisses and mica schists vary within a narrow range of +2 to +8 ‰, which indicates that the ori-

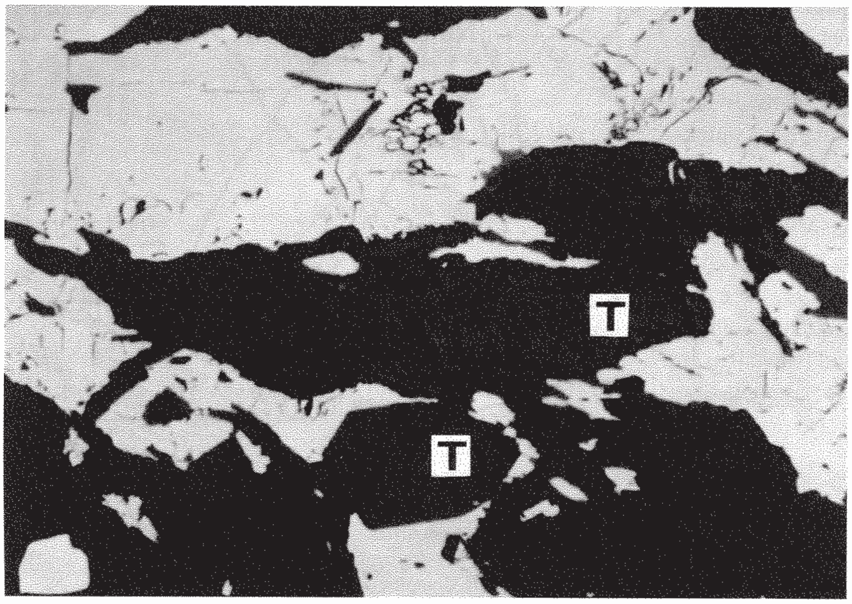

Fig. 3. Euhedral dravite II columns (T) up to 1 x 3 mm long in massive pyrrhotite ore from Petříkov. Polished section

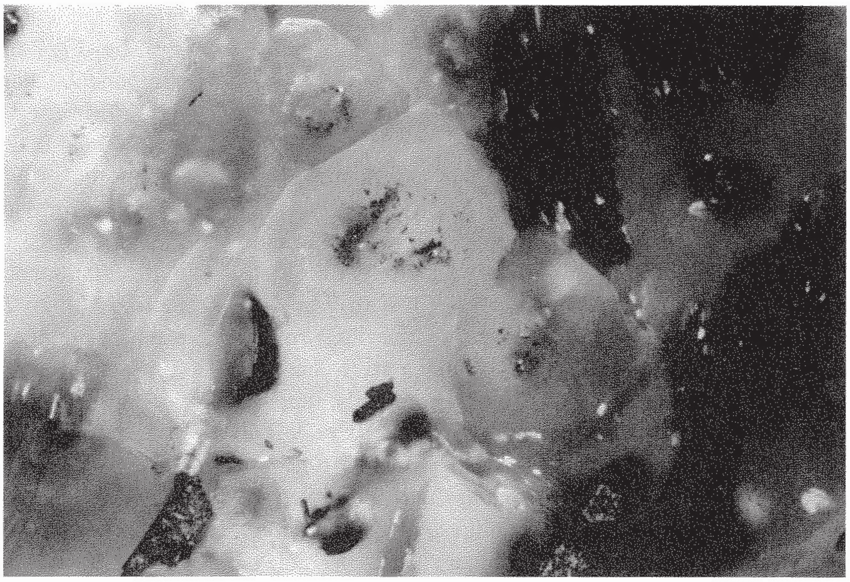

Fig. 4. Dravite I contains fine graphite inclusions (submicroscopic graphite flakes up to 0.003-0.01 mm) in cores of the crystals. Pyrite-graphite gneiss from Malé Vrbno. Polished section, crossed polars

gin of hydrogen sulphide in aqueous environment, closed to marine sulphate, had a contemporaneous lack of reactive iron in the water in an anoxic basin (Hladíková et al. 1993).

Petrography and mineralogy

Two paragenetically different types of tourmaline were recognized in the mentioned serie of graphitic rocks:

The first type (dravite I) occurs in pyrite-graphite gneisses and schists of the Petříkov (Barbora mine) and Malé Vrbno graphite deposits (Fig. 1). These rocks contain tourmaline of the dravite-uvite series. The abundance of dravite I in the graphitic gneisses is variable, with a maximum reaching up to 10-15 vol.%. Gneisses consist of dominant quartz, feldspars, graphite and pyrite subordinate tourmaline and muscovite accessory rutile, very rare zircon, apatite, pyrrhotite and chalcopyrite. Tourmaline crystals and graphite and muscovite flakes have a preferred orientation parallel to the foliation of the rocks. Dravite I from both localities occur as small euhedral columnar crystals commonly up to 0.6 mm long and up to 0.1 mm wide, subhedral grains are rare. Crystals frequently exhibit ditrigonal prismatic form with a trigonal pyramids (Figs. 2, 4, 5).

The second type of tourmaline (dravite II) is enclosed in massive pyrrhotite ores from Petříkov (Fig. 3). These metasedimentary ores are located in graphite-free dolomitic marbles in the vicinity of graphitic gneisses. Dravite II forms euhedral crystals (macroscopic columns 1 x 3 mm large) with megascopically yellow-brown colour.

In thin section, both tourmaline types are colourless. The type I dravite commonly contains fine graphite inclusions (submicroscopic euhedral graphite flakes up to 0.003-0.01 mm) in the core of the crystals (Figs. 4, 5). Similar dravites with graphite-rich cores occur in the graphite deposit Amstall in Austria (Richter et al. 1991).

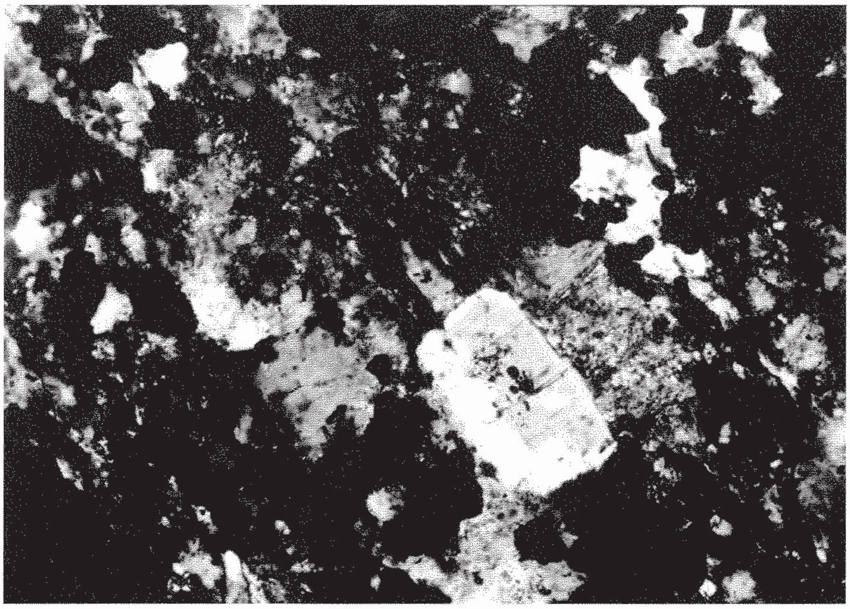

Fig. 5. The euhedral dravite I, 0.2 mm in size, with fine graphite inclusions in the core of the crystal. Pyrite-graphite gneiss from Petříkov. Thin section, crossed polars

Tourmaline chemistry

Tourmalines were analysed using an electron microprobe (Cameca Camebax SX-50) by J. B. Selway at the University of Manitoba. Analytical conditions: Beam voltage for all elements was 15 kV and spot diameter of 1 Ķm. Beam current was 20 nA for Na, Fe, Ca, Si, Al and Mg, and 30 nA for Mn, K, F, Ti, P, Zn, Cr and V. Counting times of peak and background determinations for all elements were 20 s and 10 s, respectively. The analytical data were reduced and corrected using the PAP routine (Pouchou - Pichoir 1985). The samples were analyzed using the K_a lines from the following standards: diopside (Si, Ca), titanite (Ti), kyanite (Al), chromite (Cr), V_2PO_5 (V), fayalite (Fe), olivine (Mg), spessartine (Mn), gahnite (Zn), albite (Na), orthoclase (K) and fluor-riebeckite (F).

The 41 analyses of the tourmaline crystals were evaluated. Representative compositions are listed in Tables 1 and 2.

All studied tourmalines correspond to dravite-uvite series ranging from dravite$_{95}$ uvite$_5$ to dravite$_{61}$ uvite$_{38}$ with minor, but constant, schorl component (from 0.5 to 3 mol.%) - Figs. 6, 8. Rims of crystals are enriched in uvite component. Charge balance is maintained by the substitution of Mg for Al at the Z-site, i.e. the coupled substitution Na + Al = Ca + Mg (Burt 1989, Grice - Ercit 1993, Taylor et al. 1995) - Fig 8.

Zoned dravite I (particularly rims of crystals) from graphitic gneiss in Malé Vrbno and Petříkov is enriched in uvite component (25-38 mol.%) relative to dravite II from Petříkov (up to 24 mol.%) - Fig. 6. Rims of dravite I crystals are enriched in uvite component relative to the core (Figs. 6, 8).

Dravite I and II exhibit elevated contents of Si in the T-site, commonly Si > 6 (up to 6.125 - I type and 6.205 - II type). The excess of Si may suggest that OH + F < 4 (Taylor et al. 1995). The very low X-site vacancy ranges between 8-15 % for dravite from Petřikov and 12-30 % for dravite from Malé Vrbno. Dravite from Petříkov and Malé Vrbno is Na- rich (Fig. 7) with a range from 0.50-0.79 apfu Na. The fluorine concentration in dravite I and II is similarly low with averages ranging from 0.28 to 0.34 wt.% F.

Table 1. Representative compositions of dravite I. Formula contents on a basis of 31 anions, * calculated from stoichiometry

	Crystals from Petříkov				Crystals from Malé Vrbno					
	1	2	3	5	7MV-3 rim	7MV-3 core	7MV-3 rim	7MV-5 rim	7MV-5 core	7MV-5 rim
SiO_2	37.70	37.10	37.40	37.50	38.10	37.70	37.40	38.00	38.30	37.90
TiO_2	0.59	0.52	0.49	0.44	0.46	0.31	0.42	0.43	0.20	0.47
Al_2O_3	33.10	32.20	31.80	31.60	31.40	32.40	30.90	31.00	33.70	31.10
V_2O_3	0.35	0.32	0.33	0.20	0.04	0.05	0.06	0.13	0.06	0.04
Cr_2O_3	0.06	0.30	0.18	0.00	0.00	0.00	0.01	0.07	0.00	0.28
MgO	10.30	11.20	11.40	11.70	10.90	10.80	11.50	11.00	9.64	11.00
CaO	0.41	1.36	1.21	1.95	1.25	1.11	1.89	1.61	0.20	1.40
MnO	0.00	0.03	0.04	0.03	0.10	0.06	0.06	0.10	0.04	0.09
FeO	0.11	0.34	0.38	0.34	0.32	0.13	0.34	0.29	0.05	0.29
ZnO	0.04	0.00	0.03	0.05	0.00	0.00	0.05	0.00	0.00	0.00
Na_2O	2.55	2.08	2.25	1.84	2.08	2.06	1.79	1.90	2.18	1.99
K_2O	0.02	0.02	0.04	0.02	0.05	0.02	0.05	0.03	0.00	0.03
F	0.24	0.31	0.26	0.36	0.32	0.27	0.41	0.34	0.18	0.38
B_2O_3 *	10.90	10.86	10.87	10.88	10.81	10.83	10.74	10.78	10.88	10.79
H_2O *	3.65	3.60	3.63	3.58	3.58	3.61	3.51	3.56	3.67	3.54
O=F	-0.10	-0.13	-0.11	-0.15	-0.13	-0.11	-0.17	-0.14	-0.08	-0.16
TOTAL	99.92	100.11	100.20	100.35	99.28	99.23	98.96	99.10	99.02	99.17
Si^{4+}	6.010	5.935	5.980	5.988	6.123	6.050	6.050	6.125	6.120	6.105
Ti^{4+}	0.071	0.063	0.059	0.053	0.056	0.037	0.051	0.052	0.024	0.057
Al^{3+}	6.219	6.071	5.992	5.947	5.948	6.128	5.891	5.889	6.347	5.904
V^{3+}	0.045	0.041	0.042	0.026	0.005	0.006	0.008	0.017	0.008	0.005
Cr^{3+}	0.008	0.038	0.023	0.000	0.000	0.000	0.001	0.009	0.000	0.036
Mg^{2+}	2.448	2.671	2.717	2.785	2.612	2.584	2.773	2.643	2.296	2.642
Ca^{2+}	0.070	0.233	0.207	0.334	0.215	0.191	0.328	0.278	0.034	0.242
Mn^{2+}	0.000	0.004	0.005	0.004	0.014	0.008	0.008	0.014	0.005	0.012
Fe^{2+}	0.015	0.045	0.051	0.045	0.043	0.017	0.046	0.039	0.007	0.039
Zn^{2+}	0.005	0.000	0.004	0.006	0.000	0.000	0.006	0.000	0.000	0.000
Na^+	0.788	0.645	0.697	0.570	0.648	0.641	0.561	0.594	0.675	0.622
K^+	0.004	0.004	0.008	0.004	0.010	0.004	0.010	0.006	0.000	0.006
F^-	0.121	0.157	0.131	0.182	0.163	0.137	0.210	0.173	0.091	0.194
B^{3+}	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
H^+	3.879	3.843	3.869	3.818	3.837	3.863	3.790	3.827	3.909	3.806
O^{2-}	30.879	30.843	30.869	30.818	30.837	30.863	30.790	30.827	30.909	30.806
CATSUM	18.680	18.751	18.786	18.760	18.674	18.668	18.734	18.666	18.516	18.673
AN SUM	31	31	31	31	31	31	31	31	31	31

Table 2. Representative compositions of dravite II from Petříkov. Formula contents on a basis of 31 anions, * calculated from stoichiometry

	Crystal A			Crystal B				
	rim	core	rim	rim	int	core	int	rim
P_2O_5	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00
SiO_2	37.70	37.80	38.30	37.60	38.20	38.30	38.00	38.30
TiO_2	0.63	0.32	0.68	0.62	0.42	0.44	0.43	0.65
Al_2O_3	31.60	31.10	30.50	31.00	30.80	31.10	30.70	30.30
V_2O_3	0.19	0.00	0.06	0.21	0.09	0.05	0.12	0.13
Cr_2O_3	0.07	0.00	0.11	0.00	0.11	0.02	0.21	0.00
MgO	11.30	11.10	11.40	11.30	11.10	11.00	11.20	10.80
CaO	1.17	0.60	1.19	0.99	0.73	0.54	0.65	0.94
MnO	0.00	0.03	0.00	0.02	0.00	0.00	0.00	0.00
FeO	0.34	0.63	0.37	0.66	0.53	0.66	0.59	0.59
ZnO	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
Na_2O	2.20	2.54	2.31	2.41	2.50	2.64	2.49	2.38
K_2O	0.00	0.03	0.02	0.03	0.02	0.02	0.02	0.02
F	0.23	0.45	0.21	0.18	0.33	0.23	0.30	0.25
B_2O_3*	10.86	10.73	10.83	10.79	10.78	10.81	10.76	10.73
H_2O *	3.64	3.49	3.64	3.64	3.56	3.62	3.57	3.58
O=F	-0.10	-0.19	-0.09	-0.08	-0.14	-0.10	-0.13	-0.11
TOTAL	99.83	98.63	99.54	99.41	99.03	99.34	98.91	98.56
P^{5+}	0.000	0.000	0.003	0.001	0.000	0.000	0.000	0.000
Si^{4+}	6.035	6.122	6.148	6.058	6.160	6.156	6.140	6.205
Ti^{4+}	0.076	0.039	0.082	0.075	0.051	0.053	0.052	0.079
Al^{3+}	5.962	5.936	5.771	5.887	5.854	5.891	5.846	5.786
V^{3+}	0.024	0.000	0.008	0.027	0.012	0.006	0.016	0.017
Cr^{3+}	0.009	0.000	0.014	0.000	0.014	0.003	0.027	0.000
Mg^{2+}	2.697	2.680	2.728	2.714	2.668	2.636	2.698	2.608
Ca^{2+}	0.201	0.104	0.205	0.171	0.126	0.093	0.113	0.163
Mn^{2+}	0.000	0.004	0.000	0.003	0.000	0.000	0.000	0.000
Fe^{2+}	0.046	0.085	0.050	0.089	0.071	0.089	0.080	0.080
Zn^{2+}	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000
Na^{+}	0.683	0.798	0.719	0.753	0.782	0.823	0.780	0.748
K^{+}	0.000	0.006	0.004	0.006	0.004	0.004	0.004	0.004
F^{-}	0.116	0.230	0.107	0.092	0.168	0.117	0.153	0.128
B^{3+}	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
H^{+}	3.884	3.770	3.893	3.908	3.832	3.883	3.847	3.872
O^{2-}	30.884	30.770	30.893	30.908	30.832	30.883	30.847	30.872
CATSUM	18.733	18.773	18.731	18.787	18.742	18.754	18.755	18.690
AN SUM	31	31	31	31	31	31	31	31

Vanadium contents in dravite are low. Dravite II from marbles in Petříkov has apparent zoned distribution of V contents with V-poor core (0-0.15 wt.%, average 0.07 wt.% V_2O_3) and V-enriched rim (0.04-0.21 wt.%, average 0.12 wt.% V_2O_3). Dravite I has rather irregular distribution of vanadium contents ranging from 0.18-0.40 wt.%, average 0.32 wt.% V_2O_3 for dravite I from Petřikov graphitic gneisses; and from 0.04-0.39 wt.%, average 0.10 wt.% V_2O_3 from Malé Vrbno. The average chromium contents in dravite are very low (0.14 wt.% Cr_2O_3 in Petříkov graphitic gneiss, 0.05 wt.% in Petříkov pyrrhotite ores and 0.06 wt.% in Malé Vrbno graphitic gneiss).

Tourmaline of uvite-dravite composition (MgO = 12.36 %, CaO = 2.38 %, Na_2O = 0.34 %, K_2O = 0.34 %, Fe_2O_3 tot. = 0.95 %) was described from pegmatite of Barbora mine at Petříkov (Fojt et al. 1994).

Discussion and conclusions

Two paragenetically different types of tourmaline were recognized in the studied series of graphitic rocks: dravite I from pyrite-graphite gneisses of Petříkov and Malé Vrbno graphite deposits and dravite II from massive pyrrhotite ore of dolomitic marbles from Petříkov.

The abundance of dravite I in the graphitic gneisses is variable, with a maximum up to 10-15 vol.%. Fine graphite inclusions (submicroscopic euhedral graphite flakes up to 0.003-0.01 mm) occur in the core of the dravite crystals. Paragenetically and morphologically very similar tourmalines occur in the graphite deposit Amstall in Austrian part of the Moldanubian zone (Richter et al. 1991).

Both tourmalines correspond to dravite-uvite series ranging from $dravite_{95}$ $uvite_5$ to $dravite_{61}$ $uvite_{38}$ with minor, but constant, admixture of schorl component (from 0.5 to 3 mol.%). Crystal rims are commonly enriched in the uvite component relative to the core.

Tourmaline is Na-rich with low vacancy in the X-site relative to dravite from Bítovánky enclosed in graphitic quartzite.

Tourmalines from graphitic gneisses of the Velké Vrbno Group display very low V (0.00-0.40 wt.% V_2O_3), and Cr

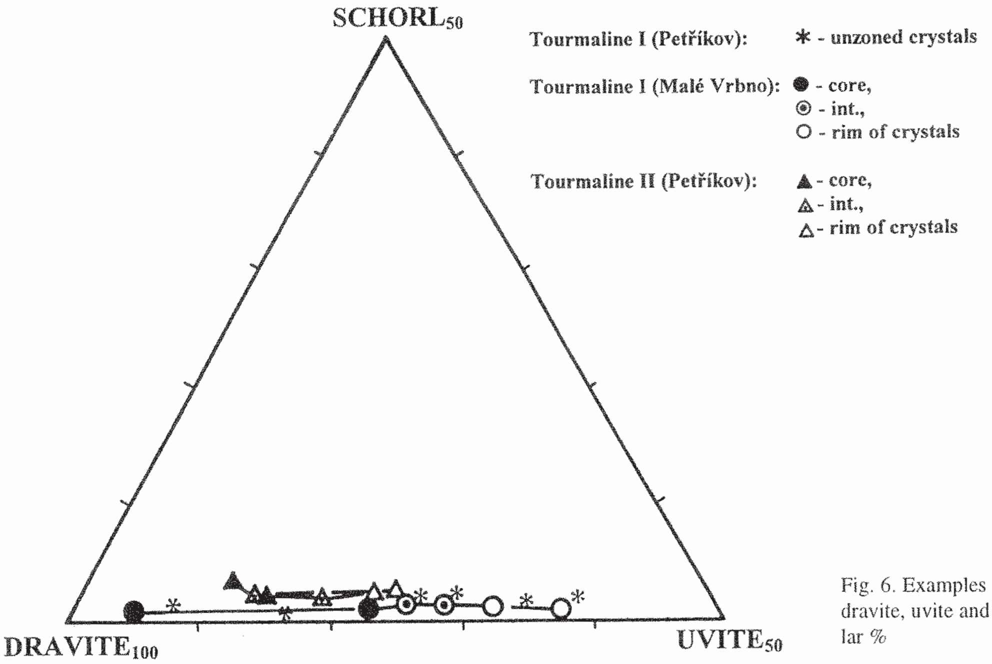

Fig. 6. Examples of tourmaline compositions in the dravite, uvite and schorl triangle. Values in molecular %

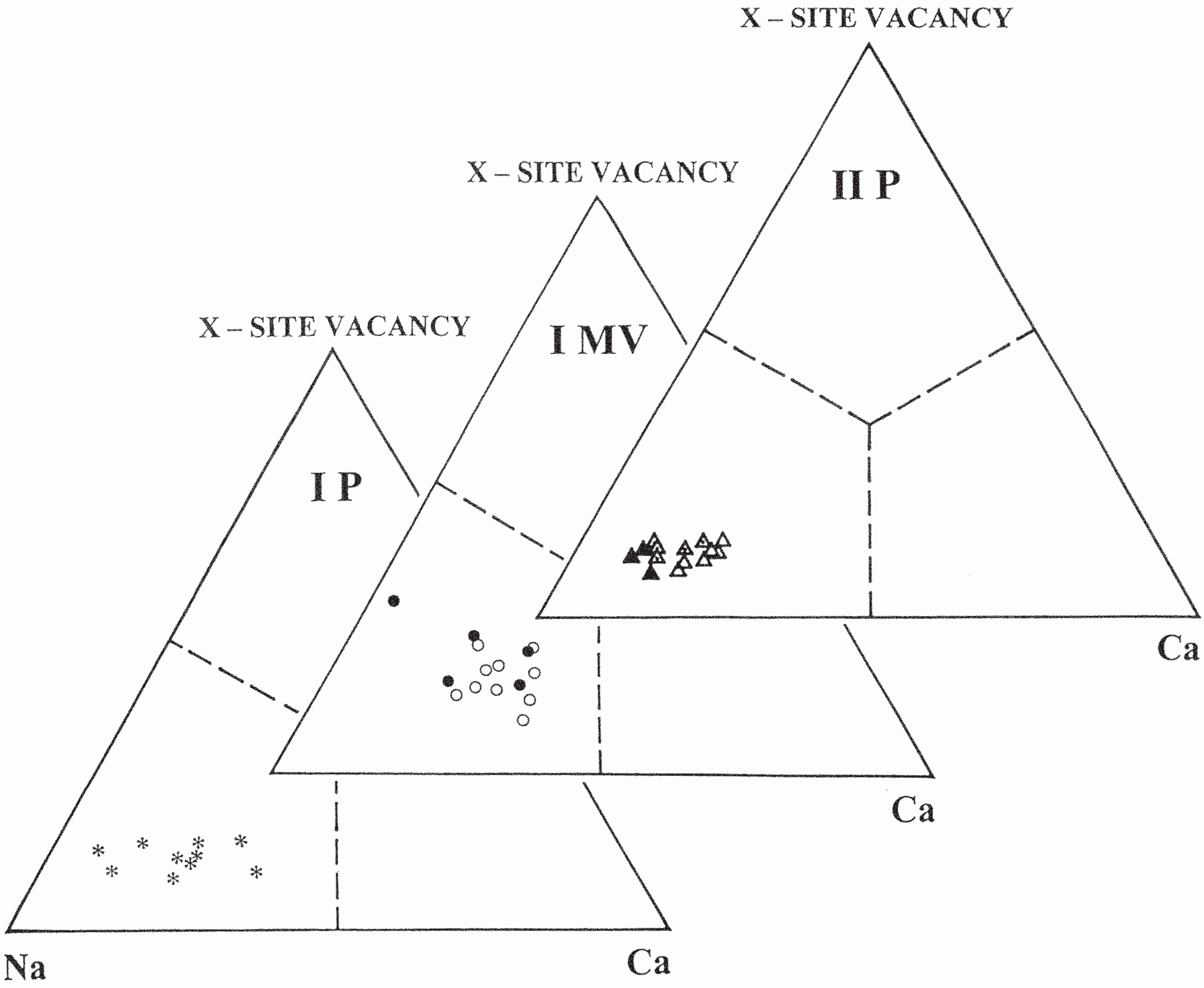

Fig. 7. Compositions of tourmaline I (from Petříkov - I P and Malé Vrbno - I MV) and II (from Petříkov) in terms of X-site vacancy, Na and Ca diagram. Symbols as in Fig. 6

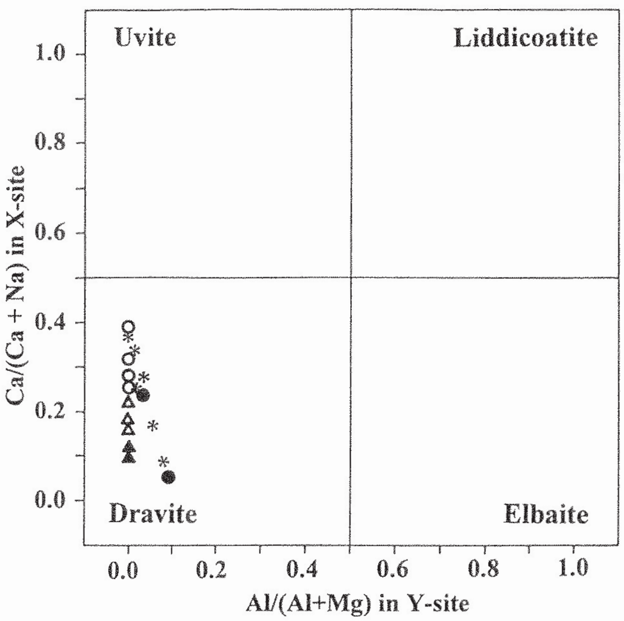

Fig. 8. Ca/(Ca + Na) in the X-site versus Al/(Al + Mg) in the Y-site diagram for tourmaline from the Petříkov and Malé Vrbno graphite deposits. Symbols as in Fig. 6

contents (0.05-0.14 wt.% Cr_2O_3). Similar low V and Cr concentrations (0.1-0.4 wt.% of V_2O_3) were found also in dravite from graphitic gneisses at Amstall, Moldanubicum (Richter et al. 1991). They are significantly lower relative to dravite from Bítovánky with 1.75 - 7.67 wt.% of V_2O_3 (Houzar - Selway 1997). The difference in concentrations of V in tourmaline between that from Velké Vrbno region and Amstall and that from Bítovánky is in apparent contrast with concentrations of V in their host rocks; up to 420 ppm (graphite gneiss from Amstall) and up to 690 ppm (graphite quarzite from Bítovánky).

The dravite-uvite and graphite of the host rocks were formed during progressive regional metamorphism at temperatures of 500-540 °C (Losos - Hladíková 1995) and pressures of about 0.5 to 0.7 GPa (Fojt et al. 1994). The tourmaline chemical composition falls in a field between low- to medium-grade metamorphosed metapelites and marbles (Henry - Dutrow 1996). Elevated Ca-contents are related to the presence of marbles within the host graphitic rock sequence. The $\delta\ ^{13}C$ values of graphites range from -23.1 to -25.0 ‰ from carbonate free rocks (i.e., graphitic gneisses with tourmaline) which corresponds to organic matter of marine sediments (Losos - Hladíková 1995). The primary boron content in these sediments can be explained by an increase in salinity within a regressive sea-shelf.

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Turmalíny dravit-uvitové řady z grafitických hornin velkovrbenské skupiny (silesikum, Česká republika)

Pro grafitické ruly velkovrbenské skupiny silesika, metamorfované v nižší amfibolitové facii (granátové až staurolitové zóně), jsou charakteristická lokální nabohacení turmalínem (dravit I). Byla zjištěna na ložiskách grafitu u Petříkova (důl Barbora) a v Malém Vrbně. Sloupečkovité krystaly dravitu I uzavírají v centrech jemné grafitové inkluze (automorfní vločky grafitu o velikosti 0.003-0.01 mm). Parageneticky odlišný typ turmalínu (dravit II) se vyskytuje v masívní pyrhotinové rudě z dolomitických mramorů grafitového ložiska v Petříkově.

Oba typy turmalínu odpovídají chemismem dravit-uvitové řadě a jsou charakterizovány složením $dravit_{95}\ uvit_5$ až $dravit_{61}\ uvit_{38}$ s malou, ale stabilní příměsí skorylové komponenty v množství 0.5-3 mol.%. Okrajové zóny krystalů turmalínu jsou většinou obohaceny uvitovou složkou o 2-27

mol.%, vzhledem k jádrům krystalů. Obsahy vanadu (0.00-0.40 wt.% V_2O_3) a chromu (0.05-0.14 wt.% Cr_2O_3) ve studovaných turmalínech jsou velmi nízké.

Turmalín společně s grafitem rul krystaloval během progresívní regionální metamorfózy, pravděpodobně za teplot 500-540 °C a tlaků 0.5 až 0.7 GPa. Prakticky stejné chemické složení turmalínů obou paragenetických typů odpovídá chemismu turmalínů z nízko až středně metamorfovaných hornin na hranici mezi metapelity a mramory. Obsahy boru pravděpodobně indikují zvýšenou salinitu vody v závěru sedimentace grafitonosného souvrství velkovrbenské skupiny za podmínek regrese šelfového moře.