BARIUM-VANADIUM MUSCOVITE AND VANADIUM TOURMALINE FROM MARIPOSA COUNTY, CALIFORNIA

KENNETH G. SNETSINGER, *Department of Geology, Stanford University.*[1]

ABSTRACT

Barium-vanadium muscovite and zoned vanadium tourmaline occur in quartz-graphite schist in the northwest part of the Bass Lake quadrangle, Mariposa County, California.

Appreciable barium has substituted for potassium in the large cation formula group of the muscovite, and the positive charge thus induced has required excess substitution of tetrahedral aluminum for silicon to maintain electrical neutrality of the mineral. Physical properties are similar to those recorded for chromian muscovite.

The inner zone of the tourmaline contains considerable trivalent vanadium as well as the divalent cations commonly present in schorl or dravite, and substitution of oxygen for hydroxyl and fluorine has taken place to compensate the excess positive charge. Similar substitution has occurred in the outside zone of the tourmaline. Cell dimensions of the inner zone plot precisely on the schorl-dravite join, suggesting trivalent vanadium is acting isostructurally with respect to ferrous iron. The outer zone plots off the join in the direction of elbaite, probably due to substitution of aluminum for larger iron and magnesium ions in octahedral structural sites.

It is suggested the vanadium and other heavy metals present in these minerals were primary constituents concentrated with organic material in the original unlithified sediment, and were not introduced hydrothermally or metasomatically.

INTRODUCTION

During study of igneous and metamorphic rocks exposed 20 miles south of the Yosemite Valley, California (Snetsinger, 1965), a bluish-green muscovite-like mica, initially identified as chromian muscovite, was found in a quartz-graphite schist together with crystals of tourmaline, the green color of which also suggested a chromiferous variety. Subsequent chemical analysis of these minerals showed, however, that chromium was present in only small amounts, that the chromian muscovite was actually an example of barium-vanadium muscovite, and the tourmaline was a vanadium-bearing type. In this report results of chemical, optical and x-ray study of the muscovite and tourmaline are given, together with a suggested origin of the vanadium and other heavy metals present in these minerals.

OCCURRENCE; PETROGRAPHY

The quartz-graphite schist constitutes a 100 by 200 foot lens within one of a series of pendants made up of quartz-mica schist that occur in granitic rocks in the northwest part of the U.S. Geological Survey's 15

minute Bass Lake quadrangle. The area is 5 miles south of the southern-most park boundary of Yosemite National Park. Quartz-graphite rock crops out only at the top of a prominence called Silver Knob in the south-east corner of Section 4, T.6S., R.21E.; graphite-bearing schists do not occur elsewhere in the area.

The quartz-mica schists are fine-grained and homogeneous in composition; thin section modes give the following average values: quartz, 53 per cent; potash feldspar, 8 per cent; plagioclase, 4 per cent; biotite and muscovite, 33 per cent (with the biotite/muscovite ratio about 3:1); opaques, 2 per cent. In contrast to these micaceous rocks, the quartz-graphite schist is poor in mica, rich in graphite, and lacks feldspars; modal analysis gives: quartz, 53.5 per cent; graphite 30.4 per cent; barium-vanadium muscovite, 10.2 per cent; vanadium tourmaline, 5.3 per cent; biotite, 0.6 per cent. Graphite forms a planar fabric, and platelets may be included in quartz grains or occur between them; the schist is fine-grained, but muscovite and tourmaline occur porphyro-blastically with respect to other constituents, and average 2 mm in their largest dimension. Muscovite, which displays strong preferred orientation, very commonly contains graphite inclusions and is occasionally sieved by quartz. Tourmaline is aligned in the plane of orientation of graphite and muscovite, has fewer graphite inclusions than muscovite and only rarely includes quartz. The tourmaline is zoned, with a main inner zone and a very thin rim at either end of the crystals. The muscovite does not appear zoned in thin section and this was verified by careful refractive index work.

Separatory Procedures

Purification of muscovite for chemical analysis was accomplished by preliminary concentration using a Frantz electromagnetic separator, followed by fine grinding of the concentrate thus obtained and repeated centrifuging in bromoform-methylene iodide mixtures. All graphite inclusions could not be removed, so elemental carbon was determined analytically and calculated out of the analysis. About 3 gm of pure mica were obtained for analysis.

It was found possible to separate the outside from the inside zone of the tourmaline. Purification involved handpicking of coarse fragments followed by fine grinding and centrifuging in bromoform-methylene iodide mixtures of carefully adjusted density. Chemical treatment with HF was used to dissolve quartz and muscovite contaminants. After purification a small percentage of graphite inclusions remained in both zones. Sufficient material of the inner zone (2.5 gm, *ca.*) was at hand so that carbon could be quantitatively determined and cast out of the

analysis. Only a small amount (about 100 mg) of the outer zone was available, and carbon was not determined in this case.

ANALYTICAL PROCEDURES

Muscovite and inner zone of tourmaline. The muscovite and inner zone of the tourmaline were analyzed in the laboratories of the U.S. Geological Survey at Washington, D.C. A combination of x-ray fluorescence and wet chemical methods were employed. John Marinenko was analyst in both cases, with x-ray fluorescence determinations by H. Rose, Robena Brown and Marinenko.

The following oxides were determined by x-ray fluorescence: SiO_2, Al_2O_3, CaO, K_2O, TiO_2, MnO, Cr_2O_3 and BaO. MgO and P_2O_5 were determined respectively by the clayton-yellow and heteropoly-blue spectrophotometric procedures. Fluorine was determined spectrophotometrically by the thoron-thorium method. Iron was assumed to be in the ferrous state in both minerals. Fe^{2+}, V^{3+} and V^{4+} were determined as follows: the samples were decomposed by fusion in a nitrogen atmosphere with sodium metafluoborate flux containing ferric iron. The Fe^{2+} equivalent of V^{3+} was titrated to the o-phenanthroline end point and corrected for ferrous iron originally present in the sample. The difference between total vanadium found by a separate procedure and the V^{3+} gave the V^{4+} value. Because of the refractory nature of the tourmaline there is a possibility of unavoidable error in determination of valence states of vanadium. Carbon was determined in a combustion train and reported as elemental carbon. Boron in the tourmaline was distilled as the menthyl ester and after hydrolysis determined by titration with standard base in the presence of mannitol.

Outer zone of tourmaline. The outer zone of the tourmaline was analyzed by Norman Suhr and C. O. Ingamells of Pennsylvania State University.

MgO, CaO, V_2O_5, Cr_2O_3 and TiO_2 were determined spectrographically by Suhr; values for the other oxides were obtained wet chemically by Ingamells. Owing to the small amount of sample, water and ferrous iron determinations had to be omitted.

NOMENCLATURE

A satisfactory mineral name for the muscovite is not available, because the notable percentages of vanadium and barium suggest affinities with both the vanadium muscovite roscoelite and the barium muscovite oellacherite. Schaller's (1930) modifiers would in this case be unwieldy,[1] and the mineral is described as barium-vanadium muscovite. Chemical analysis of the inner zone of the tourmaline showed it contains more vanadium than has previously been recorded for tourmaline, and thus a new name might have been proposed. It seems inappropriate, however, to assign a different name to a compositional variant of a common mineral; both inner and outer zones are referred to as vanadium tourmaline.

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[1] If strictly applied, Schaller's system would lead to "barian vanadylian vanadoan muscovite."
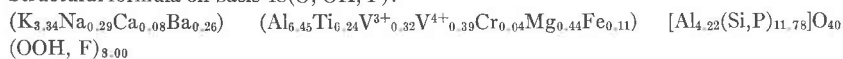
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COMPOSITION AND PHYSICAL PROPERTIES
OF THE MUSCOVITE

Analytical data for the muscovite are given in Table 1. Vanadium, titanium and barium are present in appreciable amounts; of particular interest is the determination of vanadium in two valence states. Chromium is minor. Calculation of empirical cell contents from the analysis using cell volume and density shows close agreement with the theoretical 48 (O, OH, F) per unit cell, and the numbers of ions on this basis to-

TABLE 1. ANALYSIS AND STRUCTURAL FORMULA OF BARIUM-VANADIUM MUSCOVITE

Oxide	Weight Percent[1]	Numbers of Ions	
SiO_2	43.7	Si	11.77
P_2O_5	0.05	P	0.013 ⎱ 16.00
		Al	4.217
Al_2O_3	33.5		
		Al	6.453
TiO_2	1.18	Ti	0.243
V_2O_3	1.48	V^{3+}	0.324
V_2O_4	1.95	V^{4+}	0.389
Cr_2O_3	0.21	Cr	0.043 ⎰ 8.01
MgO	1.08	Mg	0.438
FeO[2]	0.48	Fe	0.114
MnO	0.01	Mn	0.002
CaO	0.25	Ca	0.081
BaO	2.39	Ba	0.259 ⎰ 3.97
Na_2O	0.56	Na	0.292
K_2O	9.71	K	3.340
H_2O^+	4.30	OH	7.749
H_2O^-	0.04		⎰ 7.83
F	0.10	F	0.081
Total	100.99		
Less O for F	0.04		
	100.95		

Structural formula on basis 48(O, OH, F):
$(K_{3.34}Na_{0.29}Ca_{0.08}Ba_{0.26})$ $(Al_{6.45}Ti_{0.24}V^{3+}_{0.32}V^{4+}_{0.39}Cr_{0.04}Mg_{0.44}Fe_{0.11})$ $[Al_{4.22}(Si,P)_{11.78}]O_{40}$
$(OOH, F)_{8.00}$

[1] Analysis recalculated to eliminate 0.57 per cent C.

[2] Total iron as FeO.

Analyst: John Marinenko; x-ray fluorescence determinations by H. Rose, Robena Brown and Marinenko.

gether with the structural formula are given in Table 1. Clearly, excess substitution of aluminum for silicon has taken place, the Al:Si ratio in the tetrahedral group being greater than the ideal 1:3. This is unusual because, as Foster (1960) has observed, most dioctahedral micas have divalent as well as trivalent metals replacing octahedral aluminum, giving the octahedral layers a relative negative charge, and requiring more Si to substitute for Al in the tetrahedral layers; the Al:Si ratio is therefore usually less than the ideal 1:3 relation. In the barium-vanadium muscovite, however, the effect of divalent cations proxying for aluminum has been offset by entry of quadrivalent titanium and vanadium; calculation of the number of positive charges in the octahedral formula group[1] gives 24.07, in close agreement with the value 24.00 for ideal muscovite. The octahedral layer is, therefore, of its own accord close to neutral. The large cation group on the other hand has, owing to entry of barium, a positive charge of 4.31, as compared with the theoretical 4.00. Thus, while excess substitution of Al for tetrahedral Si has porduced a relative negative charge of 0.22 in the tetrahedral group, electrical balance of the mineral is maintained, within limits of analytical error, by entry of divalent barium substituting for monovalent metals in the large cation formula positions.

Two previous analyses of muscovite in which the tetrahedral Al:Si ratio is slightly greater than 1:3 occur in the literature (Bauer and Berman, 1933;[2] Hutton, 1940). The charge relations in Bauer's mica are similar to the current example, but the octahedral formula group has a negative charge. The analysis recorded by Hutton appears to be impeccable, but there is no clear reason for increased substitution of Al.

Kultiassov and Dubinkina (1946) describe three varieties of barium- and vanadium-bearing muscovite but these show considerable deviation from the theoretical formula and are not given further consideration.

Calculation of cell parameters (Table 2) and d-spacings (Table 3) of the barium-vanadium muscovite was done by the computer program devised by Evans *et al.* (1963), using repeated least-squares refinement of data.[3] Twenty-eight reflections within the 2θ range 7 to 77° were selected for these calculations. Intensities of reflections were estimated visually from a powder photograph which exhibited no evidence of preferred orientation. Because of preferred orientation of the diffractometer smear or coincidence with quartz internal standard peaks, a few reflec-

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[1] Done by multiplying the numbers of each of the ions in the structural formula by their charges, and summing the results.

[2] Analysis of oellacherite.

[3] The hkl-generating option to the program was not put in use, the reflections being indexed "by hand" from data in the literature.

tions could not be measured by diffractometer; values for these were obtained from film. The cell dimensions are somewhat expanded compared with pure muscovite, but are similar to values reported by Whitmore *et al.* (1946) for chrome-bearing mica. The muscovite has the common $2M_1$ structure, amounts of barium and vanadium present in it being insufficient to cause it to crystallize as the 1M polymorph. The latter structure has been found by Heinrich and Levinson (1955) in oellacherite (BaO = 9.89 per cent) and roscoelite (V_2O_3 greater than 17 per cent), but these writers noted that the $2M_1$ structure can accommodate small amounts of Ba and V.

TABLE 2. PHYSICAL DATA FOR BARIUM-VANADIUM MUSCOVITE

a	5.202 ± 0.004 Å
b	9.035 ± 0.006 Å
c	20.056 ± 0.007 Å
β	$95°48' \pm 4'$
Cell volume	937.8 ± 0.8 Å³
Structure type	$2M_1$
Density (obs.)	2.925 ± 0.005 gm/cc
Optical properties	
α	1.571 ± 0.001
β	1.608 ± 0.001
γ	1.611 ± 0.001
2V (calc.)	$(-)$ 34°
2V (obs.)	$(-)$ 29°–32°
X = colorless (pale yellow in thick section)	
Y = pale greenish-yellow	
Z = pale robin's-egg blue	
Dispersion: $r > v$, distinct	

Physical data for the muscovite are listed in Table 4 together with what other data are available for examples of barium- and vanadium-bearing muscovite. The effect of barium seems to be that of raising density, whereas vanadium tends to increase refractive indices and birefringence. Substitution of trivalent and quadrivalent vanadium deepens pleochroism and results in green colors. The pleochroic scheme for the barium-vanadium muscovite is no different from that of typical chromian muscovite (*cf.* Whitmore *et al.*, 1946), especially with regard to the distinctive robin's-egg blue Z color. Hutton (1940) has observed that a very small percentage of Cr_2O_3 (0.27 per cent) is sufficient to cause considerable coloration of muscovite, but it is suggested that in the present example vanadium is influencing pleochroism to a far greater degree than is chromium.

TABLE 3. X-RAY DATA FOR BARIUM-VANADIUM MUSCOVITE

Calculated[1]		Measured[2]	
hkl	d(Å)	d(Å)	I[3]
002	9.977	9.969	90
004	4.988	4.986	20
110	4.491	4.479	80
111	4.301	4.293	20
022	4.115	4.125	50
11$\bar{3}$	3.883	3.882	50
023	3.737	3.737	50
11$\bar{4}$	3.493	3.494	60
114	3.201	3.203	60
025	2.991	2.990	60
115	2.861	2.861	30
11$\bar{6}$	2.792	2.791	30
13$\bar{1}$	2.598	2.602	20
20$\bar{2}$	2.569	2.569	100
132	2.488	2.493	10
20$\bar{4}$*	2.398	2.395	30
134*	2.261	2.251	20
204	2.208	2.209	10
20$\bar{6}$	2.150	2.151	30
135*	2.131	2.128	30
0.0.10	1.995	1.994	40
13$\bar{9}$	1.732	1.733	10
0.0.12*	1.663	1.668	10
312	1.644	1.647	80
313*	1.604	1.602	10
245	1.529	1.524	10
060*	1.506	1.504	90
0.0.16	1.247	1.247	20

[1] Calculated from the refined unit cell parameters given in Table 2.

[2] Diffractometer data obtained at scanning speed of $\frac{1}{4}°$ 2θ per minute and chart speed of $\frac{1}{2}$ inch per minute using nickel-filtered copper radiation with Brazil quartz as internal standard.

[3] Visual intensities.

* Reflection measured by camera method.

COMPOSITION AND PHYSICAL PROPERTIES
OF VANADIUM TOURMALINE

Analyses of the inner and outer zones of the tourmaline are given in Table 5. The inner zone contains the highest percentage of vanadium yet recorded for tourmaline, and the element is present mainly in the trivalent oxidation state. The outer zone contains appreciable vanadium.

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Both zones are chromiferous and both have boron contents slightly in excess of the average for tourmaline. Table 6 shows results of calculation of empirical cell contents of the two examples of tourmaline, compared with theoretical values. The numbers of (O, OH, F) are in both cases comparable to the theoretical value of 93, and structural formulae calculated on that basis are given in Table 5.

Octahedral cations present in common iron-magnesium tourmaline are mainly divalent, but considerable trivalent and appreciable quadrivalent metals are present in the octahedral group of the inner zone tourmaline. Excess positive charge thus produced has resulted in substitution of

TABLE 4. PHYSICAL PROPERTIES OF BARIUM- AND VANADIUM-BEARING MUSCOVITES

	BaO = 9.89[1] V=O (1)	BaO = 2.39 V₂O₃+ V₂O₄ = 3.43 (2)	BaO = 7.15 V₂O₃ = 6.18 (3)	BaO = 5.27 V₂O₃ = 17.92 (3)	BaO = 7.20 V₂O₃ = 16.44 (3)	BaO = 1.35 V₂O₃ = 12.84 (4)	Ba = O V₂O₃ = 23.59 (5)
α	—	1.571	—	1.620	—	1.610	—
	(Mean r.i.						
β	1.59)	1.608	1.625	1.664	1.627	1.685	—
γ	—	1.611	1.634	1.676	1.634	1.704	—
$2V(-)$	—	34°	40°, *ca.*	40°, *ca.*	40°, *ca.*	25–40°	—
D(gm/cc)	—	2.925	—	3.106	2.964	2.92–2.94	2.90
X	—	colorless		not determined		greenish-brown	—
Y	—	pale greenish-yellow		pale green		olive green	—
Z	—	pale robin's-egg blue		yellowish green		olive green	—

[1] Weight percent. (1) Oellacherite; Bauer and Berman (1933). (2) Barium-vanadium muscovite, present report. (3) Vanadium-bearing oellacherite; Kultiassov and Dubinkina (1946) (4) Barium-bearing roscoelite; Hillebrand and Ransome (1900); optics from Wright (1914). (5) Roscoelite (cited in Wells and Brannock, 1945).

O^{2-} for OH^- and F^- to maintain electrical balance of the mineral, as evidenced by oxygens in excess of the ideal number of 81 and hydroxyl and fluorine summation less than 12 (Table 6). The same situation is apparent with the outer zone formula, except that the very small number of univalent anions may in this case in part be due to non-determination of structural water. Thus while the barium-vanadium muscovite adjusts for excess positive charge in large cation formula positions by changing the Al:Si ratio in tetrahedral layers, tourmaline, its structure unable to allow substitution of Al for tetrahedral Si (Lowenstein, 1956), compensates for positive octahedral charge mainly by substitution of O^{2-} for univalent anions. Proxying of B^{3+} for Si^{4+} has taken place in both tourmalines: this substitution may also be in response to excess positive

octahedral charge. Summations of large cation groups are in both cases considerably less than the ideal 3, and this is considered due to positive octahedral charge, fewer large cations then being needed to maintain electrical neutrality.

On the tentative assumption it is substituting for Al as well as Si, boron in excess of 9 ions is apportioned to both these elements in the inner zone formula. The number of ions of Si+B is, in the outer zone tourmaline, greater than the ideal 18, but in both minerals the numbers of octahedral cations are close to the theoretical 9.

Tourmaline with appreciable vanadium content is rare, but two pre-

TABLE 5. ANALYSIS AND STRUCTURAL FORMULA OF INNER AND OUTER
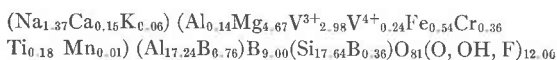ZONE OF VANADIUM TOURMALINE

Inner Zone			
Oxide	Weight Percent[1]	Numbers of Ions	
SiO_2	35.6	Si	17.64 ⎫ 18.00
			0.36 ⎬
B_2O_3	11.8	B	9.00
			0.76 ⎫ 18.00
Al_2O_3	29.7	Al	17.24 ⎫ 0.14
Cr_2O_3	0.89	Cr	0.357
V_2O_3	7.45	V^{3+}	2.975
V_2O_4	0.58	V^{4+}	0.238
MgO	6.33	Mg	4.671 ⎫ 9.11
TiO_2	0.46	Ti	0.179
FeO^2	1.32	Fe	0.536
MnO	0.02	Mn	0.009
Na_2O	1.43	Na	1.369
CaO	0.25	Ca	0.149 ⎬ 1.58
K_2O	0.1	K	0.06
H_2O^+	2.56	OH	8.449 ⎫ 9.16
F	0.46	F	0.714 ⎭
Total[3]	98.95		
Less O for F	0.19		
	98.81		

TABLE 5—(*Continued*)

Outer Zone			
Oxide	Weight Percent	Numbers of Ions	
SiO_2	39.8	Si	19.55 ⎫ 20.12
B_2O_3	11.3	B	⎧ 0.57 ⎫ ⎩ 9.00
Al_2O_3	32.3	Al	⎧ 18.00 ⎩ 0.72
Cr_2O_3	0.10	Cr	0.040
V_2O_5[4]	1.8	V	0.59
MgO	9.4	Mg	6.88 ⎫ 8.91
TiO_2	0.41	Ti	0.148
Fe_2O_3[5]	1.5	Fe	0.53
MnO	0.01	Mn	0.003
Na_2O	1.05	Na	1.004
CaO	1.4	Ca	0.74 ⎫ 1.79
K_2O	0.07	K	0.041
H_2O	n.d.	F	1.359 ⎫ 1.36
F	0.87		
Total	100.01		
Less O for F	0.37		
	99.64		

Structural formula on basis 93 (O, OH, F):

Inner Zone

$(Na_{1.37}Ca_{0.15}K_{0.06})$ $(Al_{0.14}Mg_{4.67}V^{3+}_{2.98}V^{4+}_{0.24}Fe_{0.54}Cr_{0.36}$
$Ti_{0.18}$ $Mn_{0.01})$ $(Al_{17.24}B_{6.76})B_{9.00}(Si_{17.64}B_{0.36})O_{81}(O, OH, F)_{12.06}$

Outer Zone

$(Na_{1.00}Ca_{0.74}K_{0.04})$ $(Mg_{6.88}V_{0.59}Fe_{0.13}Cr_{0.04}Ti_{0.15}$
$Al_{0.72})$ $Al_{18.00}B_{9.00}(Si_{19.55}B_{0.57})O_{81}(O, OH, F)_{12.00}$
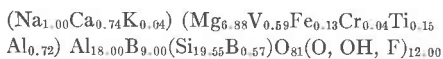
[1] Analysis recalculated to eliminate 0.06 percent C.

[2] Total iron as FeO.

[3] P_2O_5 and H_2O^-, less than 0.02 and 0.03 percent respectively, are not included in summation. No barium found by x-ray fluorescence.

[4] Total vanadium as V_2O_5.

[5] Total iron as Fe_2O_3.

Inner zone analysts as with barium vanadium muscovite; outer zone analysts N.H. Suhr and C. O. Ingamells.

TABLE 6. EMPIRICAL CELL CONTENTS OF VANADIUM TOURMALINES

	Inner Zone	Outer Zone	Theoretical (Donnay and Buerger, 1950, p. 380)
Numbers of cations	56.78	57.09	57
Numbers of O^{2-}	90.17	91.07	81
Numbers of (OH, F)	5.03	1.35	12
Numbers of (O, OH, F)	95.20	92.42	93
Total atoms per unit cell	151.98	149.51	150

vious examples have been recorded;[1] one contains 5.76 per cent V_2O_3 (Badalov, 1951) and the other (Basset, 1956) contains 1.50 per cent.

X-ray study of vanadium tourmaline was carried out in the same way as with barium-vanadium muscovite; results are listed in Tables 7 and

[1] Lacroix (1918) states that iochroite of Nordenskiold (1863), containing 7.53 per cent V_2O_3, is tourmaline, but Nordenskiold's early analysis, while it shows good summation, contains no boron and iochroite is herewith rejected as an example of vanadium-bearing tourmaline.

TABLE 7. PHYSICAL DATA FOR ZONED VANADIUM TOURMALINE

Inner Zone	
a	15.983 ± 0.003 Å
c	7.190 ± 0.001 Å
Cell volume	1590.6 ± 6 Å³
Density (obs.)	3.131 ± 0.005 gm/cc
Optical properties	
ϵ	1.643 ± 0.001
ω	1.675 ± 0.001
ϵ = pale grass green	
ω = dark reddish-brown	

Outer Zone	
a	15.938 ± 0.006 Å
c	7.173 ± 0.003 Å
Cell volume	1578.0 ± 1.0 Å³
Density (obs.)	3.065 ± 0.005 gm/cc
Optical properties	
ϵ	1.628 ± 0.001
ω	1.653 ± 0.001
ϵ = palest yellowish-green	
ω = pale brown	

TABLE 8. X-RAY DATA FOR ZONED VANADIUM TOURMALINE

Inner Zone

hkl	Calculated[1] d(Å)	Measured[2] d(Å)	I[3]
101	6.380	6.394	50
021	4.986	5.000	25
300	4.614	4.620	25
211	4.230	4.238	70
220	3.996	3.999	80
012	3.479	3.485	70
122	2.963	2.964	80
321	2.905	2.904	5
312	2.624	2.624	5
051	2.584	2.584	100
003	2.397	2.396	10
232	2.380	2.380	10
511	2.350	2.349	10
502	2.193	2.195	20
431	2.170	2.169	20
342	1.923	1.922	50
413	1.877	1.878	10
621	1.855	1.855	10
333	1.782	1.783	20
024	1.740	1.739	1
603*	1.662	1.662	40
271	1.646	1.646	20
550	1.598	1.598	45
054	1.508	1.507	45
244	1.481	1.481	10
514*	1.457	1.457	50
015	1.430	1.431	10

Outer Zone

hkl	Calculated[1] d(Å)	Measured[2] d(Å)	I[3]
101	6.365	6.365	50
021	4.973	5.002	25
300	4.601	4.608	25
211	4.219	4.234	70
220	3.985	3.988	80
012	3.471	3.470	70
122	2.956	2.957	80
321	2.897	2.899	5
312	2.617	2.618	5
051	2.576	2.574	100
502	2.188	2.188	20

TABLE 8 (*Continued*)

	Outer Zone		
hkl	Calculated[1] d(Å)	Measured[2] d(Å)	I[3]
431	2.164	2.164	20
342	1.918	1.917	50
413	1.873	1.872	10
621	1.849	1.850	10
333	1.777	1.777	20
024	1.736	1.733	1
603*	1.658	1.657	40
271	1.642	1.642	20
550	1.594	1.594	45
054	1.504	1.503	45
244	1.478	1.477	10
514*	1.453	1.453	50
015	1.427	1.426	10
205	1.405	1.406	20

[1] Calculated from the refined cell parameters given in Table 7. All reflections listed were used in unit cell refinement.

[2] Measuring procedure as with barium-vanadium muscovite (Table 3).

[3] Visual intensities.

* Reflection measured by camera method.

8, and cell dimensions are plotted on Figure 1 for comparison with the elbaite-schorl-dravite series. The inside zone, with its high vanadium content, plots precisely on the schorl-dravite join, suggesting trivalent vanadium is acting isostructurally with respect to ferrous iron, V^{3+} and Fe^{2+} having identical ionic radii (0.74Å).[1] The outside zone and Basset's tourmaline, however, both plot off the join in the approximate direction of elbaite, and this is considered due to substitution of aluminum for larger iron and magnesium ions in octahedral structural positions.

Physical properties of chromium- and vanadium-bearing tourmaline are listed in Table 9. The general effect of these two metals is to increase refractive indices and birefringence; Badalov's tourmaline is an exception. As with barium-vanadium muscovite, pleochroism deepens as vanadium increases over chromium.

ORIGIN OF BARIUM-VANADIUM MUSCOVITE AND VANADIUM TOURMALINE

It is suggested that the vanadium, barium and chromium present in these minerals were primary constituents initially concentrated with
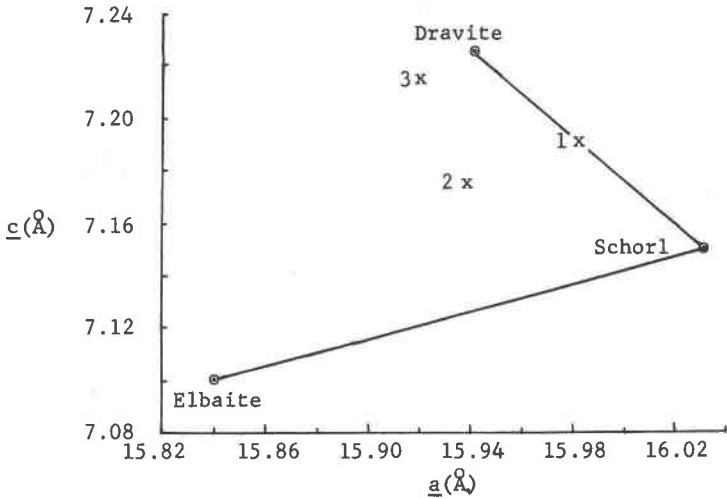
[1] Ahrens (1952).

Fig. 1. Cell dimensions of vanadium tourmalines. 1: inner zone of vanadium tourmaline; 2: outer zone of vanadium tourmaline; 3: vanadium-bearing tourmaline from Tanganyika (McKie, 1958). Cell dimensions of end members from Deer *et al.* (1962).

organic material in the unlithified sediment, and were not introduced hydrothermally by the granitic intrusives. Several considerations support this, the first of which is association of the minerals only with the graphite schist: where graphite is absent from the metamorphic rocks, barium-vanadium muscovite and vanadium tourmaline are also lacking. Indeed, common tourmaline is completely absent elsewhere in the metamorphic rocks, and this suggests boron in the vanadium-bearing type

TABLE 9. PHYSICAL PROPERTIES OF VANADIUM- AND CHROMIUM-BEARING TOURMALINES

	$V=O$[1] $Cr_2O_3=10.86$ (1)	$V=O$ $Cr_2O_3=1.60$ (2)	$V_2O_3=1.50$ $Cr=O$ (3)	$V_2O_5=1.8$ $Cr_2O_3=0.10$ (4)	$V_2O_3=5.76$ $Cr=O$ (5)	$V_2O_3+V_2O_4=$ 9.02 $Cr_2O_3=0.89$ (4)
ϵ	1.669	1.650	1.644	1.653	1.635	1.675
ω	1.637	1.625	1.622	1.628	1.618	1.643
D(gm/cc)	3.120	3.13	3.125	3.065	3.058	3.131
ϵ	yellow	light yellow	green but non-pleo-chroic	pale yellowish green	light green	pale grass green
ω	green	colorless		pale brown	brown	dark reddish brown
a (Å)	—	—	15.92	15.938	--	15.983
b (Å)	—	—	7.215	7.173	—	7.190
a/c	2.215	---	2.207	2.222	—	2.223

[1] Weight percent. (1) Cossa and Arzruni, 1883. (2) Shenderova, 1955. (3) Basset, 1956; cell parameters by McKie, 1958. (4) Vanadium tourmaline, present report. (5) Badalov, 1951.

was also preferentially concentrated in the original carbonaceous sediment. Second, spectrographic investigation of tourmaline and muscovite in pegmatites of the area shows no concentration of vanadium, barium or chromium. Finally, it is well known that carbonaceous materials (such as coal ash, asphalt, petroleum ash and black shale) commonly bear appreciable percentages of these metals, as well as boron (Goldschmidt, 1954; Rankama and Sahama, 1950; Krauskopf, 1955; Mason, 1958); shungite is an example of organic-derived graphitic material which contains barium and is especially high in vanadium (Sudovikov, 1937; Lokka, 1943).

The original sediment is therefore considered to have been a poorly argillaceous quartz sandstone with considerable organic material (since graphite equals 30.4 volume per cent of the present rock), boron and the heavy metals initially being "fixed" with the carbonaceous matter, possibly in the form of organo-metallic compounds (Krauskopf, 1955, p. 421). Subsequently, during metamorphism and recrystallization, boron and the metals were set free and incorporated in the structures of muscovite and tourmaline. Thus the barium-vanadium muscovite and vanadium tourmaline have what Heinrich (1965) refers to as a metamorphic in contrast to a hydrothermal or metasomatic origin.

The mineral assemblage in the quartz-graphite schist is not a diagnostic one for judging metamorphic facies, but minerals of surrounding quartz-mica schists suggest conditions equivalent to the hornblend-hornfels facies of contact metamorphism. Using recent experimental data of Ito (1965, Fig. 5), which relate valence states of vanadium in roscoelite and some other vanadium silicates to temperature, the V^{3+}/V^{4+} ratio in the barium-vanadium muscovite implies a temperature of formation of roughly 600° C., and this value is compatible with the hornblende-hornfels facies.

An origin suggested by Badalov (1951) for his vanadium-bearing tourmaline and garnet combines hydrothermal and metamorphic origins in an interesting way and is mentioned for comparison with the present occurrence: Badalov postulates that post-magmatic solutions mobilized vanadium from a black quartz-graphite hornfels and deposited the metal in the contact zone of quartz veins, where it was incorporated in tourmaline and garnet.

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