

VANADIAN–CHROMIAN GARNET IN MAFIC PYROCLASTIC ROCKS OF THE MALÉ KARPATY MOUNTAINS, WESTERN CARPATHIANS, SLOVAKIA

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ABSTRACT

Unusual examples of vanadian–chromian garnet have been discovered in Lower Paleozoic metamorphosed mafic pyroclastic rocks, enriched in V, Cr and organic carbonaceous matter, in the Pezinok – Pernek crystalline complex of the Malé Karpaty Mountains, Slovakia. The emerald-green euhedral grains of garnet, 0.5 mm in size, with $a = 11.98 \pm 0.01$ Å, $n = 1.810 \pm 0.003$, $D_x = 3.75$ g/cm³, contain 9.5–22.1 wt.% V₂O₃, 5.5–10.9% Cr₂O₃, and 0.4–7.6% Al₂O₃, which corresponds to 27–65 mol.% goldmanite, 19–34 mol.% uvarovite, 1.5–33 mol.% grossular, and 2–5 mol.% yamatoite. The associated hydromica contains up to 9.2% V₂O₃ and between 0.5 and 7.2% Cr₂O₃. The coexisting chlorite and tremolite also exhibit elevated levels of V and Cr. The assemblage of V,Cr-rich minerals formed at approximately 500°C as a result of thermal metamorphism induced by intrusions of granitic magma in Hercynian times.

Keywords: vanadian–chromian garnet, goldmanite, uvarovite, grossularite, vanadian–chromian mica, mafic metapyroclastic rocks, organic matter, thermal metamorphism, Western Carpathians, Slovakia.

SOMMAIRE

Nous avons trouvé un grenat vanadifère et chromifère dans des roches métapyroclastiques mafiques d'âge paléozoïque inférieur, enrichies en V, Cr et matière organique, du massif cristallin de Pezinok – Pernek, dans les montagnes Malé Karpaty, en Slovaquie. Les grains de grenat sont vert émeraude, ont une taille d'environ 0.5 mm, avec un paramètre réticulaire a de 11.98 ± 0.001 Å, $n = 1.810 \pm 0.003$, et une densité D_x de 3.75; ils contiennent entre 9.5 et 22.1% (poids) de V₂O₃, entre 5.5 et 10.9% de Cr₂O₃, et entre 0.4 et 7.6% de Al₂O₃, ce qui correspond, en termes molaires, à 22–65% de goldmanite, 19–34% uvarovite, 1.5 et 33% de grossulaire et 2–5% de yamatoïte. L'hydromica associé contient jusqu'à 9.2% de V₂O₃ et entre 0.5 et 7.2% de Cr₂O₃. La chlorite et la trémolite associées montrent aussi des teneurs élevées en V et Cr. Cet assemblage de minéraux vanadifères et chromifères aurait été stabilisé à environ 500°C suite à un métamorphisme de contact lié à la mise en place de massifs granitiques hercyniens.

(Traduit par la Rédaction)

Mots-clés: grenat vanadifère et chromifère, goldmanite, uvarovite, grossulaire, mica vanadifère et chromifère, roches métapyroclastiques mafiques, matière organique, métamorphisme de contact, chaîne des Carpatés occidentales, Slovaquie.

INTRODUCTION

Garnet compositions characterized by a high level of V³⁺ are rare and poorly studied. Since the first discovery and definition of goldmanite Ca₃V₂(SiO₄)₃ by Moench & Meyrowitz (1964), several occurrences of V-enriched garnet have been reported, some of them approaching the goldmanite end-member (Wang *et al.* 1974, Hallsworth *et al.* 1992). Von Knorring *et al.* (1986) have shown that V³⁺ is commonly replaced by Cr³⁺ (uvarovite component), but only to a limited extent. On the other hand, the level of Al³⁺ (grossular

component) in the Y-site may vary considerably.

Dark green garnet designated as uvarovite was first described in the Malé Karpaty Mountains by Čillík *et al.* (1959). The results of a mineralogical study presented here show that the composition of such garnet differs from that reported in the literature; there is a substantial amount of Cr³⁺ in addition to V³⁺ and Al³⁺. These samples thus represent a new series, from a goldmanite–uvarovite solid solution with a low proportion of grossular to intermediate members of the goldmanite – uvarovite – grossular ternary solid solution.

GEOLOGICAL SETTING

ANALYTICAL TECHNIQUES

The V–Cr–Ca-bearing garnet has been found to occur at three localities in the Pezinok – Pernek metamorphic complex, located approximately 20 km north-northeast of Bratislava in southwestern Slovakia (Figs. 1, 2). The complex represents a part of the pre-Alpine basement of the Malé Karpaty Mountains, which involves mainly Silurian to Lower Carboniferous metapelites to metapsammites, with intercalations of black shales, actinolite–tremolite schists and amphibolites (Cambel & Khun 1983). These rocks are associated with syngenetic pyrite – pyrrhotite and with locally exploited epigenetic $Sb \pm Au$ mineralization (Chovan *et al.* 1992). During the Hercynian orogeny, the Pezinok – Pernek complex underwent a low-grade greenschist-facies regional metamorphism and a medium-grade amphibolite-facies thermal metamorphism induced by intrusion of Carboniferous granitic magma of the Bratislava and Modra massifs (Korikovsky *et al.* 1984).

The garnet-bearing actinolite – tremolite schists characteristically display a nematoblastic texture, with porphyroblasts of actinolite – tremolite (up to 2 mm in diameter), less common garnet, and sporadic plagioclase and micas. The matrix is composed of quartz, sericite, amphibole and plagioclase. Pyrite and organic matter are mostly aligned along the schistosity. The rocks have been subjected to hydrothermal alteration connected with the formation of secondary quartz, sericite and carbonates. Limonite and gypsum are common precipitates in oxidation zones near the surface.

X-ray powder-diffraction data on the garnet were obtained with help of a DRON 3 UM–1 diffractometer using $CuK\alpha$ radiation and NaCl as an internal standard. Quantitative electron-microprobe analyses (EMPA) of the silicates were carried out on a JEOL JXA 733 Superprobe with an accelerating voltage of 15 kV and a beam current of 20 μA . The following standards were used: albite for $SiK\alpha$, $AlK\alpha$ and $NaK\alpha$, TiO_2 for $TiK\alpha$, chromite for $CrK\alpha$ and $FeK\alpha$, metallic V for $VK\alpha$, Mn-bearing willemite for $MnK\alpha$, MgO for $MgK\alpha$, wollastonite for $CaK\alpha$, and orthoclase for $KK\alpha$. Concentrations of V, Ni, Cr, and Mo were determined by optical emission spectroscopy. The content of organic carbon (C_{org}) was estimated by differential combustion.

MINERALOGY

Grains of vanadian–chromian garnet form either aggregates, up to 2 cm in diameter, or single subhedral to euhedral grains, up to 0.5 mm in diameter, in a tremolite-rich matrix (Fig. 3). The euhedral grains show {110} faces, exceptionally in combination with {211} forms (Fig. 4). They are emerald-green, with a vitreous luster. Weathered specimens are somewhat paler. In transmitted light, the grains are either isotropic, or rarely anomalously anisotropic, particularly those collected from the Rybníček adit. The index of refraction n and density D_x are 1.810(3) and 3.75 g/cm³, respectively. The unit-cell parameter corresponds closely to that of other samples of V-rich



FIG. 1. Map of Slovakia and location of area under study (solid rectangle).

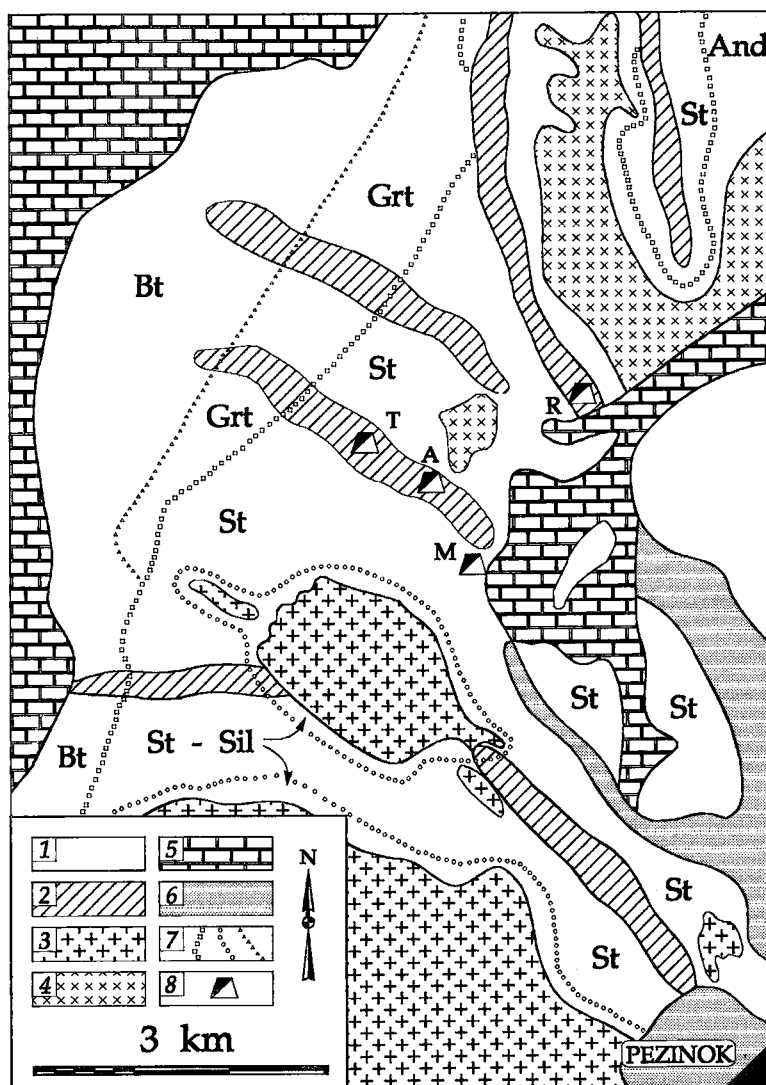


FIG. 2. Geological sketch of the Pezinok – Pernek crystalline complex, with metamorphic zones and locations of vanadian–chromian garnet occurrences (modified after Polák & Rak 1980, Korikovsky *et al.* 1984). Explanations: 1 biotite schist, paragneiss and amphibolite, 2 zones of black shale and actinolite–tremolite schist, 3 granite of the Bratislava Massif, 4 granodiorite of the Modra Massif, 5 Mesozoic limestone, dolomite and quartzite, 6 Tertiary and Quaternary sediments, 7 boundaries of regional and periplutonic metamorphic zones (Bt biotite, Grt garnet, St staurolite – chlorite, St–Sil staurolite – sillimanite, And andalusite – biotite – cordierite zones), 8 occurrences of V,Cr silicates (M: the Michal adit, A: the Augustín adit, T: the Trojárová adit, R: the Rybníček adit).

garnet and synthetic uvarovite (Table 1).

Representative results of electron-microprobe analyses of the garnet are listed in Table 2 and plotted in terms of the Al^{3+} , V^{3+} and Cr^{3+} cations in Figure 5, together with available compositional data on occur-

rences of V-rich garnet from the literature. The highest Al and Cr contents have been estimated in the garnet from the Rybníček adit (Table 2, anal. 1–3), where the levels of the goldmanite component are at a minimum. Similarly, the maximum concentrations of V in garnet,

from the Michal and Augustín adits, are accompanied by a concomitant decrease of Cr and especially Al, to the minimum recorded values (Table 2, anal. 7–9).

Optically and chemically zoned crystals of garnet have been observed in the Augustín adit. Lighter-colored rims are depleted in V and Al and enriched in Cr (Table 2, anal. 12) in comparison with dark green centers (Table 2, anal. 11).

A tentative infrared-absorption analysis of garnet from the Rybníček adit, performed and interpreted at the University of Vienna, has not corroborated the presence of substantial amounts of structurally bound OH^- , as indicated by the absence of the band near 3600 cm^{-1} in the spectrum. Consequently, the H_2O^+ content is not considered significant.

Vanadian–chromian hydromica occurs only in the Rybníček adit in the form of flaky dark green crystals 0.02–0.3 mm in diameter. Apart from exhibiting up to 9.2% V_2O_3 and 7.2% Cr_2O_3 , the hydromica (Table 3, anal. 1–3) is characterized by a high water content (as indicated by low oxide totals in the electron-microprobe analyses) and high deficiencies in K. The hydromica from other two localities (Table 3, anal. 4,5) shows Cr_2O_3 concentrations one order of magnitude lower than those reported from the Rybníček adit, and their V_2O_3 contents are near to or even below the detection limit by EMPA. This V,Cr-poor hydromica is usually associated in the Trojárová adit with clusters of green chlorite, up to 5 mm in size, arranged along the schistosity. Electron-microprobe analyses have

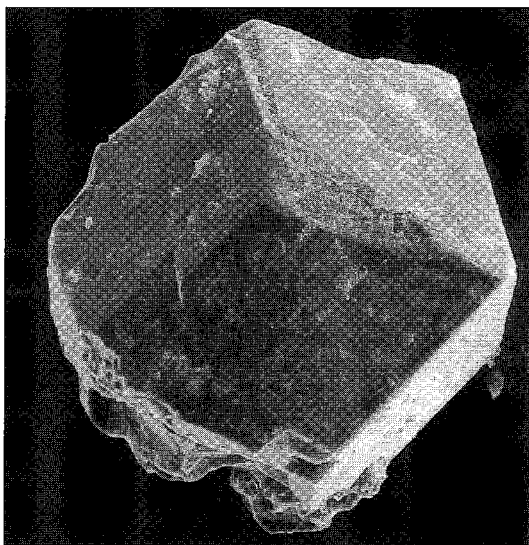


FIG. 4. Euhedral crystal of vanadian–chromian garnet from the Rybníček adit. (SEM photo, crystal diameter 0.33 mm).

also revealed detectable, although low amounts of V and Cr in the chlorite (anal. 6). In addition, relatively high concentrations of V and Cr concentrations have been locally determined in porphyroblasts of rock-forming tremolite (Table 3, anal. 7–8).

DISCUSSION AND CONCLUSIONS

Occurrences of V-rich garnet reported from various localities throughout the world invariably involve rocks enriched in organic carbon and thermally modified owing to emplacement of magmatic bodies (Moench & Meyrowitz 1964, Shepel & Karpenko 1970, Filippovskaya *et al.* 1973, Benkerrou & Fonteilles 1989, among others). Such garnet could thus be considered as indicative of the protoliths with high concentrations of Ca, V and organic carbon, and relatively undersaturated with respect to Al.

Occurrences of vanadian–chromian silicates in the Pezinok – Pernek crystalline complex also are intimately connected with metamorphic suites containing various proportions of pelitic and volcanoclastic components. Previous geochemical studies conducted in this region have confirmed the high concentrations of V, Cr, Mo and Ni in these sequences (Cambel & Khun 1983, Oružinský *et al.* 1990). Additional analytical data have also shown that the highest concentrations of V are indeed related to maximum contents of organic carbon in typical black shales. On the contrary, chromium is preferably bound in silicates from mafic volcanic rocks and their pyroclastic equivalents, all with a lower content of organic carbon (Table 4).

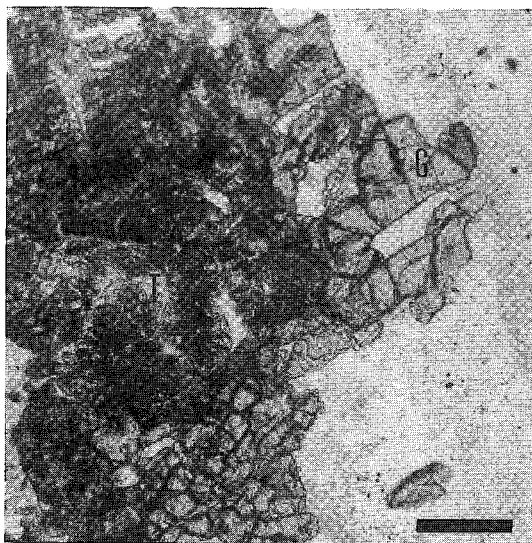


FIG. 3. Optically anisotropic vanadian–chromian garnet (G) coexisting with tremolite (T) from the Rybníček adit (transmitted light, plane-polarized light). Scale bar represents 0.1 mm.

TABLE 1. UNIT-CELL PARAMETER OF V-Cr-BEARING GARNET

	<i>a</i> (Å)	Locality	Reference
V-Cr garnet	11.969(4)*	Rybníček	this study
V-Cr garnet	11.969(1)	Rybníček	this study
V-Cr garnet	12.000(6)	Rybníček	this study
Goldmanite	12.011	Laguna, New Mexico	Moench & Meyrowitz (1964)
V-rich garnet	12.02	Ishimskaya Luka, Kazakhstan	Filippovskaya <i>et al.</i> (1973)
Uvarovite	11.99	synthetic	JCPDS

*Standard deviation in parentheses.

During thermal metamorphism caused by the intrusion of Hercynian granitic bodies, vanadian-chromian garnet and tremolite have crystallized in mixed V,Cr-rich mafic pyroclastic rocks characterized by a substantial admixture of the carbonaceous organic matter at temperatures of approximately 500°C, as estimated for the staurolite-chlorite metamorphic zone in this

region by Korikovsky *et al.* (1984). The derived temperature of formation is in good agreement with the temperature of 530°C at which end-member goldmanite, $\text{Ca}_3\text{V}_2(\text{SiO}_4)_3$, has been synthesized (Strens 1965). V,Cr-rich hydromica and chlorite have probably originated at somewhat lower temperatures, during retrograde or late hydrothermal alteration.

TABLE 2. REPRESENTATIVE COMPOSITION OF VANADIAN-CHROMIAN GARNET

	1	2	3	4	5	6	7	8	9	10	11	12
	Rybníček adit			Michal adit					Augustín adit			
SiO ₂	36.53	36.13	36.72	35.34	36.91	36.16	35.78	35.57	35.27	34.90	35.90	35.74
TiO ₂	0.19	0.00	0.18	0.14	0.18	0.00	0.00	0.05	0.21	0.00	0.42	0.19
Al ₂ O ₃	7.63	4.98	6.18	5.15	3.41	2.46	0.45	2.34	4.97	2.38	5.75	4.46
Cr ₂ O ₃	10.08	10.90	9.52	6.61	7.87	6.81	7.54	6.30	5.47	6.67	6.58	9.40
V ₂ O ₃	9.55	14.02	13.46	16.84	16.25	20.25	22.11	21.09	16.48	21.02	16.07	14.02
FeO	0.26	0.18	0.21	0.37	0.27	0.17	0.17	0.41	0.44	0.08	0.23	0.28
MnO	2.07	1.46	1.54	1.27	1.00	0.96	0.80	1.23	1.46	1.24	1.45	1.20
MgO	0.18	0.08	0.19	0.03	0.04	0.05	0.03	0.07	0.07	0.04	0.15	0.07
CaO	32.93	33.48	33.31	33.26	33.19	33.10	32.46	33.15	33.71	33.51	33.71	33.87
Na ₂ O	0.00	0.07	0.00	0.00	0.08	0.00	0.00	0.09	0.00	0.00	0.09	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01
Σ (wt.%)	99.45	101.34	101.35	99.06	99.26	99.98	99.38	100.35	98.11	99.89	100.39	99.30
Si*	2.96	2.91	2.94	2.90	3.04	2.97	2.99	2.92	2.92	2.87	2.91	2.93
Al ^{IV}	0.03	0.08	0.05	0.09	0.00	0.02	0.00	0.07	0.07	0.12	0.08	0.06
Al ^{VI}	0.69	0.38	0.52	0.40	0.33	0.21	0.03	0.15	0.40	0.11	0.46	0.37
Cr	0.64	0.69	0.60	0.43	0.51	0.44	0.49	0.41	0.35	0.43	0.42	0.61
V	0.62	0.90	0.86	1.11	1.07	1.33	1.48	1.39	1.09	1.39	1.04	0.92
Fe ³⁺	0.01	0.01	0.00	0.02	0.01	0.00	0.00	0.02	0.03	0.00	0.01	0.01
Fe ²⁺	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Mn	0.14	0.09	0.10	0.08	0.07	0.06	0.05	0.08	0.10	0.08	0.10	0.08
Mg	0.02	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Ca	2.86	2.89	2.86	2.93	2.93	2.91	2.90	2.92	2.99	2.96	2.93	2.98
Goldm	26.92	40.98	39.61	51.96	53.77	64.38	71.20	65.42	53.23	65.11	49.29	44.49
Uva	33.25	34.07	30.18	21.36	26.97	22.18	24.70	20.20	18.68	21.35	21.36	31.44
Gros	33.07	20.57	25.29	22.20	15.52	10.36	1.51	9.80	22.48	10.04	24.45	19.77
Yam	5.30	3.53	3.78	3.19	2.67	2.43	2.04	3.05	3.88	3.07	3.65	3.11
Alm	0.00	0.00	0.36	0.00	0.00	0.24	0.39	0.00	0.00	0.00	0.00	0.00
Pyr	0.60	0.27	0.61	0.10	0.15	0.17	0.12	0.25	0.24	0.16	0.50	0.24
Andr	0.82	0.54	0.14	1.16	0.90	0.20	0.00	1.26	1.47	0.25	0.71	0.91

*Normalized on the basis of 8 oxygen atoms

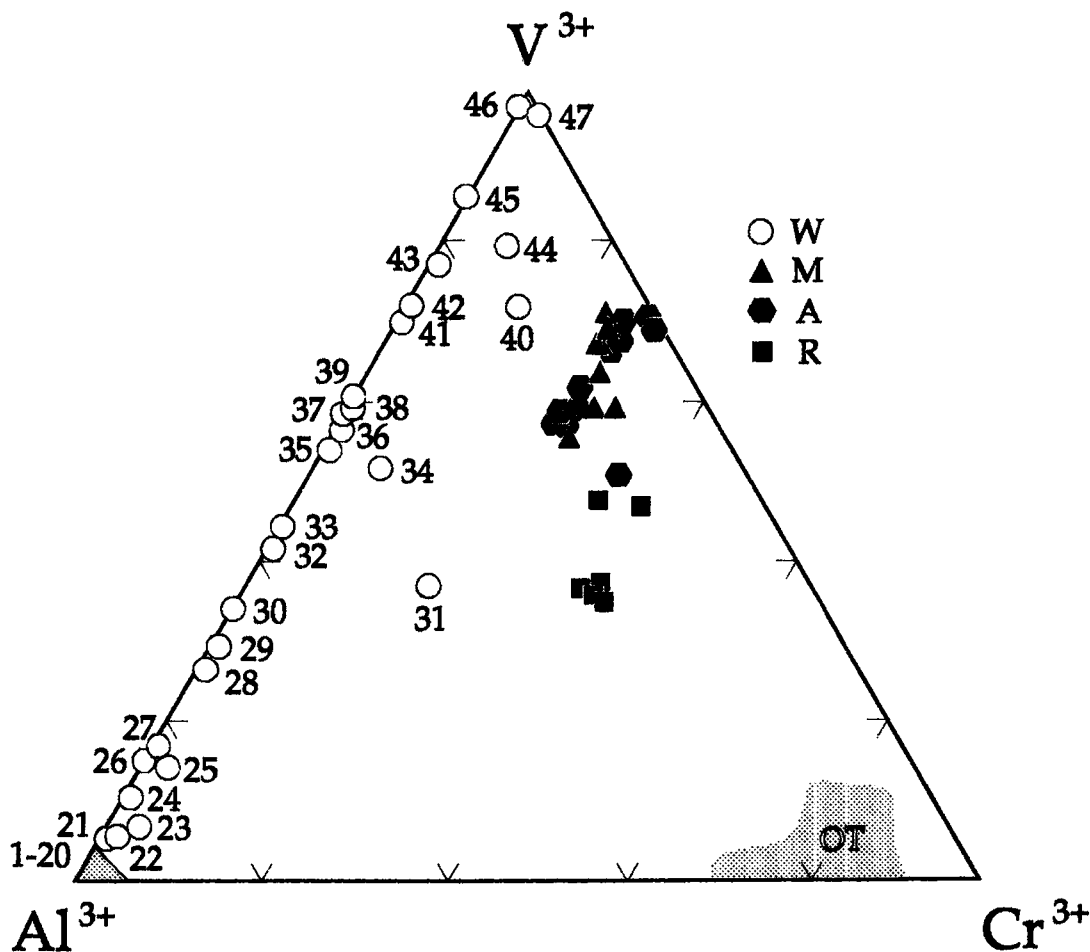


FIG. 5. Projection of chemical compositions of garnet in terms of V, Cr and Al (atomic proportions). Explanations: W world localities, A the Augustín adit, M the Michal adit, R the Rybníček adit. Localities: 1, 7, 14, 15, 23: Uмба Valley, Tanzania (Schmetzer & Ottemann 1979); 2–6, 12, 16, 17, 19: Cazadero, California (Lee *et al.* 1963); 8, 25: Tanzania (Schwitzer 1974); 9, 26–28, 32, 36–38, 41: Coat-an-Noz, France (Benkerrou & Fontelles 1989); 10, 20, 21: Kenya (Schwitzer 1974); 11: Merelani, Tanzania (Schmetzer & Ottemann 1979); 13, 22: Ratnapura, Sri Lanka (Schmetzer & Ottemann 1979); 18: Tsavo, Kenya (Schmetzer & Ottemann 1979); 24: Lualenyi, Kenya (Gübelin & Weibel 1975); 29, 31: Orton, Russia (Karev 1974); 33, 35: Yilgarn Block, Australia (Mueller & Delor 1991); 34, 39: Ishimskaya Luka, Kazakhstan (Filippovskaya *et al.* 1973); 40: Laguna, New Mexico (Moench & Meyrowitz 1964); 42: Mramornoye, Russia (Shepel & Karpenko 1970); 44: Struhadlo, Czech Republic (Litochleb *et al.* 1985); 45: Yamatō, Japan (Momoi 1964); 46: China (Wang *et al.* 1974); 47: North Sea (Hallsworth *et al.* 1992); OT: field of chromian garnet from Outokumpu, Finland (von Knorring *et al.* 1986).

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TABLE 3. REPRESENTATIVE COMPOSITION OF VANADIAN-CHROMIAN SILICATES FROM THE PEZINOK-PERNEK CRYSTALLINE COMPLEX

	1	2	3	4	5	6	7	8
	Hydromica				Chlorite		Amphibole	
SiO ₂	47.10	47.07	47.33	54.08	51.02	27.44	56.81	52.80
TiO ₂	0.00	0.03	0.06	0.18	0.09	0.00	0.17	0.00
Al ₂ O ₃	23.90	24.19	24.23	31.58	28.67	22.88	2.26	5.79
Cr ₂ O ₃	7.18	6.58	5.78	0.51	0.68	0.28	0.21	0.75
V ₂ O ₃	9.16	6.91	8.24	0.00	0.37	0.10	1.59	2.51
FeO	0.15	0.26	0.21	0.41	0.43	15.80	0.31	0.57
MnO	0.16	0.00	0.06	0.00	0.02	0.00	0.04	0.24
MgO	1.98	2.07	2.97	1.74	2.81	19.55	22.45	20.65
CaO	0.01	0.00	0.00	0.06	0.01	0.07	13.74	12.67
Na ₂ O	0.47	0.38	0.42	0.46	0.32	0.00	1.14	2.17
K ₂ O	4.13	5.72	4.13	4.16	9.89	0.03	0.03	0.07
Σ (wt.%)	94.23	93.21	93.44	93.18	94.31	86.15	98.75	98.22
Si	3.19*	3.22*	3.21*	2.38*	3.39*	2.77 ⁺	7.70 ^o	7.27 ^o
Al ^{IV}	0.81	0.78	0.79	1.62	0.61	1.23	0.30	0.73
Al ^{VI}	1.09	1.12	1.11	2.07	1.63	1.50	0.06	0.21
Cr	0.39	0.36	0.31	0.04	0.04	0.02	0.02	0.08
V	0.50	0.38	0.45	0.00	0.02	0.01	0.17	0.28
Fe ²⁺	0.01	0.02	0.01	0.03	0.02	1.34	0.04	0.07
Mn	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Mg	0.20	0.21	0.30	0.26	0.28	2.95	4.53	4.24
Ca	0.00	0.00	0.00	0.01	0.00	0.01	1.99	1.87
Na	0.06	0.05	0.06	0.09	0.04	0.00	0.30	0.58
K	0.36	0.50	0.36	0.53	0.84	0.00	0.01	0.01

* Normalized on the basis of 11 oxygen atoms

⁺ Normalized on the basis of 14 oxygen atoms^o Normalized on the basis of 23 oxygen atoms

TABLE 4. TRACE ELEMENTS AND ORGANIC CARBON CONTENT IN METAMORPHIC ROCKS FROM THE TROJÁROVÁ ADIT

Element	N	Average	Range
Black shales			
V (ppm)	16	1114	250-3600
Cr	16	127	48-224
Ni	16	650	257-1040
Mo	16	133	21-420
C _{org} (wt.%)	14	4.64	0.58-7.82
Actinolite-tremolite schists, amphibolites			
V (ppm)	14	312	214-440
Cr	14	268	166-525
Ni	14	69	23-316
Mo	14	<10	-
C _{org} (wt.%)	14	<0.05	-

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