VANADIUM-BEARING TOURMALINE IN METACHERTS FROM CHVOJNICA, SLOVAK REPUBLIC: CRYSTAL CHEMISTRY AND MULTISTAGE EVOLUTION

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Abstract

Vanadium-bearing tourmaline was found in Paleozoic metacherts near Chvojnica in the Strážovské vrchy Mountains, Slovakia. The geochemistry of metacherts suggests that the protolith was deposited under anoxic conditions. Tourmaline from Chvojnica displays strong chemical zoning, with high Mg and a very low Fe content. The core has the composition of magnesio-foitite with a low V content, and is mainly controlled by alkali-deficient substitution $[^X\square(Al,V)(NaMg)_{-1}]$. The other zones have a dravitic composition considering ordering of all Mg to the Y sites, but they may reach the composition of olenite if one proposes strong Al–Mg disorder (not proven by structural refinement). The intermediate zone is mostly enriched in V (up to 3.3 wt.% V_2O_3, 0.42 *apfu* V), and V is considered to be incorporated into the structure by VAl_{-1} substitution. Two rim zones were observed. Rim 1 is depleted in V but is enriched in Al. Rim 2 is similar in composition to the intermediate zone, with increased V. The increased content of trivalent cations, including Al, V and Cr in comparison to divalent Mg and Fe, suggests a deprotonation of $(OH)^-$ by the proton-deficient substitution $^Y(Al,V)O^YMg_{-1}(OH)_{-1}$. The increase of Ca, Ti and Mg content from core to rim may be the result of several substitutions, including $TiMg(Al,V)_{-2}$, $CaMgO^X\square_{-1}(Al,V)_{-1}(OH)_{-1}$. The V-bearing tourmaline from Chvojnica is the result of multistage Pre-Alpine regional metamorphism. The core of the grains is a product of the lower-grade M1 metamorphic event, whereas the intermediate zone corresponds to the second metamorphic event, M2. Medium-grade metamorphism (580 < T < 600°C) remobilized V from the organic matter present in the protolith of the metacherts. Rim 1 may be the result of reheating of the host rock due to the intrusion of the Malá Magura granitic massif (M3 event). The chemical composition of rim 2 was most likely influenced by the remobilization of V from older V-bearing silicates during the M3 (M3b stage?) metamorphic event.

Keywords: tourmaline-group minerals, dravitic tourmaline, magnesio-foitite, vanadium, metachert, metamorphism, Western Carpathians, Slovakia.

Sommaire

Nous décrivons la tourmaline vanadifère découverte dans des métacherts paléozoïques près de Chvojnica, montagnes Strážovské vrchy, Slovaquie. D'après la géochimie de ces roches, le protolithe aurait été déposé en conditions anoxiques. La tourmaline de Chvojnica fait preuve d'une zonation chimique importante, avec des compositions fortement enrichies en Mg et une teneur en Fe très faible. Le noyau a la composition de magnésio-foïtite à faible teneur en V, et sa composition répond à la substitution impliquant une déficience en alcalins $[^X\square(Al,V)(NaMg)_{-1}]$. Les autres zones possèdent une composition dravitique si tout le Mg est placé au site Y, mais pourraient atteindre le champ de l'olénite si on propose un fort désordre dans la distribution des atomes Al–Mg, ce qui n'est pas encore documenté avec un affinement de la structure. La zone intermédiaire est enrichie en V (jusqu'à 3.3% V_2O_3, poids, 0.42 *apfu* V), et le V serait incorporé dans la structure selon la substitution VAl_{-1}. Il y a deux zones distinctes à la bordure. La bordure 1 a une faible teneur en V mais est enrichie en Al. La bordure 2 est semblable à la zone intermédiaire en composition, avec une augmentation en V. L'augmentation de la concentration des cations trivalents, y inclus

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Al, V et Cr, par rapport aux cations bivalents Mg et Fe, fait penser à une déprotonation de $(OH)^-$ selon la substitution $^Y(Al,V)$ $O^YMg_{-1}(OH)_{-1}$. L'augmentation de la teneur en Ca, Ti et Mg du noyau jusqu'à la bordure pourrait être le résultat de plusieurs substitutions, y inclus $TiMg(Al,V)_{-2}$ et $CaMgO^X\square_{-1}(Al,V)_{-1}(OH)_{-1}$. La The tourmaline vanadifère de Chvojnica serait le résultat d'une évolution métamorphique régionale pré-Alpine en plusieurs étapes. Le noyau des grains serait le produit d'une recristallisation précoce lors de l'événement M1, de faible intensité, tandis que la zone intermédiaire correspondrait au second événement, M2. Un métamorphisme d'intensité moyenne ($580 < T < 600°C$) aurait remobilisé le vanadium par déstabilisation de la matière organique présente dans le protolithe des métacherts. La bordure 1 serait le résultat de réchauffage de la roche hôte dû à la mise en place du pluton Malá Magura (événement M3). La composition chimique de la bordure 2 a probablement été influencée par la remobilisation du V à partir de silicates antérieurs contenant le vanadium au cours de l'événement M3 (stade M3b?).

INTRODUCTION

Occurrences of V-bearing tourmalines are rather unusual. Vanadiumdravite, $NaMg_3V_6Si_6O_{18}(BO_3)_3$ $(OH)_4$, the end member of the tourmaline group with V predominant at the Z site, was only first formally described at the beginning of the 21st century in V–Cr-bearing calcite – quartz – diopside metamorphic rocks of the Slyudyanka complex, Russia (Reznitsky *et al.* 2001). However, occurrences of V-bearing dravitic tourmalines have been studied for more than half a century. Vanadian dravitic tourmaline is usually associated with quartz-rich rocks containing organic matter (graphite). Badalov (1951) reported the occurrence of V-bearing tourmaline in black quartz–graphite hornfels from Uzbekistan. Vanadium-bearing tourmaline also occurs in Tanga Province, Tanzania (Basset 1956), Mariposa County, California (Snetsinger 1966, Foit & Rosenberg 1979), the Kwal district, Kenya (Schmetzer *et al.* 1979), Bítovánky, Czech Republic (Houzar & Šrein 1993, Cempírek *et al.* 2006), Primorye, Russia (Kazachenko *et al.* 1993), and Amstall, Lower Austria (Ertl *et al.* 2008).

Vanadium-bearing tourmaline in association with V-bearing micas (muscovite to roscoelite: Méres & Ivan 2007) also occur in Paleozoic metacherts from the Pre-Alpine basement of the Strážovské vrchy Mountains, near the village of Chvojnica, Slovakia. In this paper, we describe the crystal chemistry and zoning of the V-bearing tourmaline. The geochemistry of metacherts may be helpful in revealing the protolith and the source of the elements from which this tourmaline formed. On this basis, we present a model for the multistage evolution of this V-bearing tourmaline.

GEOLOGICAL SETTING

The Western Carpathians constitute the northernmost west–east-trending orocline of the European Alpides. Basement complexes of the central Western Carpathians (Tatra-Fatra and Vepor belts) represent the inner Variscan zones with medium- to high-grade metamor-phism and abundant granitoid plutons. The Strážovské vrchy Mountains (SVM) are part of the Tatra–Fatra Belt of core mountains; they comprise the Tatric pre-Alpine Lower Paleozoic crystalline basement and its Late Paleozoic to Mesozoic sedimentary cover (Plašienka *et al.* 1997). The pre-Alpine crystalline basement of the SVM consists of granitic rocks, migmatites, metapelites to metapsammites and amphibolites (Fig. 1).

Gneisses, graphitic gneisses and metacherts represent metamorphosed sedimentary rocks of the SVM. They underwent Hercynian regional metamorphism at amphibolite-facies conditions (Hovorka & Méres 1991). The distinct chemical composition of the gneisses, graphitic gneisses and metacherts reflects differences in the protolith and sedimentary environment.

The dark grey to black graphitic gneisses and metachert in the SVM display schistose structures and predominantly a granoblastic texture. Plagioclase, quartz, white micas and metamorphosed organic matter (graphite) are common mineral components, whereas tourmaline, almandine, sillimanite and sulfide minerals (pyrite, pyrrhotite) are relatively rare. The chemical composition of the graphitic gneisses and metacherts indicates that their protolith (pelagic clays, deep siliceous marine sediments and organic matter) was derived from the young undifferentiated arc (Méres 2005, 2007). This protolith was deposited on the abyssal ocean floor in the Early Paleozoic. The sedimentation was accompanied by oceanic rift basaltic volcanism producing N–MORB-type basalts, and by hydrothermal activity, which formed the stratiform hydrothermal massive sulfide bodies. Graphitic gneisses, metachert and amphibolites of the SVM are analogous to other Devonian ophiolite sequences of the Western Carpathians, *e.g.*, the Pernek Group in the Malé Karpaty Mountains (Ivan *et al.* 2001, Méres 2005, 2007, Méres & Ivan 2008).

ANALYTICAL METHODS

The chemical composition of the metachert was determined at the ACME Analytical Laboratories
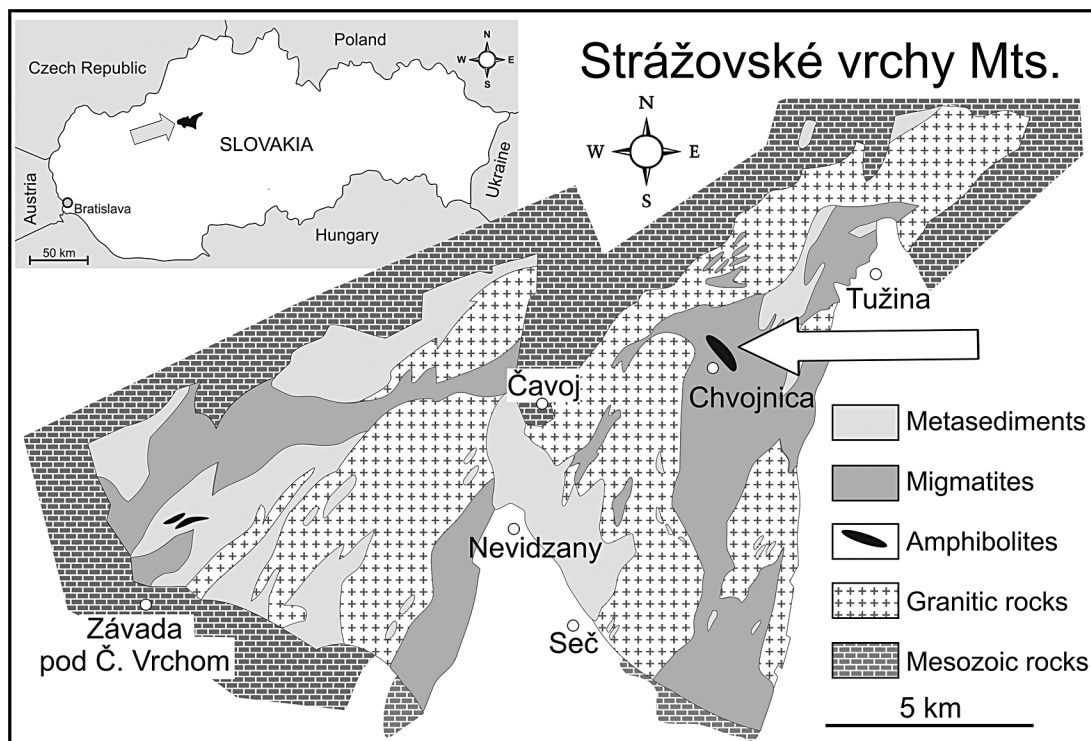
FIG. 1.   Simplified geological map of the Strážovské vrchy Mountains modified after Mahel' *et al*. (1982), with location (arrow) of the V-bearing tourmaline occurrence in metacherts related to the amphibolite body near the village of Chvojnica.

(Vancouver, Canada). The total abundance of the major oxides in metachert was determined by inductively coupled plasma – emission spectrometry (ICP–ES) following lithium metaborate–tetraborate fusion and digestion in dilute nitric acid. Loss on ignition (LOI) was calculated from the difference in weight after ignition to 1000°C. The total carbon (TOT/C) and sulfur analysis (TOT/S) was performed by LECO analysis; the samples were heated in an induction furnace to >1650°C, which caused the volatization of all C- and S-bearing phases. The vapors were carried through an infrared spectrometric cell, wherein the concentrations of C and S were determined by the absorption of specific wavelengths in the infrared spectra (ORG/C = TOT/C minus graphite C and carbonate). The concentrations of trace elements, including the rare-earth elements, were determined by ICP mass spectrometry (ICP–MS).

The composition of tourmaline was established with a CAMECA SX100 electron microprobe in wavelength-dispersion mode at the Dionýz Štúr State Geological Institute, Bratislava, Slovakia, under the following conditions: accelerating voltage 15 kV, beam current 20 nA, beam diameter 2 to 5 μm, and peak-counting time 15 to 40 s. The samples were analyzed using LPC, TAP,

LLIF, and LPET crystals, and the following standards: wollastonite (Si$K\alpha$, Ca$K\alpha$), synthetic TiO_2 (Ti$K\alpha$), synthetic Al_2O_3 (Al$K\alpha$), metallic Cr (Cr$K\alpha$), metallic V (V$K\alpha$), fayalite (Fe$K\alpha$), rhodonite (Mn$K\alpha$), forsterite (Mg$K\alpha$), willemite (Zn$K\alpha$), metallic Ni (Ni$K\alpha$), albite (Na$K\alpha$), orthoclase (K$K\alpha$), BaF_2 (F$K\alpha$) and NaCl (Cl$K\alpha$). Lower limits of detection for the measured elements vary between 0.01 and 0.05 wt.%; Mn, Zn, Ni, F and Cl were invariably below their detection limits. Matrix effects were corrected by the PAP routine. The formula of tourmaline was calculated on the basis of 15 $Y + Z + T$ cations exclusive of X-site cations, including Na, Ca and K. The proportion of Li was not calculated; the proportion of Li in the deep ocean-floor metasediments is negligible, and the amount of Li in tourmaline related to them is considered to be insignificant. The amount of B_2O_3 was calculated from stoichiometric constraints assuming B = 3 *apfu*. A very low Fe content allowed estimation of $(OH)^-$ and O^{2-} from the charge-balanced formula (Henry & Dutrow 1996). Owing to the likely Mg–Al disorder (Hawthorne *et al*. 1993, Ertl *et al*. 2008) and V occupancy at both Y and Z sites (Foit & Rosenberg 1979), we decided to treat the Y and Z sites as united in the chemical formula.

Geochemistry of the metacherts

The bulk chemical composition of the representative metachert sample was determined (Table 1); it has high contents of SiO_2 (~84 wt.%) and TOT/C (9 wt.%), as well as low contents of Al_2O_3 (~4 wt.%), FeO (<0.3 wt.%), MgO (<0.3 wt.%), CaO (~0.01 wt.%), Na_2O (~0.07 wt.%) and K_2O (~1.5 wt.%). In comparison to the Post-Archean average Australian Shale (PAAS, Taylor & McLennan 1985), the metachert from Chvojnica is enriched in U (~10 ppm), V (~950 ppm) and depleted in Sr, Ti and LREE (Table 1). The PAAS-normalized REE patterns display a negative Ce anomaly, a negative Eu anomaly, and low LREE/HREE ratio (Fig. 2).

Chemical composition, zoning and substitutions in tourmaline

The tourmaline from Chvojnica is an accessory mineral occurring in association with quartz and V-bearing muscovite (up to 21 wt.% V_2O_3, Méres & Ivan 2007). It forms euhedral to subhedral prismatic crystals up to 1 mm in size (Fig. 3). Tourmaline grains are crossed by mostly irregular fissures. Color zoning of tourmaline, with a light yellow-green core and light green rim, with a light yellow-green to green pleochroism, is visible in thin section.

The crystals display a strong chemical zoning, with a chemically distinct core, an intermediate zone, and two rim zones (Fig. 4). However, these zones are not uniformly developed in all tourmaline crystals exam-
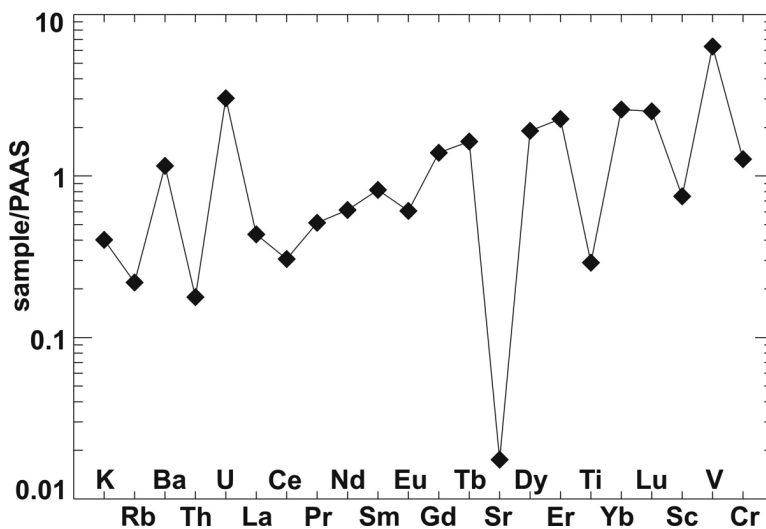

FIG. 2.   Multi-element PAAS-normalized pattern of the metachert (Chvojnica, sample MM–05–2).

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITION OF METACHERT (SAMPLE MM–05–2) FROM CHVOJNICA

sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total	TOT/C	ORG/C	TOT/S
MM-05-2	83.95	0.29	4.41	0.25	0.01	0.25	0.01	0.07	1.49	0.01	9.20	99.94	9.13	1.43	0.01

sample	Sc	V	Cr	Co	Ni	Rb	Sr	Y	Zr	Nb	Ba	Hf	Ta	Th	U
MM-05-2	12	950	140	<0.5	20	35	3.5	82	121	3.5	752	2.1	0.4	2.6	9.4

sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
MM-05-2	16.5	24.5	4.57	19.7	4.60	0.67	6.54	1.26	8.39	2.10	6.53	0.96	7.21	1.08

Concentrations of the major and minor elements, acquired with an ICP–ES, are reported in wt.%; concentrations of the trace elements, including the rare-earth elements, acquired with ICP–MS, are reported in ppm.
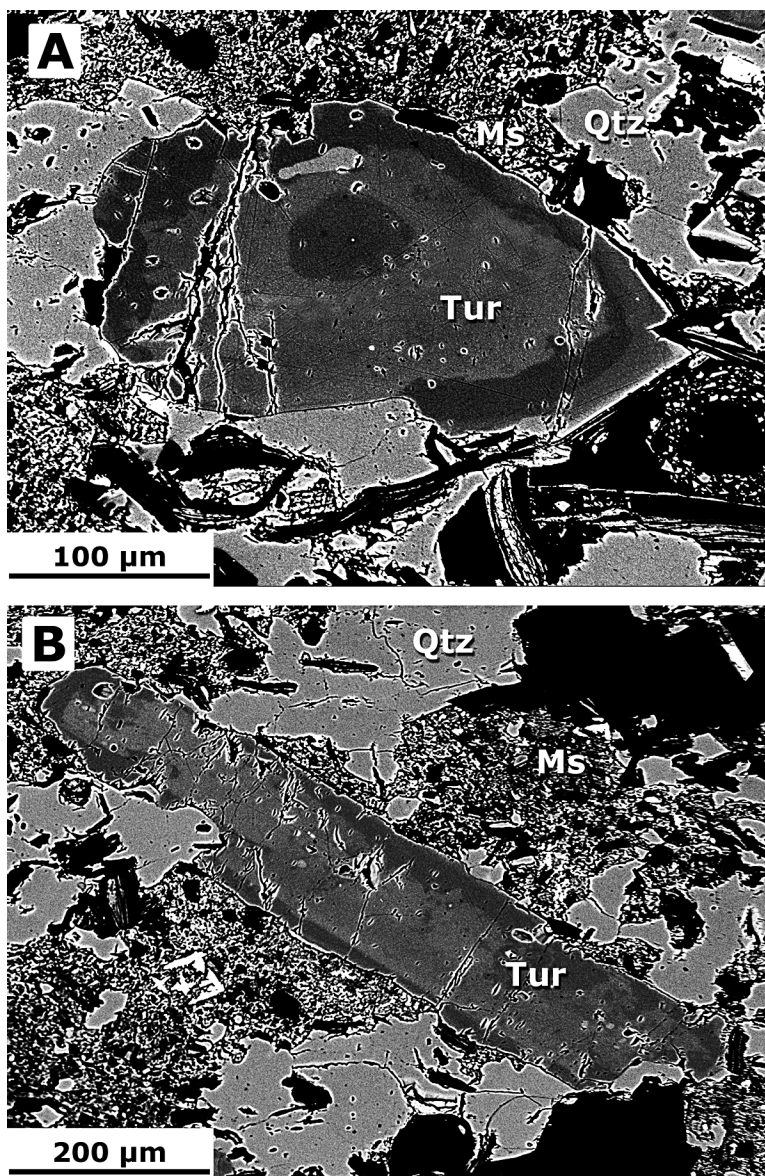
Fig. 3. BSE images of V-bearing tourmaline (Tur) in association with quartz (Qtz) and V-bearing muscovite (Ms) in metachert from Chvojnica.

ined. There is some similarity among the sequences from core to intermediate zone and rim 1 to rim 2, which suggests multistage formation of the crystals. The several zones and borders between them are irregular (Fig. 4), which suggests partial dissolution and replacement by a later generation of tourmaline formed under different geochemical conditions.

The tourmaline from Chvojnica belongs to the alkali subgroup except for the core, where some compositions belong to the X-site-vacant subgroup (Fig. 5A) and have a composition of magnesio-foitite (Table 2). The other zones are dravitic, but if we consider Al–Mg disorder at both octahedral sites, they might have the composition of Mg-rich olenite. Generally, all zones are extremely

low in Fe (up to 0.01 *apfu*), with Mg, Al and V occupying the majority of the octahedral sites (Table 2). The content of Na is almost constant throughout the whole grain (0.41 to 0.56 *apfu*). The tourmaline is relatively rich in Ca (up to 0.30 *apfu*), which is in negative correlation with $^X\square$. The content of Cr (0.02 to 0.07 *apfu*) is significantly lower than V (0.10 to 0.41 *apfu*), but they are correlated positively (Table 2).

The anhedral to subhedral core has a lower content of V, Ca, Na, and Ti (Fig. 4), and higher Al content (up to 6.41 *apfu*). The *X* site is 42–46% vacant, more so than in the outer zones, where *X* site on average is 25% vacant. The core approaches the magnesio-foitite composition (Figs. 5A–B). The intermediate zone constitutes the majority of the grain (Fig. 4). It is the most enriched in V (up to 3.3 wt.% V_2O_3; 0.42 *apfu*),
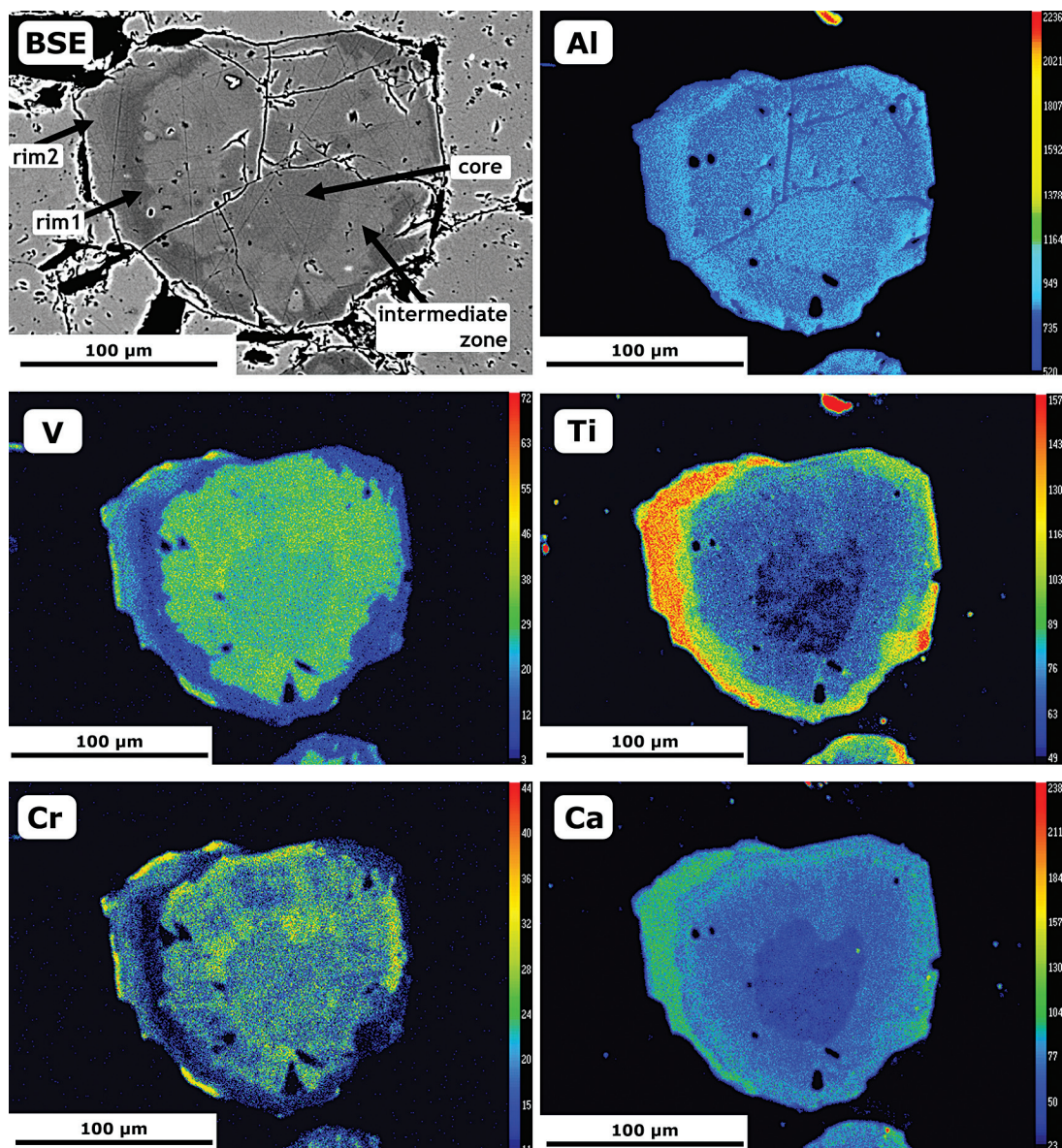

FIG. 4.   BSE image and X-ray distribution maps of Al, V, Ti, Cr, and Ca, in V-bearing tourmaline crystal from Chvojnica. In the color scale of X-ray maps, red indicates the highest and dark blue the lowest concentration of the element.

Cr (up to 0.64 wt.%; 0.08 *apfu*) and Na. The content of Ca (up to 0.34 *apfu*) and that of Ti (up to 0.05 *apfu*) are higher, and that of Al, lower (up to 2.00 *apfu*) in the intermediate zone. The first rim zone is Al-rich (up to 6.50 *apfu*). In this zone, the Ca and Ti contents are also higher. In contrast, the V content is the lowest of all zones, with 0.13 *apfu* or less (Fig. 4), whereas the content of Cr is less than 0.03 *apfu*. The second rim zone is enriched in V and Cr and depleted in Al with respect to the previous zone, but it attains the highest contents of Ca (0.30 *apfu*) and Ti (0.09 *apfu*) (Table 2, Fig. 4).

The increased content of trivalent cations, including Al, V and Cr in comparison to divalent Fe and Mg, results in the shift of tourmaline compositions over the ideal trend-line between dravite and magnesio-foitite (Fig. 5B). The majority of compositions fall into the field of "oxy-dravite". It suggests deprotonation of $(OH)^-$ group by some of proton-deficient substitutions including $^Y(Al,V)O^YMg_{-1}(OH)_{-1}$, mainly in the intermediate and rim zones (Fig. 6A). However, the charge excess of trivalent cations at the *Y* site may also be balanced by the *X*-site vacancy owing the substitutions $^X\square(Al,V)(NaMg)_{-1}$ (Fig. 6B). The low concentration of Fe (up to 0.1 wt.%) results in a negligible role of $FeMg_{-1}$ substitution typical of the schorl–dravite series. Instead, the Chvojnica tourmaline appears to belong to a series between dravite and vanadiumdravite, in which there is significant VAl_{-1} substitution at the octahedral sites (Fig. 6C). The multistage formation of tourmaline zones is reflected in two parallel trends of V increase at the expense of Al. The steeper trend-line of both trends reflects the decrease of trivalent cations and the slight increase of Mg and Ti (Fig. 4) during formation of tourmaline [$TiMg(AlV)_{-2}$ substitution, Fig. 6D]. Calcium increases from the core to the rim, and *X*-site

vacancy decreases (Figs. 4, 6F), whereas the Na content is roughly constant (Table 2). The decrease of trivalent cations is not accompanied by the adequate decrease of calculated content of O^{2-} at the *W* site (Table 2). It suggests the influence of more complex substitutions, *e.g.*, $CaMgO^X\square_{-1}(Al,V)_{-1}(OH)_{-1}$ (Fig. 6E).

DISCUSSION AND CONCLUSIONS

The chemical composition of V-bearing tourmaline occurring in metacherts from Chvojnica is typical of this type of genetic environment. Its V content (up to 3.3 wt.% V_2O_3; 0.42 *apfu*) is intermediate relative to other world occurrences, *e.g.*, 1.5 wt.% V_2O_3 in the tourmaline from the Tanga province, Tanzania (Basset 1956) and 8.5 wt.% V_2O_3 in tourmaline from Mariposa County, California (Foit & Rosenberg 1979). Vanadium is generally considered to be concentrated in the organic matter of deep ocean sediments (Snetsinger 1966), where it is subsequently remobilized from black cherts and incorporated in silicate minerals during medium-grade metamorphism (Badalov 1951, Houzar & Šrein 2000). This appears to be a general scenario for the origin of vanadium in tourmaline from Chvojnica.

The VAl_{-1} substitution, which was reported by several authors, including Reznitsky *et al.* (2001) and Cempírek *et al.* (2006), seems to be the preferred mode of incorporation of V also in the structure of Chvojnica tourmaline. Although V was assigned to the *Z* site in the ideal formula of the vanadiumdravite end-member (Reznitsky *et al.* 2001), a structural refinement of V-bearing dravite from Mariposa County, California proved the presence of V at both *Y* and *Z* octahedral sites (Foit & Rosenberg 1979). In contrast, V was fully assigned to the *Y* site in V-bearing, Mg-rich olenite from
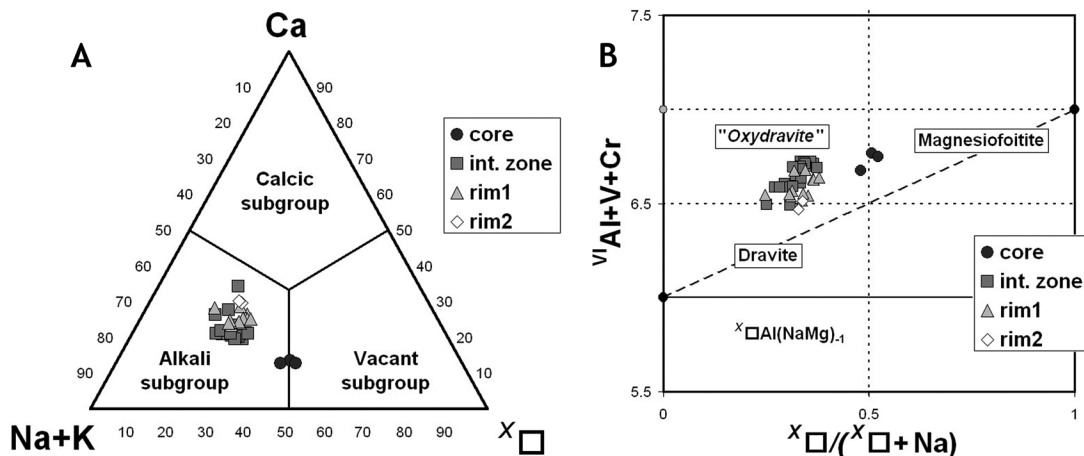

FIG. 5. Classification diagrams for V-bearing tourmaline from Chvojnica. (A) Triangular Ca – Na + K – $^X\square$ diagram. (B) Quadrilateral ^{VI}Al + V + Cr *versus* $^X\square$ / $^X\square$ + Na) diagram.
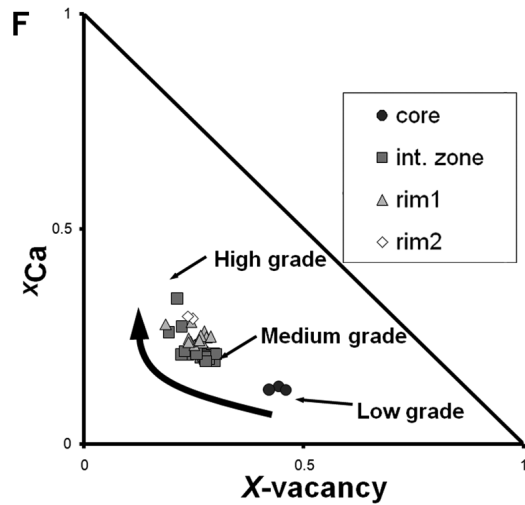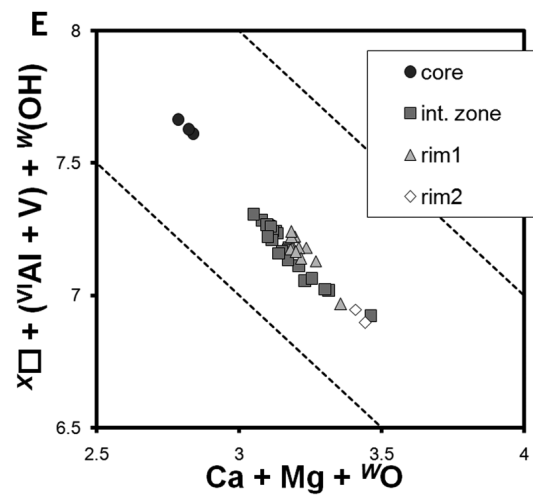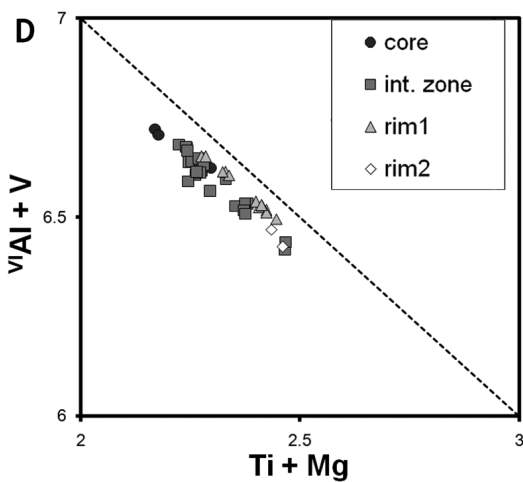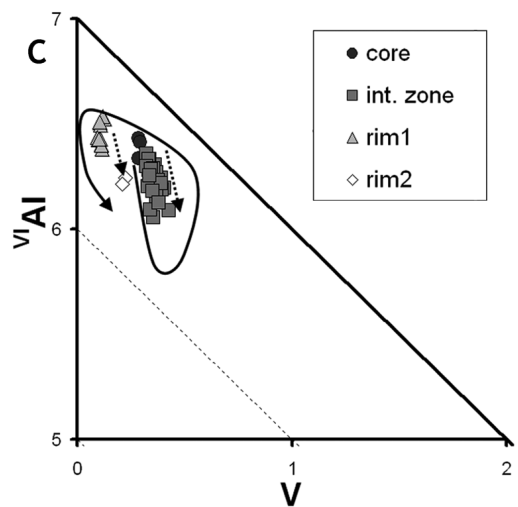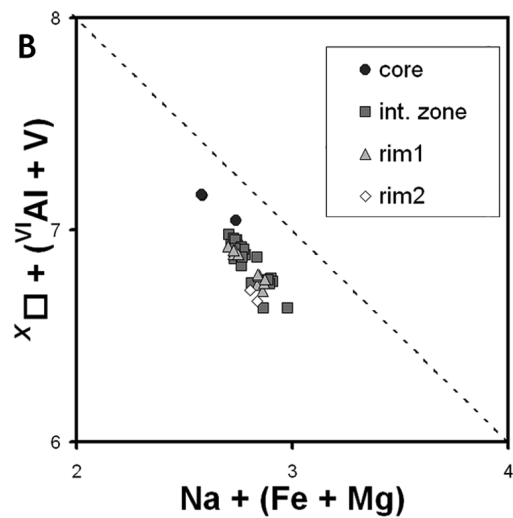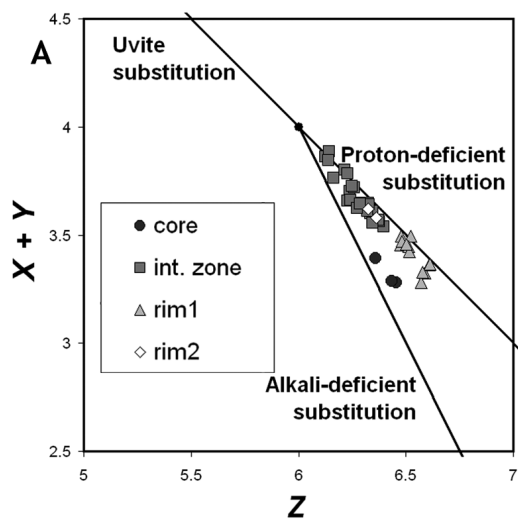
TABLE 2. REPRESENTATIVE COMPOSITIONS OF V-BEARING TOURMALINE
FROM CHVOJNICA, WESTERN CARPATHIANS, SLOVAKIA

	Crystal 1 core	Crystal 1 int. z.	Crystal 1 rim 1	Crystal 1 rim 2	Crystal 2 core	Crystal 2 int. z.	Crystal 2 rim 1	Crystal 2 rim 2
SiO_2 wt.%	37.11	37.13	36.62	37.26	37.33	36.17	36.05	37.32
TiO_2	0.26	0.26	0.44	0.68	0.14	0.37	0.59	0.74
B_2O_3*	10.75	10.68	10.76	10.75	10.75	10.54	10.55	10.8
Al_2O_3	33.23	32.29	34.09	32.6	33.63	31.78	33.42	32.9
Cr_2O_3	0.32	0.33	0.18	0.32	0.33	0.58	0.17	0.35
V_2O_3	2.64	3.15	0.89	1.64	2.27	2.83	0.76	1.76
FeO	0.06	0.06	0.06	0.06	0.07	0.07	0.08	0.05
MgO	9.30	9.33	9.95	10.02	9.06	9.51	9.64	9.93
CaO	1.18	1.24	1.47	1.74	0.73	1.57	1.61	1.71
Na_2O	1.66	1.65	1.52	1.47	1.33	1.57	1.65	1.47
K_2O	0.02	0.03	0.06	0.07	0.02	0.04	0.07	0.06
H_2O**	3.05	2.99	3.19	3.00	3.22	2.98	2.97	3.02
Total	99.64	99.17	99.26	99.61	98.91	98.08	97.6	100.14
Si *apfu*	6.00	6.05	5.91	6.03	6.04	5.97	5.94	6.01
Al	0	0	0.09	0	0	0.03	0.06	0
Σ T	6.00	6.05	6.00	6.03	6.04	6.00	6.00	6.00
B	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Ti	0.03	0.03	0.05	0.08	0.02	0.05	0.07	0.09
Al	6.33	6.20	6.40	6.21	6.41	6.15	6.43	6.24
Cr	0.04	0.04	0.02	0.04	0.04	0.08	0.02	0.04
V	0.34	0.41	0.12	0.21	0.29	0.37	0.10	0.23
Fe^{2+}	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	2.24	2.27	2.40	2.42	2.18	2.34	2.37	2.38
Σ $Y + Z$	9.00	8.95	9.00	8.97	8.96	9.00	9.00	8.99
Ca	0.20	0.22	0.25	0.30	0.13	0.28	0.28	0.30
Na	0.52	0.52	0.47	0.46	0.42	0.5	0.53	0.46
K	0	0.01	0.01	0.01	0	0.01	0.02	0.01
$^X\square$	0.27	0.26	0.26	0.22	0.45	0.21	0.17	0.23
ΣX	0.73	0.74	0.74	0.78	0.55	0.79	0.83	0.77
$O^{..}$	0.72	0.76	0.56	0.76	0.54	0.73	0.74	0.77
OH**	3.28	3.24	3.44	3.23	3.46	3.27	3.26	3.23
Σ cations	18.73	18.74	18.74	18.78	18.55	18.79	18.83	18.77

The analytical data, acquired with an electron microprobe, are first reported in wt.%, and then converted to atoms per formula unit on the basis of 15 anions per formula unit. A component is not considered significant unless its value exceeds the uncertainty. * B_2O_3 was calculated assuming 3.00 *apfu*; ** OH and ^wO were calculated from the charge-balanced formula; H_2O was calculated for OH + O = 4 *apfu*.

FIG. 6. Substitution diagrams for V-bearing tourmaline from Chvojnica. (A) ($X+Y$) *versus* Z diagram, where X = Ca + Na; Y = Fe + Mg + V + Cr; Z = Al + 1.33*Ti. Lines radiating from the point of the ideal schorl–dravite composition represent uvite, alkali-deficient and proton-deficient substitutions (after Trumbull & Chaussidon 1999). (B) $^X\square$(Al,V)Na$_{-1}$(Fe,Mg)$_{-1}$ substitution. Dotted line is parallel with the ideal substitution trend. (C) VAL$_{-1}$ substitution. Solid curve with arrow represents the general trend of tourmaline evolution; dotted arrows represent two distinct parallel trends between four zones. (D) TiMg(Al,V)$_{-2}$ substitution. Dotted line is parallel with the ideal substitution trend. (E) CaMgO$^X\square_{-1}$(Al,V)$_{-1}$(OH)$_{-1}$ substitution. Dotted lines are parallel with the ideal substitution trend. (F) Ca *versus* $^X\square$ diagram, with estimated grade of metamorphism (after Henry & Dutrow 1996).

Amstall, Lower Austria (Ertl *et al*. 2008). Olenite from Amstall has a very similar composition to tourmaline from Chvojnica, but there is a strong Al–Mg disorder between Y and Z sites, which gives Al > Mg at the Y site. Similarity of chemical composition and the genetic features suggests that the intermediate and rim zones of tourmaline from Chvojnica might also be olenite, as at Amstall. Consequently, it is not possible to determine the occupancy of V, Mg and Al at the Y and Z sites and clearly classify tourmaline from Chvojnica without structure-refinement data.

Kazachenko *et al*. (1993) and Cempírek *et al*. (2006) suggested a substitution of V for Mg. This trend is not pronounced in tourmaline from Chvojnica; Mg substitutes for both V and Al, but variations of the V

content seem to be independent on the general trend of enrichment in Mg from the core to the rim (Figs. 6C–D). The slight enrichment in Mg and Ca during the formation of tourmaline seems to depend on the increasing metamorphic grade (Henry & Dutrow 1996) and could be described as $CaMgO^X\square_{-1}(Al,V)_{-1}(OH)_{-1}$ substitution (Henry & Dutrow 1990). The increase of Ti content along with Mg may also reflect increasing P–T conditions and could be represented by $TiMg(Al,V)_{-2}$ substitution, which only affects the octahedral Y site (Burt 1989).

Tourmaline from Chvojnica contains less Cr (up to 0.6 wt.% Cr_2O_3, 0.08 *apfu*) compared to tourmaline in other occurrences, which contains more than 1.5 wt.% Cr_2O_3 (Foit & Rosenberg 1979, Kazachenko *et al.* 1993). However, the Cr content is similar to that in tourmalines from Bítovánky (Houzar & Šrein 1993) and the Kwal District (Schmetzer *et al.* 1979). The proportion of Cr may depend on the geochemistry of the protolith and the surrounding rocks. Chromium enrichment is mainly of magmatic origin, and it is fixed in the ultrabasic to basic rocks of the ophiolitic complexes or into the stratiform massive sulfide bodies (*e.g.,* Treloar 1987). However, metacherts from Chvojnica are surrounded by metabasic rocks that contain less Cr in comparison to meta-ultrabasic rocks. Moreover, Fe and Cu sulfide minerals (pyrite, pyrrhotite, and chalcopyrite) are only scarce and disseminated.

Low Fe contents are typical of V-bearing tourmaline from metacherts, *e.g.,* 0.3–1.6 wt.% (Snetsinger 1966, Kazachenko *et al.* 1993, Houzar & Šrein 1993). The main reason for the low Fe content may be the geochemistry of the host rock; metacherts are usually associated with a deep ocean environment and nearby Mg-rich metabasic suites (*e.g.,* Méres & Ivan 2008). Moreover, the majority of Fe could be concentrated in sulfide minerals, mainly pyrite and pyrrhotite. Iron-deficient silicate minerals have been recorded in several localities from the analogous meta-ophiolite Pernek Group in the Malé Karpaty Mountains, where tourmaline does not occur, but the amphiboles, diopside, dissakisite-(La), and goldmanite garnet are also very Fe-poor (Uher *et al.* 2008, Bačík & Uher 2010).

Vanadium-bearing tourmaline from Chvojnica is the product of several processes, including sedimentation of the protolith and subsequent polystage Pre-Alpine regional metamorphism, which took a place in the SVM. The negative Ce anomaly and PAAS-depleted contents of Th and Ti in metacherts suggest a chemical or biochemical origin of the protolith, whereas low contents of CaO and Sr suggest the absence of the carbonates in the protolith. The low Th:U ratio, the high contents of V and U, and the TOT/C enrichment in metacherts provide strong evidence for sedimentary deposition under distinctly anoxic conditions (*cf.* Méres 2005). The trace-element distribution (La/Sc, Th/Sc, Th/Yb, Ta/Yb, LREE/HREE) and the common occur-

rence of metacherts with metabasic rocks in the SVM indicate an ocean-floor sedimentary environment for the protolith of the metacherts, close to the active oceanic spreading center producing N–MORB-type basalts (Méres & Ivan 2008).

The multistage metamorphic evolution of tourmaline is displayed by its compositional zoning (Fig. 6F). The core, with a higher proportion of the X-site vacancy, corresponds to the initial relatively lower-grade metamorphic event (M1). It may be correlated with the grossular- and spessartine-rich almandine core of garnet in the surrounding gneisses (Hovorka & Méres 1991). The intermediate zone of the tourmaline crystals formed during the subsequent regional metamorphic event (M2) and partially replaced the core. The P–T conditions of this stage correspond to the amphibolite facies, in the range from 580 to 600°C (Hovorka & Méres 1991). At this stage, the proportion of the X-site vacancy decreased, and V may have been remobilized from sedimentary organic matter. The transition of the intermediate zone to rim 1 is not continuous, and as their margins are irregular, the rim 1 seems to have replaced the intermediate zone (Fig. 4). Rim 1 thus seems to be the product of a subsequent metamorphic event (M3). The slightly increased contents of Ca, Mg and Ti in tourmaline generally indicate P–T conditions analogous to high-amphibolite facies (Henry & Dutrow 1996). The M3 metamorphic event can be related to the intrusion of the Malá Magura granite massif, which quickly increased the thermal gradient in surrounding rocks. This is also well documented by the presence of a pyrope-rich almandine rim on garnet crystals and also by the formation of fibrolitic sillimanite from primary biotite in the adjacent paragneisses (Hovorka & Méres 1991). Rim 2 is considered to be the product of the continuing M3 metamorphic event (M3b stage?), which is documented by the Ti- and Ca-enrichment of the rim-2 zone (Fig. 4). However, the amount of V in the rims is lower than in the intermediate zone, and may be the result of change in the source of V. Vanadium from the organic matter in the matrix was already fixed in silicate minerals formed during the previous metamorphic events (M1 and M2), including roscoelite, V-bearing muscovite and tourmaline. Older V-bearing silicates could have been reactivated during the M3 stage of metamorphism, which is also evident in the dissolution of the intermediate zone in tourmaline (Figs. 3, 4) and then became the source of V, which again increased in rim 2.

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