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VANADIAN–CHROMIAN TOURMALINE AND VANADIAN MUSCOVITE IN CONTACT-METAMORPHOSED CARBONACEOUS ROCKS, PRIMORYE, RUSSIA

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ABSTRACT

Vanadian–chromian tourmaline (as much as 4.06 wt.% V_2O_3 and 2.38% Cr_2O_3) and vanadian muscovite (as much as 2.73% V_2O_3) occur in contact-metamorphosed carbonaceous metasediments of the Pribrezhnaya anticlinal zone in Primorye, Russia. Crystals are compositionally zoned, showing depletion in V and Cr, and enrichment in Al, Mg and Fe, from core to rim. Zoning is attributed to progressive decrease of V and Cr contents in the host rock during the course of crystal growth. Cr and V are incorporated according to the schemes: $Cr^{3+} \leftrightarrow Al^{3+}$ and $V^{3+} \leftrightarrow (Mg^{2+},Fe^{2+},Mn^{2+})$. The charge increase that results from the latter exchange is considered to be compensated by the concomitant substitution of ^{IV}Al for Si and by the appearance of vacancies in the *X* site. The associated vanadian muscovite contains minor amounts of Mg, Fe, Ti and Na. An empirical formula calculated from results of an electron-microprobe analysis is $(K_{1.94}Na_{0.09})_{\Sigma 2.03}(Al_{3.34}V_{0.29}Mg_{0.26}Ti_{0.05}Fe_{0.04})_{\Sigma 3.98}(Si_{6.27}Al_{1.73})_{\Sigma 8.00}O_{22}(OH)_2$. Both minerals are products of contact metamorphism of V–Cr-bearing carbonaceous rocks.

Keywords: vanadian–chromian tourmaline, vanadian $2M_1$ muscovite, electron-microprobe analysis, carbonaceous rocks, contact metamorphism, Primorye, Russia.

SOMMAIRE

Nous avons trouvé une tourmaline vanadifère et chromifère (jusqu'à 4.06% de V_2O_3 et 2.38% de Cr_2O_3, en poids) et une muscovite vanadifère (jusqu'à 2.73% V_2O_3) dans des métasédiments carbonacés d'une auréole de contact dans la zone anticlinale de Primorye, en Russie. Les cristaux montrent une zonation chimique, avec appauvrissement progressif en V et Cr, et enrichissement en Al, Mg et Fe, du coeur vers la bordure. Nous attribuons cette zonation à la pénurie progressive en V et Cr dans la roche hôte pendant la croissance des cristaux. Le Cr et le V seraient incorporés dans la structure de la tourmaline selon les couples $Cr^{3+} \leftrightarrow Al^{3+}$ et $V^{3+} \leftrightarrow (Mg^{2+}, Fe^{2+}, Mn^{2+})$. L'augmentation des charges positives impliquée par le deuxième couple serait compensée par le remplacement de Si par ^{IV}Al et par la présence de lacunes dans la position *X*. La muscovite vanadifère associée contient de faibles concentrations de Mg, Fe, Ti et Na. Une formule empirique, calculée à partir de données obtenues à la microsonde électronique, serait $(K_{1.94}Na_{0.09})_{\Sigma 2.03}(Al_{3.34}V_{0.29}Mg_{0.26}Ti_{0.05}Fe_{0.04})_{\Sigma 3.98}(Si_{6.27}Al_{1.73})_{\Sigma 8.00}O_{22}(OH)_2$. Les deux minéraux sont le produit du métamorphisme de contact de roches carbonacées porteuses de chrome et de vanadium.

(Traduit par la Rédaction)

Mots-clés: tourmaline vanadifère et chromifère, muscovite $2M_1$ vanadifère, données à la microsonde électronique, roches carbonacées, métamorphisme de contact, Primorye, Russie.

INTRODUCTION

Only a few examples of tourmaline with significant contents of vanadium (>1.0 wt.% V_2O_3) have been recorded in the literature. Badalov (1951) reported the occurrence of V-rich tourmaline (5.76% V_2O_3) in black quartz–graphite hornfels in contact with a quartz vein from Uzbekistan. Vanadiferous tourmaline (1.5% V_2O_3) from Tanga Province, Tanzania, was described by Basset (1956); it occurs in gneiss associated with dolomite and ultrabasic rocks as well as granulite-facies metasediments. Snetsinger (1966) described a Cr-bearing (0.89% Cr_2O_3) and exceedingly V-rich (7.45% V_2O_3, 0.58% V_2O_4) tourmaline from a quartz–graphite schist, Mariposa County, California. Electron-microprobe analysis of an additional specimen from this locality gave 1.48% Cr_2O_3 and 8.52% V_2O_3 (Foit & Rosenberg 1979). Schmetzer *et al.* (1979) gave chemical data on Cr-bearing, V-rich tourmaline (0.55% Cr_2O_3, 4.03% V_2O_3) from the Kwal district, Kenya. Nickel & Grey (1986) reported the occurrence of a vanadian schorl (2.7% V_2O_3) within the gold-bearing lodes from Kalgoorlie, Western Australia. Pan & Fleet (1992) have recently noted that tourmaline from the Hemlo gold deposit, Ontario, contains 1.48% V_2O_3. High-chromium tourmaline found in Finland (9.6% Cr_2O_3) (Peltola *et al.* 1968) and Swat, western Pakistan (Alpurai: 8.5% Cr_2O_3, Mingora: 8.78% Cr_2O_3) (Jan *et al.* 1972, Hammarstrom

1989) contain up to 1.0% V_2O_3. Published data on chromian dravite and chromian varieties of tourmaline from world-wide locations have been compiled mainly by Dunn (1977), Nuber & Schmetzer (1979), Rumyantseva (1983) and King & Kerrich (1989).

Relatively few examples of vanadiferous $2M_1$ muscovite have been reported in the literature. A V-bearing, Ba-rich muscovite (1.48% V_2O_3, 1.95% V_2O_4, 2.39% BaO), coexisting with the V–Cr-bearing tourmaline mentioned above, was reported by Snetsinger (1966). V–Cr-bearing muscovite (5.09% V_2O_3, 0.8% Cr_2O_3) from the Janggun mine area, Republic of Korea, was described by Imai *et al.* (1980). It occurs in close association with quartz, vanadian tourmaline (about 3% V_2O_3) and graphite. These minerals are regarded by the authors as being the products of regional metamorphism of orthoquartzite. Recent investigations include the description of Cr–V-bearing micas from southern Karelia, Russia, by Rumyantseva *et al.* (1984). Amongst the other micas composing metasomatic veins, nests and solid masses in dolomites, slates and diabases, muscovite (3.0% Cr_2O_3, 10.4% V_2O_3) is present.

This paper documents the occurrence of chromian V-rich tourmaline and vanadiferous muscovite found in contact-metamorphosed carbonaceous rocks of the Pribrezhnaya anticlinal zone in Primorye, in the Far-Eastern region of Russia.

GEOLOGICAL SETTING

Carbonaceous rocks are a minor but integral part of the basement of the East Sikhote – Alin volcanogenic belt. The basement rocks, exposed between two Late Cretaceous granitic massifs, comprise Late Paleozoic, Triassic and Jurassic marine deposits such as arkosic sandstones, siltstones, cherts, siliceous shales and reef limestones (Fig. 1). Amongst these deposits occur horizons of basalt, metamorphosed and recrystallized manganese ores, iron ores and Mn- and Fe-rich calc-silicate rocks.

THE CARBONACEOUS ROCKS

Carbonaceous rocks constitute a bed about 2 m thick in Triassic cherts. They were originally siltstones and pelites (Table 1) rich in organic matter before contact metamorphism due to the intrusion of granitic magma.

Under the polarizing microscope, the low-metamorphic-grade carbonaceous ~~rocks~~ display a wavy texture, which is most distinctly reflected in the arrangement of the carbonaceous material. Rare fragments of feldspar and cement were variously replaced by muscovite. Segregations of rutile and newly formed albite and biotite are common. Xenotime and monazite also occur. The carbonaceous matter is present in cement in a finely dispersed state and as irregular fragments (phytoclasts?) up to 0.04 mm across.

TABLE 1. CARBON CONTENT* OF CARBONACEOUS ROCKS

Sample	Rock type	$C_{organic}$	$C_{carbonate}$
SH-8634	Muscovite-andalusite-cordierite slate	3.13 wt.%	0 wt.%
SH-8648	Siltstone	0.80	0.04
SH-8679A	Siltstone	2.90	0
SH-86B/N	Siltstone	4.60	0

* Determined by gasometric analysis following the procedure indicated by Kolpack & Bell (1968), on the apparatus described by Kitaev & Likht (1971). Analyst: L.Yu. Kurbatova.

More intensely metamorphosed carbonaceous rocks are represented by muscovite – andalusite – cordierite slates. They consist of cordierite and andalusite porphyroblasts extensively replaced by muscovite and a matrix of clayey and carbonaceous particles and grains of quartz; rare porphyroblasts of muscovite also are present. The carbonaceous substance was examined under a TESLA BS–540 transmission electron microscope at 120 kV. An electron-diffraction pattern obtained proved to be identical with that of graphite.

Quantitative spectrographic analyses of carbonaceous rocks revealed a wide spectrum of trace elements: V (200 to 500 ppm), Ba (≤ 600), Sr (≤ 300), Zn and Zr (≤ 200), Cr (60 to 160), Cu, Pb and Ni (≤ 100), Mo (≤ 80), Co (≤ 46), Ga (≤ 40), Y and La (≤ 30), Nb(≤ 20), Ag (≤ 9) and Sn (≤ 5). Another feature is the high content of Ti, which exceeds 1 wt.% TiO_2. The samples were analyzed by a standard emission spectrographic technique (Rusanov 1978) using a DFS–8 apparatus.

V–Cr-BEARING TOURMALINE

The V–Cr-bearing tourmaline is found in the low-metamorphic-grade carbonaceous siltstone. The mineral forms minute subhedral to euhedral grains (Fig. 2), which are sparsely scattered throughout the rock cement and do not appear to exceed 2 vol.%. The largest crystals (up to 0.4 mm in length) are confined mainly to loci of graphite masses occurring in the most intensely recrystallized matrix. In transmitted light, the tourmaline is greenish brown, with N_ε = pale green and N_ω = brown. It was not possible to isolate optically uniform fragments of the mineral owing to the minute size of the grains. Only approximate indices of refraction and cell parameters were therefore obtained, using the crystals analyzed by electron microprobe. The indices of refraction ε and ω of the tourmaline are 1.633(2) and 1.670(2), respectively. X-ray powder-diffraction studies were done in a 57.3-mm-diameter Debye–Scherrer camera using Fe$K\alpha,\beta$ radiation. Indexing of the powder pattern and computation of the cell parameters were done using the CRYST program (Nakhmanson & Antoshulsky 1985).

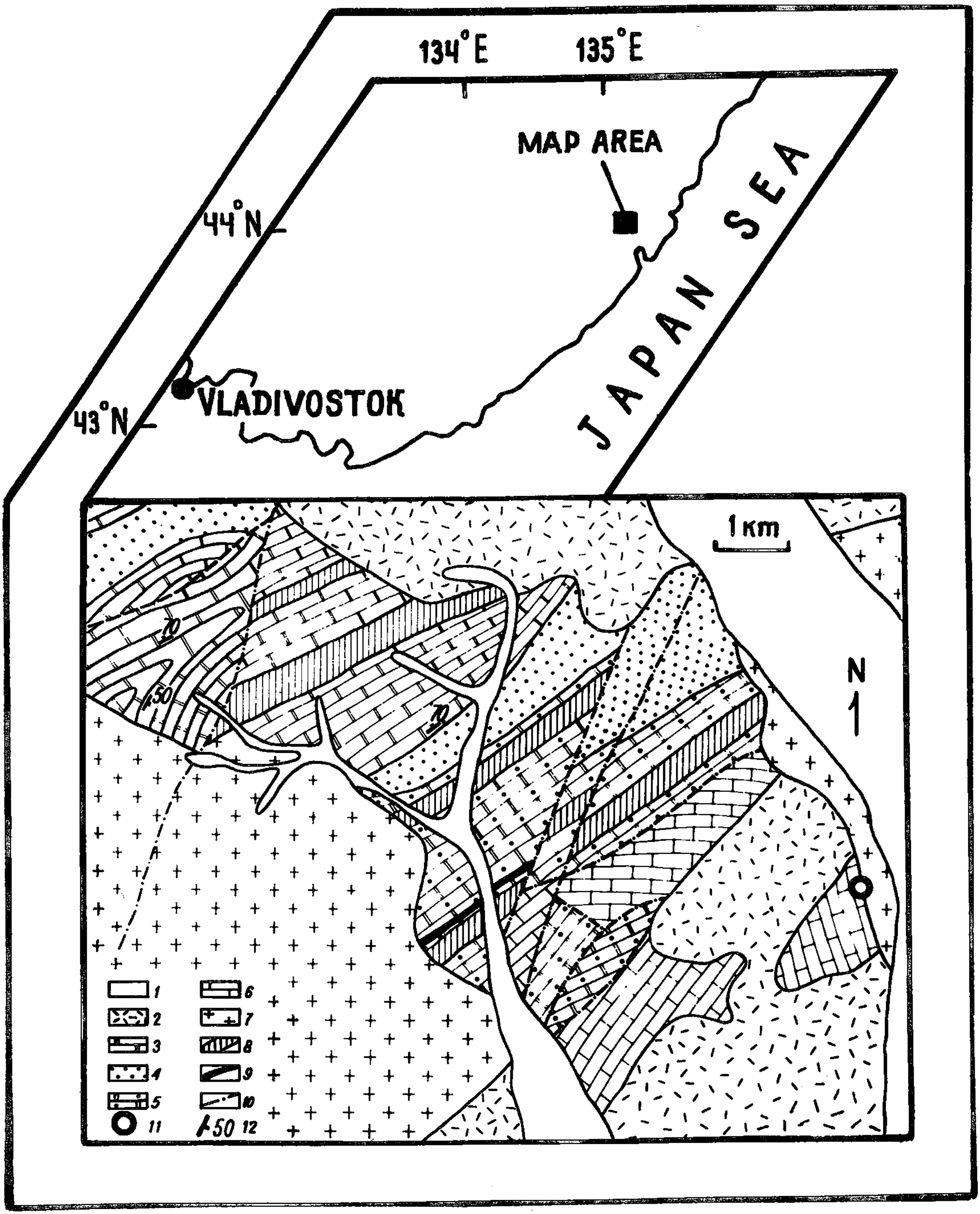


FIG. 1. Location and geological map of the study area, situated within the Primorye territory, Russia. Legend: 1 Quaternary sediments, 2 volcanogenic formations of the East Sikhote – Alin volcanogenic belt, 3 Jurassic terrigenous siliceous deposits, 4, 5 Triassic sandstones (4) and terrigenous siliceous deposits (5), 6 Carboniferous to Permian terrigenous siliceous deposits, 7 Late Cretaceous granites, 8 beds of essentially siliceous deposits containing layers and stockwork-like zones of iron–manganese mineralization, 9 carbonaceous siltstones, 10 faults, 11 Belogorskoye field of magnetite skarns, 12 strike and dip of bedding.

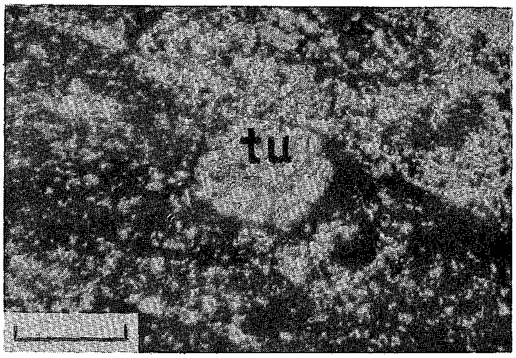
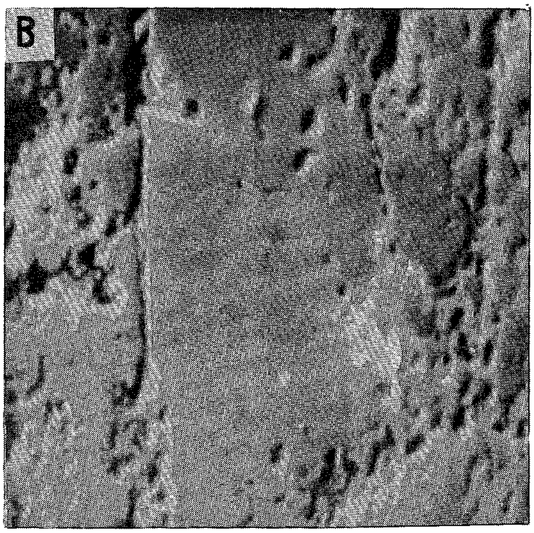
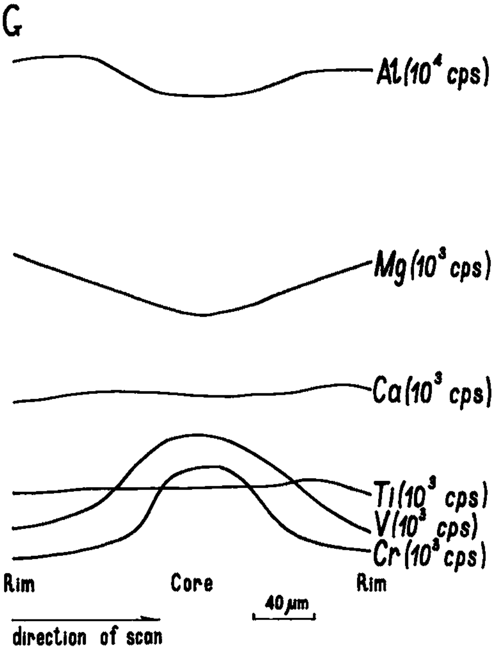


FIG. 2. Subhedral grain of tourmaline (tu) in carbonaceous siltstone. Scale bar is 40 μm. Plane-polarized light. Specimen SH–8679.

Cell dimensions of the tourmaline are: *a* 15.915(2), and *c* 7.187(3) Å.

Owing to the limited amount of material available, partial analyses were carried out for two individual grains of tourmaline in a polished section with a scanning electron microscope equipped with energy-dispersion spectrometers (Figs. 3A, B). Analytical data for the crystal (Fig. 3A) free of impurities and only slightly fractured are given in Table 2. Analyses were performed with a JXA–5A (JEOL) electron microprobe not modified for the detection of low-atomic-number elements (*Z* less than 11); concentrations of B and F were therefore not determined. The tourmaline is a chromian and V-rich variety of dravite. In other constituents, it appears to resemble normal dravite closely. The composition of the mineral is heterogeneous. Figure 4 shows





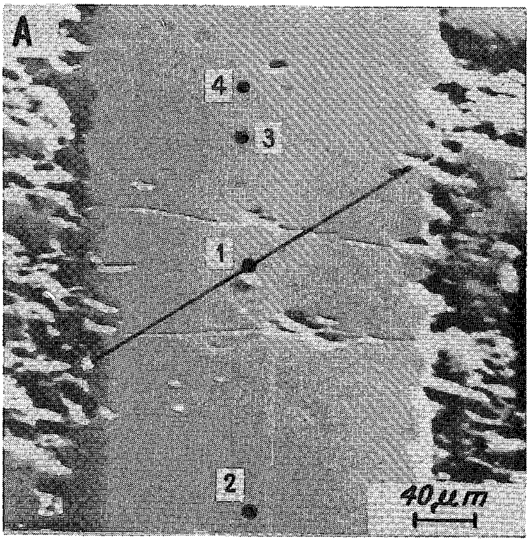
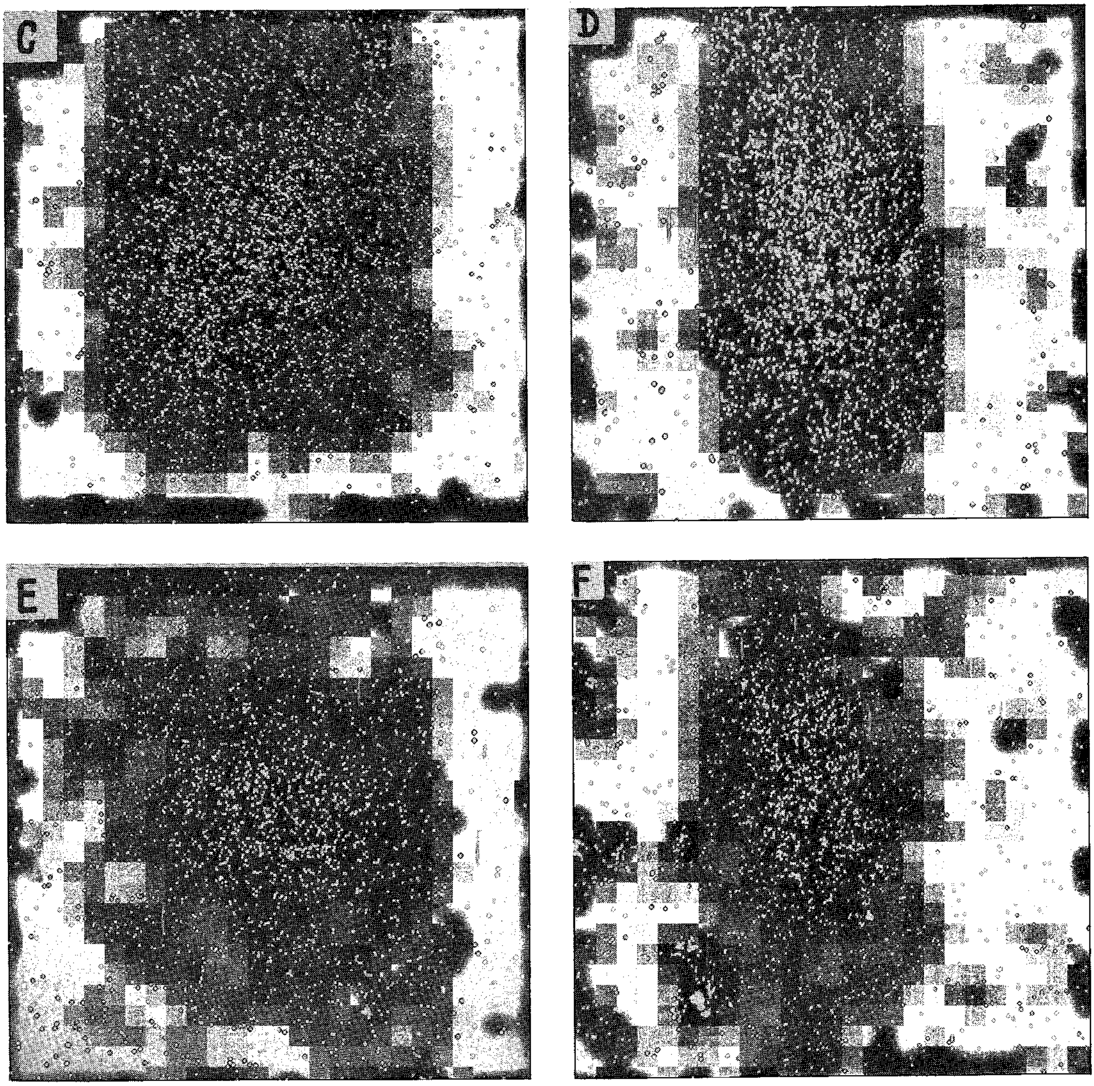


FIG. 3. Photomicrographs of two tourmaline crystals, I (A,C,E) and II (B,D,F). Specimen SH–8679. A and B. Secondary electron images. Crystals are surrounded by rock matrix. Numbers at dots (1–4) on A refer to spots analyzed by electron probe and can be used to identify specific compositions in Table 2. C and D. V*K*α X-ray images. E and F. Cr*K*α X-ray images. Scale bar is 40 μm; it applies to all photomicrographs. Note: white stains on F (left) are due to contamination. G. Simplified line-scan profiles showing the variation in intensities of characteristic *K*α X rays along the line drawn on A (cps: counts per second).



that an increase in V content is acccompanied by an increase in Cr content and decreases in Al and total Mg, Fe and Mn contents. The muscovite that coexists with the tourmaline contains no Cr or V (Table 2).

X-ray emission images V*K*α (Figs. 3C, D) and Cr*K*α (Figs. 3E, F) and scanning profiles for Al*K*α, Mg*K*α, V*K*α and Cr*K*α (Fig. 3G) illustrate the compositional zonation of the tourmaline crystals. The zonal distribution of elements is metamorphic in origin; there is a gradual change in composition from the core to the rim (Fig. 3G). The core is enriched in V and Cr (Figs. 3C–G) and depleted in Al and Mg (Fig. 3G). The contents of Al and Cr do not vary appreciably in the core and rim, but compositional gradients are steep between the two zones. Relatively steady variations from core to rim are observed for Mg and V. Such peculiarities in the behavior of Al and Cr on the one hand and of Mg and V on the other can be explained by isomorphous replacement of Al by Cr as well as of Mg by V, and can provide some indication of the preference of these element couples for occupancy of different octahedral sites. The distribution of Ca and Ti within the crystal is uniform (Fig. 3G).

In order to determine the site of Ca in the calculation of the structural formula of tourmaline (Table 3), results of about 120 chemical analyses were recalculated to an anhydrous formula containing 24.5 atoms of oxygen. The analytical data were selected from the compilations of Dunn (1977), Dolomanova *et al.* (1978), Kuzmin *et al.* (1979) and Kornetova (1981).

TABLE 2. CHEMICAL COMPOSITION OF TOURMALINE AND MUSCOVITE FROM PRIMORYE, RUSSIA

No. of spots*	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2 wt.%	35.50	37.28	36.33	36.04	35.79	36.11	35.88	35.67	36.09	35.86	45.61	46.98
TiO_2	0.61	0.92	0.59	0.51	0.65	0.60	0.61	0.70	0.54	0.23	0.40	0.47
Al_2O_3	30.59	32.52	32.24	32.41	31.89	32.41	30.89	30.99	32.57	30.74	33.32	32.24
Cr_2O_3	2.38	0.00	0.65	0.59	1.07	0.86	1.09	2.11	0.69	1.87	0.00	0.00
V_2O_3	4.06	0.00	2.67	1.62	2.37	1.77	2.51	3.81	1.84	4.00	0.00	2.73
FeO**	1.41	3.22	1.61	1.55	1.56	1.51	1.52	1.42	1.57	1.48	1.18	0.34
MnO	0.07	0.10	0.06	0.04	0.04	0.06	0.06	0.08	0.06	0.00	0.00	0.00
MgO	8.12	9.02	8.07	8.87	8.99	8.87	8.67	8.09	9.09	8.36	3.73	1.29
CaO	1.29	1.16	0.84	0.97	1.46	1.37	1.36	1.31	1.34	1.27	0.00	0.00
Na_2O	2.07	2.31	2.15	2.29	1.94	2.07	2.00	2.06	2.09	1.93	0.00	0.34
K_2O	0.05	0.02	0.09	0.07	0.08	0.09	0.08	0.10	0.08	0.06	10.42	11.38
anhydrous total	86.15	86.55	85.30	84.96	85.84	85.72	84.67	86.34	85.96	85.80	94.66	95.77

Determined by electron microprobe, model JXA-5A (JEOL). Accelerating voltage: 20 kV, specimen current: 4×10^{-8} A, beam diameter: 2 μm, measurement of X-ray intensities by fixed-time (10 s) method of counting. Standards used: sanidine (Ab_{30}) for K, Na, Al and Si, ilmenite for Ti, chromite for Cr, synthetic V_2O_5 for V, olivine (Fo_{77}) for Fe, rhodonite for Mn, diopside for Ca and Mg. Concentrations calculated and ZAF correction made using computer program of Afonin et al. (1971). Concentrations of B and F were not sought. * Arbitrary points chosen on the crystals: 1-10 tourmaline (SH-8679A), 11 and 12 muscovite (SH-8679A and SH-8634, respectively). ** All iron expressed as FeO.

A notable proportion (≈ 35%) of both the non-Ca-bearing tourmalines and the Ca-bearing ones shows full occupancy of the *Y* site. At the same time, we found that Ca occupancy of either *X* or *Y* positions is controlled by the sign (+/–) of the resulting excess charge (hereafter termed EXCH) arising from the incorporation of cations into tetrahedrally and octahedrally coordinated positions (Fig. 5). Compensation of positive EXCH leads to the appearance of vacancies in the *X* site, and Ca either does not substitute into tourmaline or occupies only the *Y* site. Negative EXCH is balanced by means of Ca accommodation in the *X* site.

A few separate data-points situated as a rule near the origin (Fig. 5) show Ca in the *X* site of tourmaline with positive EXCH values. This departure is most probably due to errors in the chemical analysis. The rest of the tourmaline compositions (≈ 65%) are, as a rule, distinguished by a high positive value of EXCH, and they have vacancies in both large cationic sites (*X* and *Y*). From the data in Figure 6, it follows that the replacement of divalent by trivalent cations is at first accompanied by an increase in the number of vacancies in the *X* site. When the number of vacancies reaches some upper limit that is presumably controlled by P–T conditions during growth, further compensation of EXCH leads to the appearance of cation deficiencies in the *Y* site. These deficiencies may explain the origin of vacancies according to the substitution $3R^{2+} \leftrightarrow 2R^{3+} + \square$. This scheme is in good agreement with the distribution of the different number of vacancies in the *X* site within the field defined by lines I and V (Fig. 6). However, if the compensation for EXCH takes place in accordance with the dehydroxylation-type of substitution proposed by Foit & Rosenberg (1977), then the deficiency of cations in the *Y* site may be a result of an error due to the normalization of the chemical data on the basis of 24.5 atoms of oxygen. In this case, the trends on Figure 6 will have nearly the same slope as those corresponding to the scheme $3R^{2+} \leftrightarrow 2R^{3+} + \square$. Thus, Figure 6 does not allow determination of the actual type of cation substitution but may be used for geothermobarometry and for classification of tourmaline-group minerals.

Structural formulae of the Cr–V-bearing tourmaline (Table 3) calculated on the basis of 24.5 atoms of oxygen, and with due regard for the above-stated considerations, imply a partial substitution of Si by Al. The presence of ^{IV}Al is confirmed by the distinct splitting of the infrared-absorption band (Fig. 7), located at 780 cm^{-1}, into two components at 783 and 764 cm^{-1} (Dolomanova *et al.* 1978). The infrared-absorption spectrum was obtained with a UR–20 spectrophotometer using a 300-mg KBr disk containing 1 mg of tourmaline.

Complete cationic occupancy of *Y* and *Z* sites means that the substitution of V for divalent cations as well as Cr for Al has taken place in a 1:1 ratio. The cationic composition of *Y* sites in tourmalines can be estimated from the infrared stretching bands located in the 3600–3400 cm^{-1} region and have been interpreted (Dolomanova *et al.* 1978, Gonzalez-Carreno *et al.* 1988) as being characteristic of OH interaction with $2Al^{3+}$ and 1 *Y* cation (Mg, Fe, Al, *etc.*).

In the IR absorption spectrum of the tourmaline examined (Fig. 7), the most intense component (3580 cm^{-1}) corresponds to Al–Al–Mg associations and is shifted toward higher frequencies relative to the analogous band in dravite (3568 cm^{-1}, according to Gonzalez-Carreno *et al.* 1988). The 3545 cm^{-1} band probably corresponds to Al–Al–V environments. The 3515 cm^{-1} has a weak intensity and a frequency similar to that of

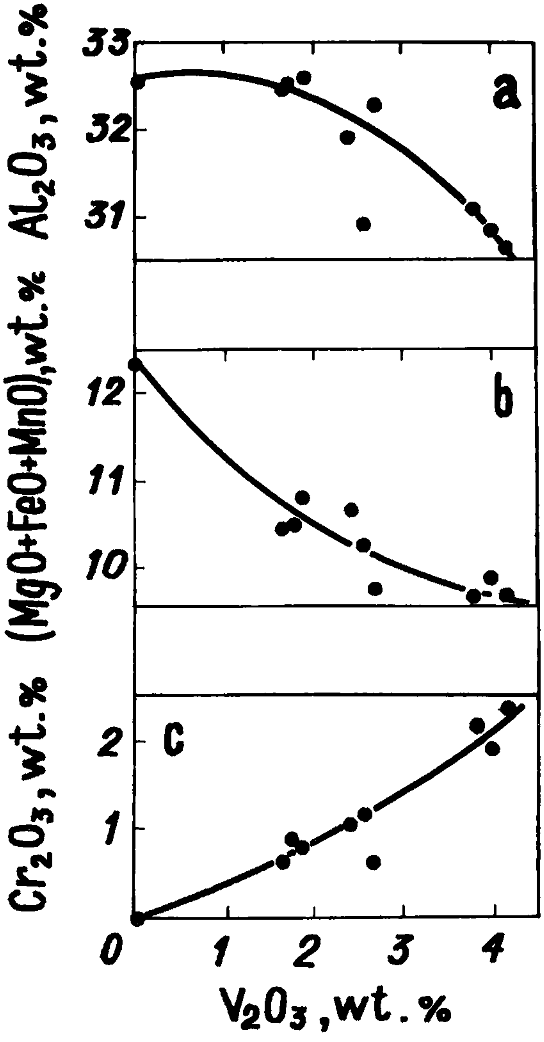


FIG. 4. Variation of V_2O_3 with a) Al_2O_3, b) MgO + FeO (total iron) + MnO, and c) Cr_2O_3 in tourmaline.

the band conforming to Al–Al–Al associations in the IR spectrum of dravite (3494 cm^{-1}, according to Gonzalez-Carreno *et al.* 1988). However, careful analysis of interrelations between IR and chemical data (normalized to 24.5 atoms of oxygen) compiled by Dolomanova *et al.* (1978) has shown that the 3494 cm^{-1} band is typical only of the samples containing more than 0.35 Al atom per formula unit in the *X* site. In view of this reasoning, one ought to assume that the amount of Al^{3+} in the *Y* site of the tourmaline analyzed is higher than that given in Table 3. Such an inference reflects the possible entry of a small amount of V^{3+} (Foit & Rosenberg 1979) as well as Mg^{2+} (Nuber & Schmetzer 1979) in the *Z* site.

V-BEARING MUSCOVITE

Vanadiferous muscovite is found in muscovite – andalusite – cordierite slate. It forms porphyroblasts (2 to 3 mm across) which, in transmitted light, are colorless to faintly greenish and are not pleochroic.

The muscovite is enriched in V and contains some Mg, Fe, Ti and Na (Table 2). Sericite in the rock matrix appears to contain V, but far less than in the muscovite porphyroblasts. Results of electron-microprobe analyses of the vanadiferous mica (Table 2) recalculated on the basis of 22 atoms of oxygen (Table 3) correspond to the structural formula: $(K_{1.94}Na_{0.09})_{\Sigma 2.03}(Al_{3.34}V_{0.29}Mg_{0.26}Ti_{0.05}Fe_{0.04})_{\Sigma 3.98}(Si_{6.27}Al_{1.73})_{\Sigma 8.00}O_{22}$. V as well as Mg and Fe have replaced ^{VI}Al. This 1:1 substitution is charge-balanced by replacement of Si by ^{IV}Al.

The muscovite was observed by transmission electron microscopy in the same specimen as graphite (see above). An electron-diffraction pattern reveals that the vanadiferous mica is of the $2M_1$ polytype modification, with cell parameters *a* 5.19(1), *b* 9.05(2), *c* 20.23(4) Å, β 95.0(5)°.

DISCUSSION

V–Cr-bearing tourmaline and V-bearing muscovite are products of contact metamorphism of carbonaceous rocks. Prerequisites for their appearance were the initial enrichment of sediments in Cr and V and a reducing environment due to a high content of organic carbon.

Concentrations of V, Cu, Ni, Mo, Ag and other elements are typical of natural organic compounds (Manskaya & Drozdova 1964). Originally, the major portion of these elements may have been connected with the organic matter of the carbonaceous rocks described. A substantial role of basic material in the detrital component seems to be a cause of high concentration of Cr and Ti in the rocks.

Chemical zoning in tourmaline crystals is apparently due to progressive depletion of V and Cr during the course of crystal growth.

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TABLE 3. STRUCTURAL FORMULAE OF TOURMALINE AND MUSCOVITE OBTAINED FROM THE CHEMICAL COMPOSITIONS GIVEN IN TABLE 2

	1	2	3	4	5	6	7	8	9	10	11	12
Si	5.78	5.96	5.89	5.86	5.80	5.83	5.89	5.79	5.81	5.84	6.12	6.27
^{IV}Al	0.13	0.04	0.11	0.14	0.20	0.17	0.11	0.21	0.19	0.16	1.88	1.73
	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	8.00	8.00
^{VI}Al	5.65	6.00	5.91	5.92	5.86	5.89	5.86	5.72	5.90	5.74		
Cr	0.31	0.00	0.09	0.08	0.14	0.11	0.14	0.27	0.10	0.24		
V	0.04	0.00										
	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00		
Mg	1.97	2.15	1.95	2.15	2.17	2.14	2.12	1.96	2.18	2.03	0.75	0.26
Fe	0.19	0.43	0.22	0.21	0.21	0.21	0.21	0.19	0.21	0.20	0.13	0.04
Mn	0.01	0.01	0.01			0.01	0.01	0.01	0.01	0.00		
Ca	0.22	0.20	0.14	0.17	0.25	0.24	0.24	0.23	0.23	0.22		
^{VI}Al		0.10	0.15	0.15	0.03	0.11			0.10		3.40	3.34
V	0.49	0.00	0.35	0.22	0.30	0.23	0.34	0.48	0.24	0.51	0.00	0.29
Ti	0.08	0.11	0.08	0.06	0.08	0.08	0.08	0.09	0.07	0.03	0.04	0.05
	2.96	3.00	2.90	2.96	3.04	3.02	3.00	2.96	3.04	2.99	4.32	3.98
Na	0.65	0.72	0.68	0.72	0.61	0.65	0.63	0.65	0.65	0.61	0.00	0.09
K	0.01		0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.01	1.78	1.94
	0.66	0.72	0.70	0.73	0.63	0.67	0.65	0.67	0.67	0.62	1.78	2.03

Calculated on the basis of 24.5 atoms of oxygen for tourmaline (1-10) and 22 atoms of oxygen for muscovite

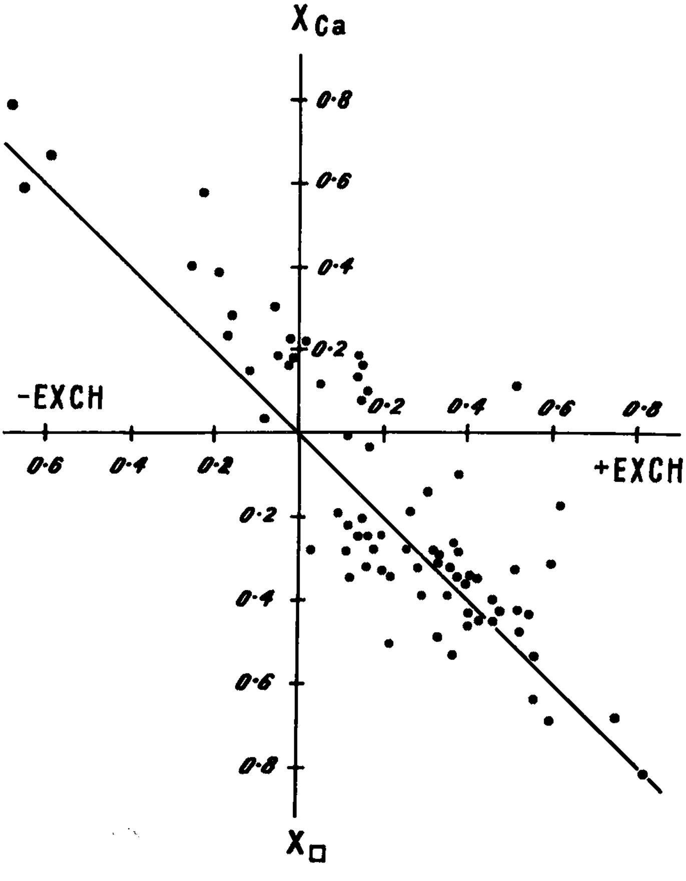

FIG. 5. Relationship between Ca (per formula unit) in X site in tourmaline and value of positive or negative excess charge (EXCH), derived from the expression $(R^{3+}_{Y} + 2\mathrm{Ti}^{4+}) - (\mathrm{Li}^{+} + \mathrm{Mg}^{2+}_{Z} + {}^{IV}\mathrm{Al}^{3+})$. $X_\square$ is the number of vacancies in the X site. Multiple points are not indicated. See text for details.

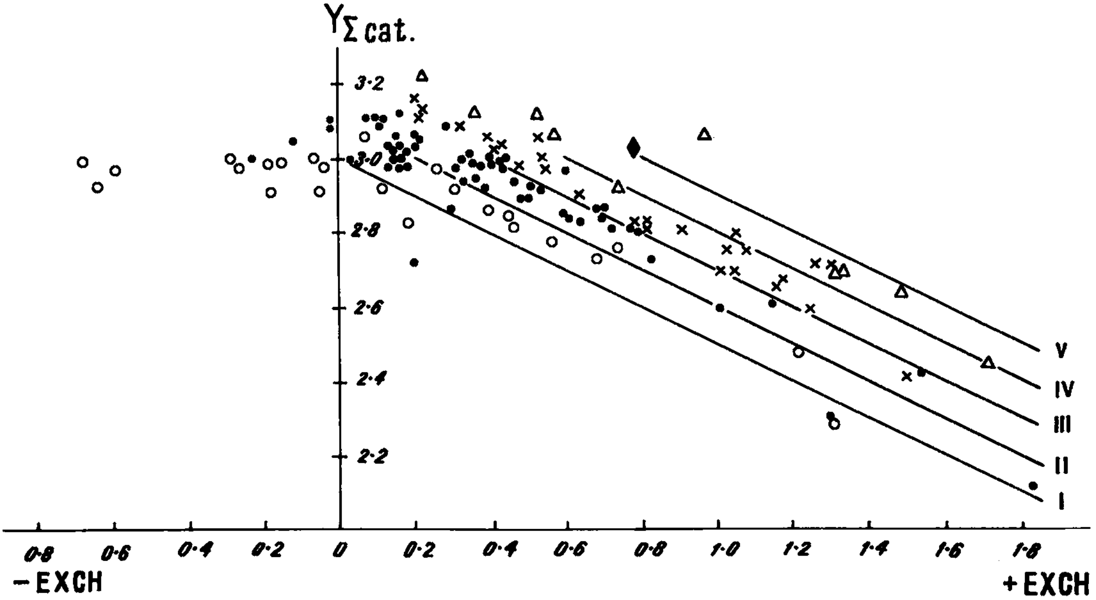

FIG. 6. Relationship between sum of Y cations in tourmaline (per formula unit) and value of positive or negative excess charge (EXCH: calculation is the same as that in the caption to Fig. 5). The parallel lines show the trends of the ideal substitution $3R^{2+} \leftrightarrow (2R^{3+} + \square)$ at different proportions of vacancies in the X site ($\square^X$): I 0, II 0.2, III 0.4, IV 0.6, and V 0.8. Symbols indicate tourmaline compositions in which $\square^X$ has five ranges of values: circle 0.0 – 0.2; dot 0.2 – 0.4; cross 0.4 – 0.6; triangle 0.6 – 0.8; rhomb 0.8 – 1.0. See text for details.

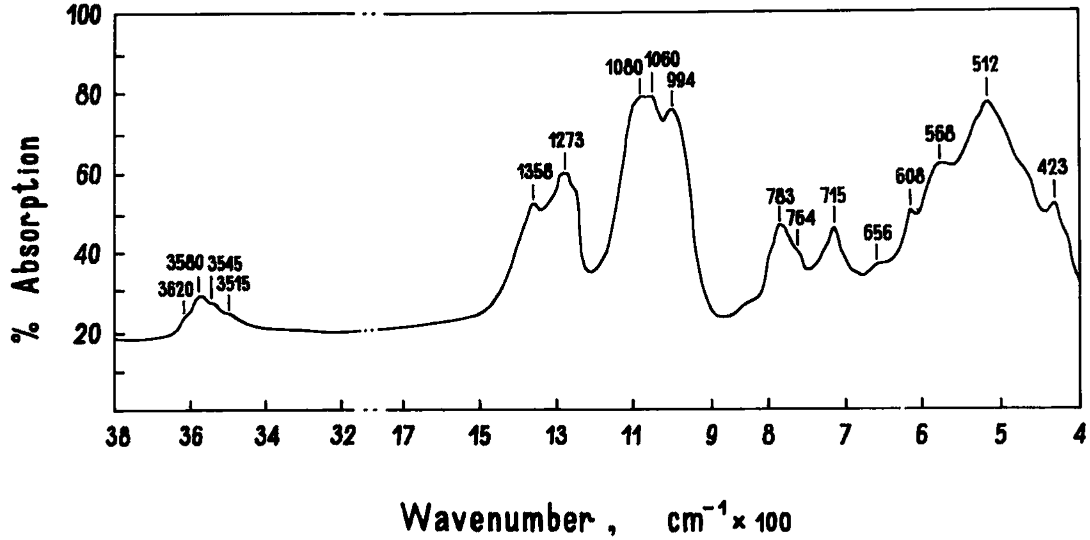

FIG. 7. Infrared absorption spectrum of V–Cr-bearing tourmaline (Primorye, Russia) in the 400 to 3800 cm^{-1} region. The principal absorption bands are indicated.

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