THE TANCO PEGMATITE AT BERNIC LAKE, MANITOBA. II. WODGINITE, TANTALITE, PSEUDO-IXIOLITE AND RELATED MINERALS

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ABSTRACT

Wodginite, tantalite, pseudo-ixiolite, microlite, tapiolite, cassiterite and ilmenite occur as disseminations in the silicate minerals in zones (3), (4), (5), (6), and (9) of Crouse & Černý (1972). Wodginite, tantalite, microlite and cassiterite are the most abundant, all four occurring mainly in the late central intermediate zone (6). The other minerals occur mainly in other earlier-forming zones.

Wodginite is brown to black, and granular to euhedral with crystals prismatic along $b[010]$. The mean cell content is $(Mn_{3.33}^{2+}Sn_{2.54}^{4+}Fe_{0.98}^{2+}Ti_{0.95}^{4+}Nb_{0.86}^{5+})Ta_{7.94}^{5+}O_{32}$ a preliminary structure analysis suggests that the Ta atoms are ordered into one site. The monoclinic space group was confirmed as $C2/c$ or Cc, and the mean cell dimensions are a 9.501, b 11.453, c 5.113 Å, β 91°0.3'. Wodginite has a sub-cell with $a' = a/2$, $b' = b/2$, $c' = c$, $\beta' = \beta$, $Z' = Z/4$, and problable space group $P2/c$. Wodginite heated in an oxidizing atmosphere showed no change in its yellow-brown colour or in its powder diffractogram, but that heated in a reducing atmosphere turned brownish-black and showed marked changes in two powder diffraction intensities.

Black tantalite and pseudo-ixiolite are almost indistinguishable except by x-ray diffraction although tantalite is normally interstitial and subhedral whereas pseudo-ixiolite tends to be euhedral and platy. The mean cell content of tantalite is $(Mn_{3.59}^{2+} Ti_{0.14}^{4+} Fe_{0.09}^{2+} Sn_{0.04}^{4+})(Ta_{5.59}^{5+}Nb_{2.43}^{5+})O_{24}$. The mean cell content of pseudo-ixiolite is $1/3$ $[(Mn_{3.68}^{2+} Ti_{0.28}^{4+}Fe_{0.06}^{2+} Sn_{0.16}^{4+}Ta_{5.14}^{5+}Nb_{2.69}^{5+})O_{24}]$. X-ray diffraction confirmed that the two minerals have similar orthorhombic cells (space group $Pbcn$) except that a of pseudo-ixiolite equals $a/3$ of tantalite, presumably due to disordering and ordering of cations in the two minerals, respectively. Tantalite has a strong pseudo-ixiolite sub-cell. Densities are: tantalite 6.76 gm/cc, pseudo-ixiolite (mean): 6.95 gm/cc. The brownish-black minerals change to yellow on heating in an oxidizing atmosphere, and to black in a reducing atmosphere. Colour suggests these Tanco minerals probably formed at $fO_2 \sim 10^{-30}$ atm. Heated pseudo-ixiolites gave tantalite x-ray patterns, the cations presumably becoming ordered on ignition.

Tapiolite yields an average formula of $(Fe_{1.86}^{2+}Mn_{0.28}^{2+}Ti_{0.02}^{4+}Sn_{0.01}^{4+})(Ta_{3.77}^{5+}Nb_{0.17}^{5+})O_{12}$. Microlite gives $Ta_2O_5 \sim 73\frac{1}{2}$ and $Nb_2O_5 \sim 6$ wt.%. Ilmenite contains ~ 9 wt.% MnO.

During the crystallization of the pegmatite, the Ta-minerals and associated phases were concentrated in late inner zones, mostly in metasomatic assemblages within these zones. The Ta/Nb ratio in these minerals increases, but the Mn/Fe ratio decreases in consecutively later zones, and wodginite, indicative of high fO_2, is concentrated in the youngest zone which also carries the highest accumulation of Sn and Ti.

INTRODUCTION

Among the minerals occurring in the Li-Cs-Be-Ta pegmatite at Bernic Lake in southeastern Manitoba are the tantalum oxides, wodginite, tantalite, pseudo-ixiolite, microlite and tapiolite. At the time of writing (late 1971), these tantalum minerals constitute the only ones being concentrated and marketed by the Tantalum Mining Corporation of Canada (TANCO). Several non-tantalum minerals, especially spodumene, pollucite, beryl and K-feldspar are being stockpiled while investigations concerning their possible marketing are in progress.

A detailed examination of the tantalum oxide minerals, the results of which are the subject of this paper, constitutes part of a larger investigation of several of the principal mineral groups in the Tanco pegmatite being carried out in the Department of Earth Sciences at the University of Manitoba. The results of the investigations of several of these other mineral groups and an up-to-date account of the geology of the mine (Crouse & Černý 1972) are given in papers that accompany this one.

Although it was shown earlier by Nickel *et al.* (1963a) that both tantalite and wodginite occur in the Tanco pegmatite, the present authors felt that a detailed investigation of many specimens of the different tantalum oxide minerals from known locations in the pegmatite would be valuable to establish the variations in the properties of these minerals, and to provide, along with the other mineralogical investigations, some petrogenetic information. The complex mineralogy of tantalum in the examined pegmatite is particularly promising in this respect. Much of this study is embodied in the M.Sc. thesis of Grice (1970) from which most of this paper has been taken.

SAMPLING AND EXPERIMENTAL METHODS

Sampling

From known localities in the mine, sixty-five oxide-bearing rock specimens were collected by J. D. G. and an additional five by P.Č. From these, the oxide minerals were separated and examined as described briefly below. Descriptions and locations of all 70 specimens and the investigations made on them are given in Grice (1970), but in the present paper we give the distribution of the minerals in the pegmatite in Table 1 and descriptions of only the 21 specimens on which detailed work was done in Tables 2, 3, and 4.

TABLE 1. DISTRIBUTION OF THE TANTALUM-OXIDE AND RELATED MINERALS IN THE PEGMATITE

	Zone (3)	Zone (4)	Zone (5)	(a)[1]	Zone (6) (b)[2]	(c)[3]
Wodginite[4]	very rare	—	—	very abundant	very abundant	rare
Tantalite	—	—	—	rare	abundant	—
Tapiolite	—	—	—	very rare	—	—
Microlite	—	rare, replaces pseudo-ixiolite	very rare, replaces pseudo-ixiolite	abundant, granular	common, granular	very rare
Pseudo-ixiolite	—	rare	very rare	—	—	—
Cassiterite[4]	—	rare	very rare	common	common	—
Ilmenite	—	—	—	(?)	subordinate (?)	—

[1] Coarse-grained K-feldspar + quartz (+ albite, beryl, spodumene) assemblage.

[2] Albitic aplite assemblage.

[3] Quartz (+ beryl) assemblage.

[4] Wodginite and cassiterite were reported also from the lepidolite zone (9), see text.

The relative abundances of minerals within individual, and among different, zones are expressed in a scale very abundant, abundant, common, subordinate, rare, very rare.

Separation

The dark oxide minerals from each rock specimen were separated by hand-picking when this was possible. When it was not, separation was effected by the heavy liquid method using bromoform on 100-200 mesh material, or by magnetic methods. It was found impossible, however, to separate wodginite, tantalite and cassiterite from each other magnetically because of the similar magnetic susceptibilities of these three minerals.

X-ray diffraction

The primary instrument used for initially identifying all the separated oxide minerals was a Philips (Norelco) x-ray powder diffractometer. Records were taken using CuKα radiation with instrument settings yielding a chart scale of 8 cm equals 3°2θ. Diffractograms with the chart scale expanded to 16cm equals 3°2θ were used to derive accurate cell dimensions for eleven of the specimens; under these conditions a given peak position could be read to within 0.01°2θ. Annealed fluorite with $a = 5.4620$Å (D. B. Stewart in Tilling 1968) was used as an internal standard. For the three runs on a given sample, reasonably well-defined peaks gave a standard deviation of ±0.02°2θ. The 2θ values derived in this manner were used in the computer program of Evans, Appleman & Handwerker (1963) as modified by D. E. Appleman for a least squares refinement of the unit cell dimensions with a weighting factor being applied to each reflection on the basis of its clarity and reproducibility. The errors quoted later for cell dimensions derived in this way are standard errors about the mean, and they were found to be less than 0.06%.

Single-crystal x-ray precession photographs of eleven of the specimens were taken using MoKα radiation. The errors quoted later for cell dimensions derived in this way are standard deviations about the mean but, because the instrument had not been calibrated, these errors are actually measurement precision. This lack of calibration probably accounts for the fact that, in Tables 2, 3 and 4, several cell dimensions derived by both the powder and the precession method are not in agreement within the separate limits of error quoted.

Electron probe microanalysis

Microprobe analyses were carried out on 21 specimens using a Philips AMR/3 microprobe at the Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, through the courtesy of Dr. A. Sawatzky and with the cooperation of Mr. S. Jones, the probe operator, who carried out most of the analyses. The operating conditions are described by Grice (1970, p. 16). The elements analyzed for were Mn, Fe, Sn, Ti, Ta and Nb, and standards

used were metals of the pure elements. Sc was sought but not found, in two of the specimens. In carrying out the analyses, care was taken to probe exactly the same spot on a given sample for all analyzed elements ; see, however, footnote 6 of Table 2. The intensity data from the electron probe were processed using a computer program, EMPADR VII, written by Rucklidge & Gasparrini (1969), and provided for us by Dr. Rucklidge.

The probe results given in Tables 2, 3 and 4 show that the total oxides for most of our specimens are high, varying mostly between 101 and 104%. Because of our high totals, we arranged to have duplicate analyses carried out on two grains of one of our wodginite specimens, No. G69-46, in another laboratory ; Dr. J. Rucklidge of the Department of Geological Sciences, University of Toronto, kindly arranged to have Miss E. Gasparrini do these analyses for us. Her results, along with ours, are given in Table 1 under this specimen number. Although her analyses were carried out on the same two grains as were ours, it was impossible for her to probe the identical spots on the grains that we had probed. The comparative results, taken along with some of our x-ray scans, indicate that compositions of these minerals vary appreciably even on a probe scale. However, her totals are also high, and so we feel that all our high totals are the result of some unknown factor in the analytical method, a factor that is probably related to our use of pure metals as standards. In view of the high totals, we regard the error in the probe analyses to be $\pm5\%$ of the weight percent quoted.

Occurrence and Distribution in the Pegmatite

The five tantalum oxide minerals (wodginite, tantalite, pseudo-ixiolite, tapiolite and microlite) and the two associated phases (ilmenite and cassiterite) occur in five of the nine zones that constitute the Tanco pegmatite (for detailed description see Crouse & Černý 1972). A summary of their distribution and abundance in these five zones is given in Table 1 which is based on the study of Grice (1970) and on later evidence gathered since the thesis was completed.

Albitic aplite of zone (3), which forms discontinuous warped sheets in the lower part of the pegmatite, contains only very rare skeletal grains of wodginite that fill interstices among albite laths. This wodginite was not studied in detail during this study.

The lower intermediate zone (4), which consists of substantial amounts of albite, quartz, K-feldspar and spodumene, and subordinate amblygonite-montebrasite and lithium micas, carriers rare platy crystals of pseudo-ixiolite and irregular grains of cassiterite. Microlite commonly replaces the pseudo-ixiolite crystals. Microlite, pseudo-ixiolite and cassiterite are asso-

TABLE 2. WODGINITE SPECIMEN DESCRIPTIONS, PROBE ANALYSES AND UNIT CELL DATA.

Spec. No.	Zone No.[1]	Associated[2] Minerals	Chemical (Probe) Analyses[3] MnO Mn+2	FeO Fe+2	SnO2 Sn+4	TiO2 Ti+4	Ta2O5 Ta+5	Nb2O5 Nb+5	Total Total	Code	Space Group	Unit Cell Data[4] a Å	b Å	c Å	β	V Å³
G69-2	(6)	KF,Ms,Q	10.4	1.0	15.7	3.8	71.8	1.0	103.7	US	C2/c	9.506(42)	11.408(20)	5.080(13)	90°54'(14')	
			3.63	0.34	2.58	1.18	8.04	0.16	15.93	UP		9.496(2)	11.455(2)	5.109(1)	91°4.0'(1.9')	555.64(17)
										HP	(1)[5]	9.491(2)	11.449(2)	5.106(1)	91°3.7'(1.0')	554.75(12)
										HP	(2)[5]	9.492(3)	11.452(3)	5.108(2)	91°4.2'(1.8')	555.15(19)
G69-8	(6)/(3)	KF,Ap,(T)	8.9	3.3	14.7	3.2	66.9	5.5	102.5							
			3.07	1.12	2.39	0.98	7.41	1.01	15.98							
G69-13	(6)	KF,Ms,(T)	10.0	1.2	13.9	3.8	72.9	1.0	102.8	US	C2/c	9.495(31)	11.437(27)	5.075(13)	90°25'(16')	
			3.52	0.42	2.30	1.19	8.24	0.18	15.85	UP		9.497(4)	11.452(4)	5.116(2)	90°56.2'(2.2')	556.39(23)
G69-17[7]	(6)	KF,Q	9.2	3.0	15.5	1.3	73.3	1.0	103.3	US	C2/c	9.436(21)	11.409(20)	5.097(11)	91°8'(5')	
			3.09	0.99	2.45	1.40	7.91	0.18	16.02	UP		9.517(2)	11.452(3)	5.112(2)	91°5.8'(1.5')	557.00(17)
G69-19	(6)	KF,Ms,Bl Q	9.4	2.7	14.0	2.5	75.3	0.2	104.1							
			3.31	0.94	2.32	0.78	8.53	0.08	15.96							
G69-21	(6)	KF,Ms,Q(T)	8.3	5.2	17.0	0.2	69.1	2.7	102.5							
			2.99	1.85	2.87	0.07	7.94	0.55	16.27							
G69-39	(6)	KF,Ms	9.8	2.1	15.4	4.0	70.2	1.5	103.0	US	C2/c	9.467(26)	11.439(14)	5.105(6)	90°33'(15')	
			3.46	0.73	2.56	1.25	7.96	0.11	16.07	UP		9.498(3)	11.454(2)	5.118(1)	90°55.9'(1.8')	556.71(16)
G69-44	(6)	KF,Ms,Q,Bl	9.2	2.8	18.9	1.2	69.4	2.0	103.5	US						
			3.26	0.98	3.15	0.38	7.90	0.38	16.05	UP						
BLM-1A	(6)	KF,Q,Ms	9.1	2.9	15.2	4.0	69.3	2.0	102.5	US	C2/c	9.503(13)	11.440(12)	5.118(9)	90°40'(12')	
			3.18	1.00	2.50	1.29	7.77	0.37	16.11	UP		9.498(3)	11.451(3)	5.112(2)	90°59.4'(1.7')	558,57(20)
G69-46[6]	(6)	KF,Ms,Bl,Q	12.0	3.2	15.1	4.0	68.7	0.5	103.5	UP						
			12.0	3.8	14.5	4.8	64.0	5.0	104.1							
			9.7	4.9	15.8	0.7	68.2	3.3	102.6							
			9.8	5.2	10.1	3.0	72.7	3.6	104.4							
			3.76	1.46	2.26	0.95	7.69	0.56	16.68							
Mean Values and Limits		Wt.%	9.8 +2.2 -1.5	3.2 +2.0 -2.2	15.1 +3.8 -5.0	2.8 +2.0 -2.6	70.1 +5.2 -6.1	2.2 +2.8 -2.0	103.2 +1.2 -.7			9.501 +0.016 -0.005	11.453 +0.002 -0.002	5.113 +0.005 -0.004	91°0.3' +5.5' -4.4'	556.86 +1.71 -1.22
		No. of atoms	3.33 +.43 -.34	0.98 +.87 -.53	2.54 +.61 -.28	0.95 +.45 -.88	7.94 +.49 -.53	0.36 +.65 -.28	16.10 +.58 -.17							

ciated mainly with pods and stringers of cleavelandite, and located along its contacts with quartz.

The upper intermediate zone (5), which occupies mostly the upper parts of the pegmatite and develops from the preceding zone (4) by gradual increase in grain size and decrease in the feldspar and mica contents, contains the same types of pseudo-ixiolite, microlite and cassiterite but in barely detectable traces. Their association with cleavelandite is also comparable to that found in zone (4).

The largest and economically important concentration of tantalum oxides and associated minerals is located in the central intermediate zone (6), which forms two lenticular bodies in the central parts of the pegmatite (see Figs. 2, 3 and 4 in Crouse & Černý 1972). This zone consists of three assemblages that differ in their Ta, Sn, and Ti mineralization.

The K-feldspar + quartz (+ albite, beryl, spodumene) assemblage (a) is penetrated by fine-grained greenish muscovite accompanied by brown

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[1] Zone numbers are those given in Crouse & Černý (1972) as follows : (3) albitic aplite zone ; (4) lower intermediate K-feldspar + albite + quartz + spodumene (+ amblygonite) zone ; (6) central intermediate K-feldspar + muscovite + plagioclase + quartz + beryl zone. The corresponding zone numbers in Table 1 in Grice (1970) are 3, 1 and 2 respectively.

[2] Code for the matrix minerals : Ab albite, Ap aplitic albite, Bl beryl, cl cleavelandite, KF K-feldspar, Ms muscovite, Q quartz, Sp spodumene. Where other oxides were found these are designated in brackets thus : T tantalite, W wodginite, Tp tapiolite, Pl pseudo-ixiolite, M microlite, C cassiterite.

[3] Chemical (probe) analyses give for each specimen, first the analysis in terms of weight percent of the oxides, and then the numbers of each cation on the bases of 32 O.

[4] Unit cell data are coded as follows : UP — unheated material, powder diffractogram data (see text), US — unheated material, single-crystal (precession) data, HP and HS — corresponding data for heated material. The cell dimensions relate to the true cell (see Table 5). The standard error in each cell dimension in $Å \times 10^{-3}$, in the β angle in minutes, and in the cell volume in $Å^3 \times 10^{-2}$ are given in brackets. The relationships between the cells adopted for wodginite, tantalite and pseudo-ixiolite is discussed in the text and shown in Table 5.

[5] The unit cell data for sample G69-2 designated HP(1) and HP(2) refer to material heated at 1000°C for 16 hours at $fO_2 = 10^{-2.5}$ atm. (HP(1)) and at $fO_2 = 10^{-17}$ atm. (HP(2)).

[6] For specimen G69-46, four probe analyses were carried out, one each on two separate grains in the same mount, done by S. Jones, Pinawa, and repeats on the same two grains (but not necessarily on identical spots) by Miss E. Gasparrini, Dept. of Geological Sciences, University of Toronto. The four analyses given in the table are in the sequence : grain 1, Jones ; grain 2, Jones ; grain 1, Gasparrini ; grain 2, Gasparrini. Below the analyses are given the numbers of cations for the means of the four analyses.

[7] Specimen G69-17 is, at the time of writing, the subject of a crystal structure analysis by Margaret Elphick, Ferguson and Grice.

TABLE 3. TANTALITE SPECIMEN DESCRIPTIONS, PROBE ANALYSES, UNIT CELL DATA AND SPECIFIC GRAVITIES.

Spec. No.[1]	Zone No.	Associated[2] Minerals	Chemical (Probe) Analyses[3]							Code	Space Group	Unit Cell Data[4]				Specific gravity
			MnO Mn^{+2}	FeO Fe^{+2}	SnO$_2$ Sn^{+4}	TiO$_2$ Ti^{+4}	Ta$_2$O$_5$ Ta^{+5}	Nb$_2$O$_5$ Nb^{+5}	Total			a Å	b Å	c Å	V Å³	
G69-8	(6)/(3)	KF,Ap,(W)	13.7 / 3.46	0.4 / 0.10	0.5 / 0.06	1.5 / 0.34	69.3 / 5.70	16.0 / 2.16	101.4 / 11.92							
			3.96				7.96									
G69-29	(4)	Ap,Q	14.5 / 3.67	0.4 / 0.11	0.2 / 0.02	0.2 / 0.05	70.0 / 5.66	17.5 / 2.38	102.8 / 11.89							
			3.85				8.04									
G69-52	(6)	KF,Ms,Q, (W,Tp)	11.3 / 3.10	3.3 / 0.91	0.0 / 0.00	0.2 / 0.05	83.5 / 7.30	4.0 / 0.62	102.3 / 12.08							
			4.06				8.02									
G69-53	(3)	Ap,Q	13.5 / 3.58	0.5 / 0.12	0.7 / 0.08	0.3 / 0.08	67.0 / 5.71	16.0 / 2.28	98.0 / 11.85	UP	(Pbcn)	14.415(9)	5.754(2)	5.116(2)	424.38(27)	
			3.86				7.99									
G69-58[7]	(4)	Q,Ms,Ab, (Pl)	14.6 / 3.66	0.2 / 0.05	0.1 / 0.01	0.4 / 0.09	64.2 / 5.12	21.0 / 2.90	100.5 / 11.83	UP, HP[5]	(Pbcn), (Pbcn)	14.403(3) / 14.430(3)	5.759(2) / 5.763(2)	5.105(2) / 5.091(1)	423.51(15) / 423.39(12)	6.76(3)
			3.81				8.02									
Mean Values and Limits		Wt.%	14.1 +0.5 -0.6	0.4 +.1 -.2	0.4 +.3 -.3	0.8 +.7 -.3	67.6 +2.4 -3.4	17.6 +3.4 -1.6	100.9 +1.9 -2.9	UP		14.409 +.006 -.006	5.756 +.003 -.002	5.110 +.006 -.005	423.94 +.44 -.43	(6.76(3))
		No. of atoms	3.59 +.08 -.13	0.09 +.02 -.04	0.04 +.04 -.03	0.14 +.20 -.09	5.59 +.16 -.43	2.43 +.47 -.27	11.85 +.07 -.02							

Footnotes

1,2 See corresponding footnotes to Table 1.

3 See corresponding footnote to Table 1; the numbers of cations correspond to 24 O.

4 See corresponding footnote to Table 1. The cell dimensions relate to the truecell (see Table 5).

5 Specimen G69-58(HP) was heated at 1000°C for 17 hours at fO$_2$ = 10^{-14} atm.

6 Because the chemical analysis of specimen G69-52 differs greatly from the other analyses, it has arbitrarily been omitted in the calculation of the Mean Values and Limits.

7 Specimen G69-58 is, at the time of writing, the subject of a crystal structure refinement by Grice and Gerguser.

TABLE 4. PSEUDO-IXIOLITE SPECIMEN DESCRIPTIONS, PROBE ANALYSES, UNIT CELL DATA AND SPECIFIC GRAVITIES.

Spec. No.	Zone No.[1]	Associated[2] Minerals		Chemical (Probe) Analyses[3]							Code	Space Group		Unit Cell Data[4]			Specific gravity
			MnO / Mn+2	FeO / Fe+2	SnO2 / Sn+4	TiO2 / Ti+4	Ta2O5 / Ta+5	Nb2O5 / Nb+5	Total			a Å	b Å	c Å	V Å3	
G69-30	(5)	Q,Cl,Ms	15.0	0.4	0.2	1.2	62.0	18.5	97.3							
			3.93	0.10	0.02	0.28	5.21	2.54	12.08							
G69-31	(4)	Q,Cl,Ms,(M)	15.1	0.5	1.8	1.7	64.0	18.0	101.1	UP	(Pbcn)	4.758(1)	5.750(2)	5.162(2)	141.22(7)	6.94(2)
			3.79	0.12	0.21	0.38	5.15	2.41	12.06							
G69-55	(4)	Cl,Q,Ms	14.4	0.1	0.6	0.8	64.0	22.0	101.9	UP5	(Pbcn)	4.763(1)	5.753(1)	5.157(1)	141.33(4)	
			3.53	0.04	0.51	0.18	5.03	2.95	12.24	HP5	(Pbcn)	4.806(1)	5.760(2)	5.091(1)	141.00(4)	
G69-59	(4)	Cl,Q,Sp,Ms,(C)	12.1	4.0	1.2	6.2	52.5	27.0	103.0							
			2.51	0.82	1.16	1.14	3.49	3.00	12.12							
G69-60	(4)	Q,Cl	14.6	0.1	0.6	0.8	64.7	21.5	102.3	UP5	(Pbcn)	4.766(1)	5.753(2)	5.153(2)	141.29(5)	6.96(3)
			3.57	0.03	0.07	0.17	5.08	2.85	11.77	HP5	(Pbcn)	4.810(1)	5.765(1)	5.093(1)	141.25(3)	
G69-61	(4)	Q,Cl	14.4	0.1	0.9	0.6	66.2	20.5	102.7	UP5	(Pbcn)	4.762(1)	5.755(1)	5.158(1)	141.35(4)	6.94(3)
			3.56	0.03	0.01	0.13	5.25	2.72	11.70	HP5	(Pbcn)	4.813(2)	5.765(2)	5.096(1)	141.74(5)	
Mean Values and Limits[6]		Wt.%	14.7 +0.4 -0.3	0.2 +.3 -.1	0.8 +1.0 -.6	1.0 +.7 -.4	64.2 +2.0 -2.2	20.1 +1.9 -2.1	101.0 +1.7 -3.3	UP	(Pbcn)	4.762 +.004 -.004	5.793 +.002 -.003	5.158 +.004 -.005	141.30 +0.05 -0.08	6.95 +0.01 -0.01
		No. of atoms	3.68 +.25 -.15	0.06 +.06 -.03	0.16 +.35 -.15	0.23 +.15 -.10	5.14 +.11 -.09	2.69 +.26 -.28	11.96 +.12 -.26							

Table 4, correction in proof for:
Correct numbers of atoms for two samples.

Spec. No.	Mn+2	Fe+2	Sn+4	Ti+4	Ta+5	Nb+5	Total
G69-55	3.56	0.02	0.07	0.18	5.07	2.90	11.80
G69-59	2.73	0.89	0.12	1.24	3.80	3.26	12.04

Footnotes

1,2 See corresponding footnotes to Table 1.

3 See corresponding footnote to Table 1; the numbers of cations correspond to 24 0 for ease of comparison with the tantalite cell contents even though the true cell of pseudo-ixiolite has only 8 oxygens.

4 See corresponding footnote to Table 1.

5 Specimens G69-55, G69-60 and G69-61(HP) were all heated at 1000°C for 17 hours at fO2 = 10^-14 atm.

6 Because the chemical analysis of specimen G69-59 differs markedly from the other analyses, it has arbitrarily been omitted in the calculation of the Mean Values and Limits.

wodginite and tantalite, yellow granular microlite, microscopic grains of tapiolite, and brownish cassiterite (Fig. 1). Wodginite is the most abundant phase, microlite and cassiterite are subordinate, tantalite and particularly tapiolite are rare. The albitic aplite (b) carries mainly skeletal grains of wodginite and tantalite, whereas granular microlite and cassiterite are present in much lesser amounts. The tantalum oxides and associated minerals are concentrated mainly along the margins of the rounded masses of aplite (Fig. 2). The quartz pods (c) rimmed by beryl contain only rarely black crystals of wodginite, occasionally associated with microlite grains.

Fine-grained ilmenite is commonly present in ore concentrates from the upper parts of zone (6), adjacent to the hanging-wall amphibolite, but has never been spotted in hand specimens. The fine grain of ilmenite suggests that this mineral comes from either assemblage (a) or assemblage (b) that carry fine-grained Ta-oxides and cassiterite ; the rare wodginite and micro-lite from assemblage (c) is always much coarser.

The metasomatic lepidolite zone (9), located within the central zone (6), is reported to contain wodginite and cassiterite, but these could not be sampled during the present study.

WODGINITE

Introduction

Bernic Lake was one of the first two localities from which wodginite was described as a new mineral by Nickel, Rowland & McAdam (1963a), the other locality being Wodgina, Australia. Since 1963 the mineral has been identified at several other localities throughout the world by different authors. The following description deals with wodginite of zone (6).

Physical properties

The brownish crystals of wodginite from assemblage (a) reach up to 4 cm across, and are frequently skeletal, with abundant inclusions of quartz and muscovite (Figs. 3, 4 ; cf. also Figs. 1 and 2 in Nickel et al. 1963a). In the aplitic assemblage (b), wodginite grains fill interstices among the albite laths. Black, euhedral crystals of wodginite may be occasionally found in quartz of the assemblages (a) and (c) ; these attain a length of 4mm. A pale red-brown streak is characteristic of all wodginite types.

Two prismatic crystals about 3mm in length were examined on the reflecting goniometer. A typical crystal is shown in Fig. 5, where it may be seen that elongation is along b[010], and that the prismatic forms are {001}, {101}, and {$\bar{1}$01} ; most crystals are terminated by the forms {111}
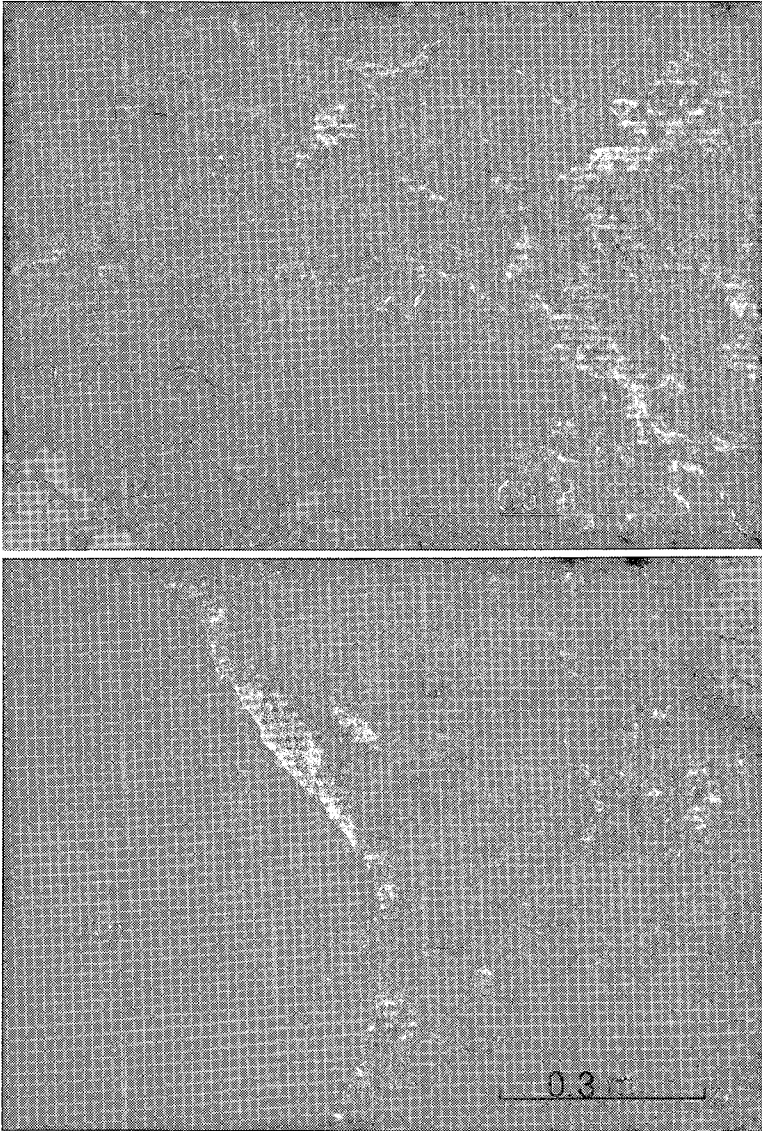
Fig. 1. (Top) A nest of microcline-perthite (K-f) partly replaced by fine-grained greenish muscovite and wodginite (W-black dots), rimmed by white crystals of beryl (B) against quartz (Q). Assemblages (a) and (c) of zone (6), first level south drift.

Fig. 2. Part of a round nodule of albitic aplite (Ap) surrounded by quartz (Q); tantalite and wodginite (T-black dots) concentrated in the marginal parts of the aplite. Assemblages (b) and (c) of zone (6), first level south drift.
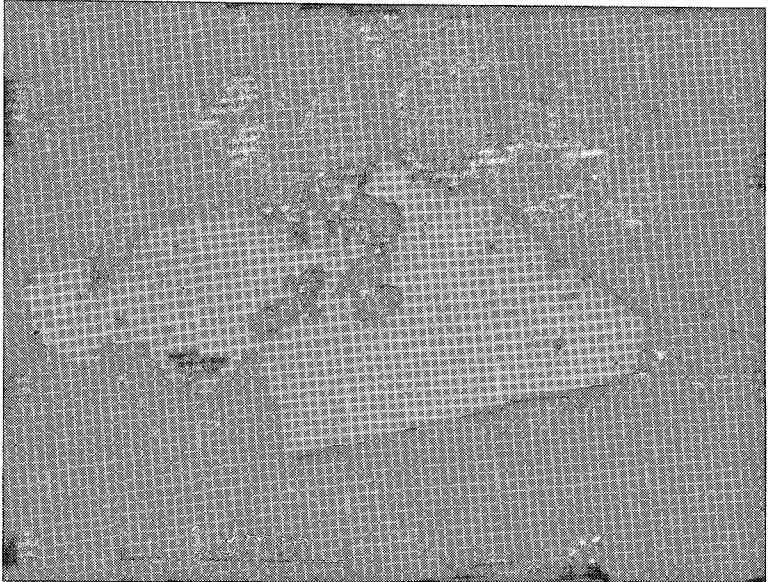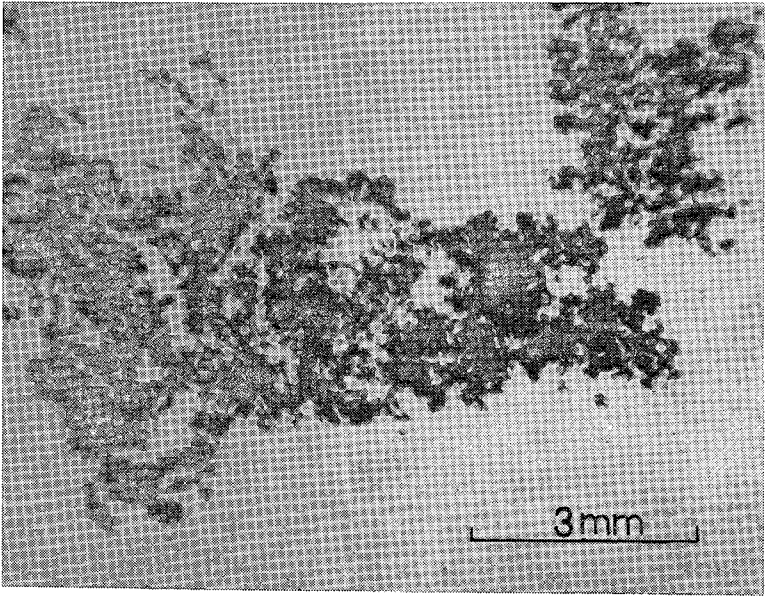
FIG. 3. (Top) Anhedral wodginite (black) with numerous silicate inclusions in muscovite and microcline-perthite. Assemblage (b) of zone (6), thin section in polarized light.

FIG. 4. Euhedral wodginite (white) in slightly muscovitized microclineperthite. Assemblage (b) of zone (6), polished section.

and {$\bar{1}11$}, but some of them are truncated by small {010}. Less common forms observed were {031} and {335}. The form indexing relates to the cell defined by the dimensions given in Table 2 ; the matter of cell orientations and dimensions for wodginite, tantalite and pseudo-ixiolite is discussed below.

In transmitted light, the wodginite is orange-brown ; the grains have a high relief (n » 1.54) and a high birefringence ; for those few grains on which it was possible to get an optical figure, it was biaxial positive. In reflected light the wodginite is grey when viewed in air with a blue filter ; under crossed polars it is slightly anisotropic, and it displays a strong internal reflection similar to the red-brown internal reflection of tantalite. We did not consider it worthwhile to try to measure specific gravities on our wodginites because of the small size of the grains and the many inclusions in them.

X-ray diffraction

Nickel *et al.* (1963a) showed that crystallographically wodginite differs from closely related tantalite by the fact that it is monoclinic (with β ~91°) rather than orthorhombic, and that the two have related but different cell dimensions. They discuss the relationship of the cell orientations, dimensions, space groups and cell contents between these two minerals, and between them and the two other closely related minerals ixiolite and olovotantalite ; they discuss these relationships further in another paper (Nickel *et al.* 1963b) in which they also propose the new species pseudo-ixiolite. The settings we have adopted for wodginite, tantalite and pseudo-ixiolite are those used by Strunz & Tennyson (1966) : wodginite is given the conventional monoclinic setting first ascribed to it by Nickel *et al.* (1963a), and orthorhombic tantalite and pseudo-ixiolite are given orientations that are structurally equivalent to that of wodginite. The relation-
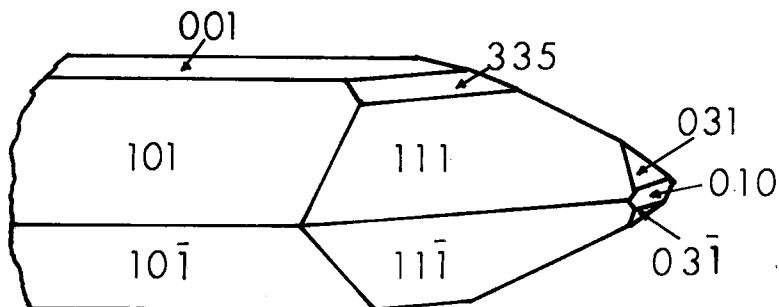

FIG. 5. Schematic drawing of a typical crystal of wodginite from the Tanco pegmatite.

ships between these minerals are further complicated by the existence of strong pseudo-cells in wodginite and in tantalite (which are discussed below). Because it is essential to know what settings are being used in any discussion of the crystallography of these minerals, we give in Table 5 our settings for these three minerals, the settings being those of Strunz & Tennyson (1966) and, for comparison, the settings of Nickel *et al.* (1963a) taken from their Table 5. Unless otherwise noted, all our crystallographic and x-ray diffraction descriptions of wodginite including the morphology described earlier and the results given in Table 2, refer to the larger true cell.

Crystals of five of the wodginite specimens were examined by means of single-crystal precession photographs and by the highly resolved powder diffractograms calibrated by an internal standard. The precession photographs confirmed the cell dimensions and the possible space groups of Nickel *et al.* (1963a) as shown in our Table 5. Table 2 gives the cell dimensions of the five specimens obtained by both the precession and the powder diffractometer methods (those obtained by the latter method being much the more accurate), and their means and ranges. It can be seen that the cell data of our five wodginite specimens show very small variations, the maximum being 0.3% and most much smaller.

The single-crystal photographs showed that wodginite has a strong pseudo-cell, the dimensions of which are shown in Table 5. This pseudo-cell gives extinction conditions corresponding to space group $P2/c$ or Pc rather than $C2/c$ or Cc of the true cell. A crystal structure analysis of wodginite by M. Elphick, Ferguson & Grice presently nearing completion in our Mineralogy Laboratory has shown that the space group of the pseudo-cell is $P2/c$ and not Pc.

Indexed powder data for two of the wodginite specimens are given by Grice (1970), but because the values are almost identical with those of Nickel *et al.* (1963a) reproduced as Powder Diffraction File card 15-795, they are not reproduced here.

Heating experiments

One wodginite sample, G69-2, was subjected to heating under two different conditions to note any possible changes which might conceivably help in the crystal-chemical understanding of the mineral. Khvostova *et al.* (1965) found that the β angle of their wodginite increased from 90°41′ to 91°02′ on heating (in an unstated atmosphere).

One portion of a powdered sample of specimen G69-2 was heated for 16 hours at 1000°C in an oxidizing atmosphere of pure CO_2 ($fO_2 = 10^{-2.5}$ atm). The sample showed no change in appearance as a result of the

TABLE 5. CRYSTALLOGRAPHIC SETTINGS FOR WODGINITE, TANTALITE AND PSEUDO-IXIOLITE

	This paper following Strunz et al. (1966)					Nickel et al. (1963a)		
	Pseudo-Ixiolite	Tantalite		Wodginite		Ixiolite	Columbite-Tantalite	
	true	true	sub	true	sub		true	sub
Axial / Lengths, Å	a 4.76	a 14.40	a/3 4.80	a 9.50	a/2 4.75	c 4.74	b 14.24	b/3 4.75
	b 5.75	b 5.76	(b) —	b 11.45	b/2 5.72	b 5.73	a 5.73	(a) —
	c 5.16	c 5.11	(c) —	c 5.11	(c) —	a 5.15	c 5.08	(c) —
β	(90°)	(90°)	(90°)	~91°	~91°	(90°)	(90°)	(90°)
V Å³	141	423	1/3 × 423 = 141	557	1/4 × 556 = 139	140	414	1/3 × 414 = 138
Space Group	Pbcn	Pbcn	Pbcn	C2/c or Cc	P2/c*	Pnab	Pcan	Pcan
Ideal Cell Content **	(A,B)₄O₈ A₄B₈O₂₄	1/3[A₄B₈O₂₄]	1/3[A₄B₈O₂₄]	A₈B₈O₃₂*	1/4[A₈B₈O₃₂]*	(A,B)₄O₈ A₄B₈O₂₄	1/3[A₄B₈O₂₄]	1/3[A₄B₈O₂₄]

*Evidence is given in the text for ordering of the Ta atoms into one site in wodginite.

** $A =$ Fe, Mn, $(+ \gg$ Sn, Ti) ; $B =$ Nb, Ta, $(+$ Sn, Ti).

heating, nor any measurable change in peak heights or peak positions in the powder diffractogram ; Table 2 shows (under G69-2, HP(1)) that the cell dimensions are almost identical with those of the unheated material, only the b values showing differences slightly greater than the limits of error.

A second portion of the same sample was heated also for 16 hours at 1000°C, but in a reducing atmosphere of pure CO ($fO_2 = 10^{-17}$ atm). After heating in this case, the powder turned from its original light yellow-brown color to a dark brownish-black ; such darkening as a result of reduction, is characteristic of Fe-Mn-Ta-Nb oxide minerals. The powder diffractogram of this heated material showed no appreciable change in spacings, and the derived cell dimensions given Table 2 (as HP(2)) are identical with those of the unheated material within the small limits of error. The diffractogram did show, however, two major changes in peak intensities : reflections 221 and 260 with d values of 2.955 and 1.771 Å increased their peak intensities by factors of two and three respectively. This change presumably results from the reduction in valence of one or more elements, probably mainly Mn, and some consequent rearrangement of the cations in the structure.

Chemistry

Microprobe analyses were carried out on nine of our wodginite specimens, and the results are shown in Table 2. Mn and Fe are arbitrarily reported as MnO and FeO since it was not possible to determine their valence states. As we pointed out earlier under Sampling and Experimental Methods, the probe work revealed marked variations in chemical compositions of the wodginites, even on the scale of the probe, over and above our estimated 5% error of the weight percentages quoted. The results in Table 2 show the extent of this variation, which is summarized at the foot of the Table where the mean values and limits of the weight percent of the oxides and the numbers of cations relative to 32 oxygens (Nickel *et al.* 1963a) are given.

The chemical analyses show that the Bernic Lake wodginites are rich in Ta, Sn, Mn and Ti, and poor in Fe and Nb, when compared with wodginites from other localities (Nickel *et al.* 1963a, Bourguignon & Mélon 1965, Khvostova *et al.* 1966, Vorma & Siivola 1967, Knorring 1968, Knorring *et al.* 1969). The only wodginite comparable to the average Tanco composition is that from the Meyer pegmatite, Karibib, S. W. Africa (Knorring 1968) which shows similarly high Mn, Ta, Sn and low Fe and Nb, but even this mineral differs by containing no TiO_2.

The chemical formula originally proposed for wodginite by Nickel *et al.* (1963a), and generally accepted, is $(Ta,Sn,Mn,Ti,Fe,Nb)_{16}O_{32}$ in terms of

the content of the true unit cell, or AO_2 in its simplest terms where A includes all the cations. However, a crystal structure analysis of wodginite specimen G69-17 in our Laboratory by Elphick, Ferguson & Grice (referred to earlier) indicates it is likely that, in the smaller pseudo-cell, all the Ta atoms are segregated into one structural site, and all the other cations into another. Pending the completion of this structure analysis, we tentatively suggest that the chemical formula be written to indicate this ordering of the Ta atoms; in its simplest terms, the formula would then be, for Bernic Lake wodginites, $(Sn,Mn,Ti,Fe,»Nb)TaO_4$.

TANTALITE AND PSEUDO-IXIOLITE

Introduction

Tantalite and pseudo-ixiolite are treated together because of the close relationship between them : pseudo-ixiolite is essentially a disordered tantalite, and such a disordered tantalite is readily converted to an ordered tantalite by heating in air for several hours at 800°C (Nickel *et al.* 1963b). (The same authors, who proposed the term "pseudo-ixiolite", suggest that the name "ixiolite" be reserved for those ixiolite-like minerals which yield olovotantalite after heating.) Both tantalite and pseudo-ixiolite are orthorhombic with similar cell dimensions, but the *a* period of pseudo-ixiolite is ⅓ *a* of tantalite (Table 5).

Strictly speaking the Bernic Lake "tantalites" should be described as "manganotantalites" because most have ~ 14% MnO and < ½% FeO. However, widespread use of the name tantalite, both in the scientific and the mining literature, for the mineral from this locality leads us to adhere to the shorter name.

Physical properties

The physical properties of tantalite and pseudo-ixiolite are very similar and in fact these minerals can be distinguished by x-ray diffraction only. However, they were found to occur in separate zones and to have different grain shapes ; on the basis of these two criteria a tentative identification may be made in hand specimens.

As noted above, tantalite is confined to zone (6), mainly to the albitic aplite assemblage (b). Skeletal tantalite normally fills interstices among albite blades (Figs. 6, 7) ; subhedral grains 1-2mm across are exceptional. In contrast, pseudo-ixiolite which occurs only in zones (4) and (5) normally forms euhedral platy crystals up to 10mm in diameter.

The density of one tantalite was measured as 6.76 gm/cc (Table 3), and the mean density of three pseudo-ixiolites was determined as 6.95 gm/cc (Table 4).
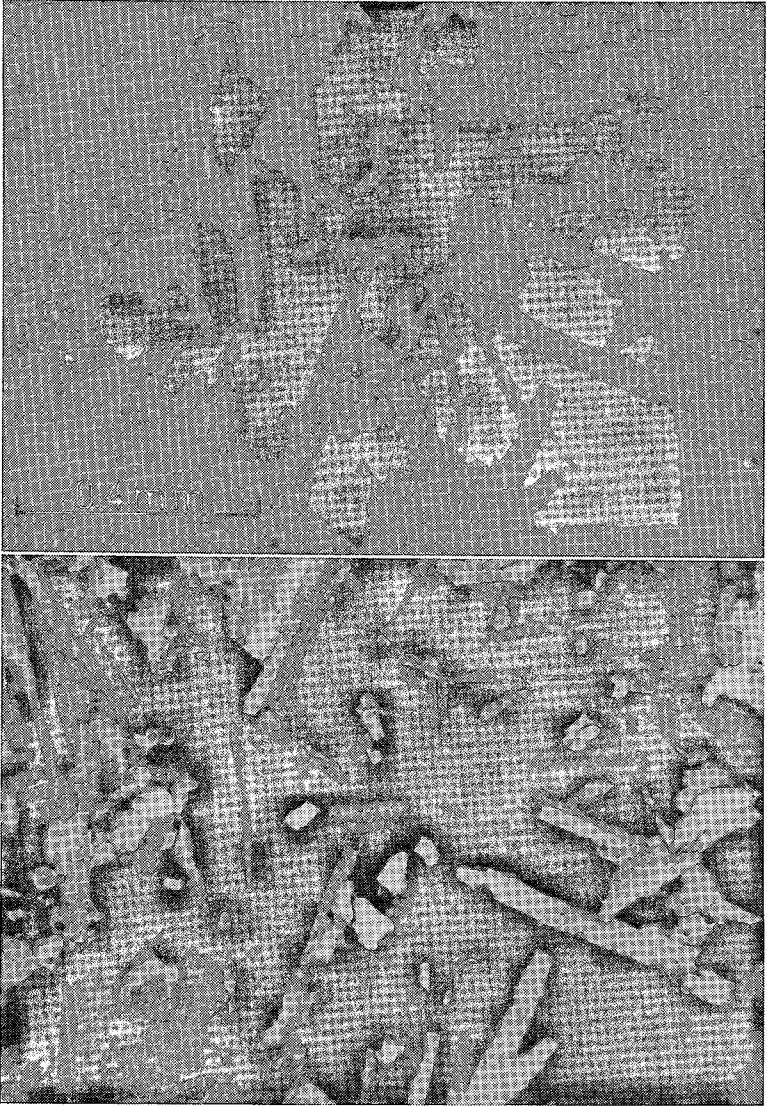
FIG. 6. Tantalite (black) fills interstices among platy crystals of albite in sodic aplite. Assemblage (b) of zone (6), thin section in polarized light.
FIG. 7. The same tantalite as in Fig. 6, nicols crossed.

Both minerals are black, and have a dark brown streak. In transmitted light, these minerals are opaque. In reflected light with a blue filter, they are bright grey, and under crossed polars they have a red-brown internal reflection which almost masks the anisotropism.

X-ray diffraction

Crystallographically the two orthorhombic minerals have, as noted above, the same cell dimensions except that the *a* period of disordered pseudo-ixiolite is $\frac{1}{3}$ *a* of ordered tantalite (Table 5). The difference between the two cells shows clearly on single-crystal photographs as weak reflections on tantalite patterns which divide into three the *a** period on pseudo-ixiolite patterns. We took precession photographs of one tantalite, four pseudo-ixiolites, and two of the same pseudo-ixiolite crystals heated. These pictures confirmed that both minerals have space group symmetry *Pbcn*. Some of the pseudo-ixiolite specimens showed, even before heating, weak extra reflections indicating some degree of ordering, that is, of transition to tantalite. The two pseudo-ixiolite crystals that were heated (for 17 hours at 1000°C at fO_2 of 10^{-14} atm.) showed intensities for the extra reflections that are comparable to those on photographs of a natural tantalite (Grice 1970).

Table 3 gives the cell dimensions for two unheated tantalites and one heated. Table 4 gives the cell dimensions for four unheated and three heated pseudo-ixiolites; the cell dimensions given relate to the true small cell of pseudo-ixiolite for all the unheated material, and to the corresponding sub-cell for the (tantalite-like) heated material. Table 4 shows that, for pseudo-ixiolites, *a* increases appreciably, *b* increases slightly, *c* decreases appreciably, and *V* remains nearly constant after heating. This relationship is emphasized by Fig. 8 which shows *a* versus *c* for our Tanco specimens, compared to the fields of a, c plots of the Greer Lake tantalites and pseudo-ixiolites (after Černý & Turnock 1971a).

Indexed powder data for one tantalite and one pseudo-ixiolite are given in Table 6 along with the data of Nickel *et al.* (1963a) for a columbite-tantalite from Tinton, South Dakota and for a true ixiolite from Skogböle, Finland. The Table shows the following:

(1) small differences in spacings between corresponding reflections of the Tanco tantalite and the Tinton columbite-tantalite, and some small differences in indexing of the reflections with $d < \sim 2.3$ Å for the two minerals;

(2) a very close similarity of the pseudo-ixiolite and ixiolite patterns but with the latter having four weak additional reflections; and

(3) identical indexing of the tantalite and pseudo-ixiolite patterns (after account is taken of the difference in the *a* periods), and the additional reflections of tantalite in relation to pseudo-ixiolite, the most valuable of which for differentiating the two minerals being 200, 110, and 400 with *d* values of 7.2, 5.3 and 3.6 Å respectively.

Heating experiments

Tables 3 and 4 indicate that one tantalite specimen and three pseudo-ixiolite specimens were heated, and the Tables give the cell dimensions measured for the minerals after heating; the conditions for the heating are given in footnotes to the two Tables (Grice 1970, Table 8, where some further details are also given). Nickel *et al.* (1963b) and Gouder de Beauregard *et al.* (1967) carried out heating experiments on pseudo-ixiolites and tantalites, but both of those authors heated their specimens in air whereas we heated ours in controlled conditions at different oxygen fugacities.
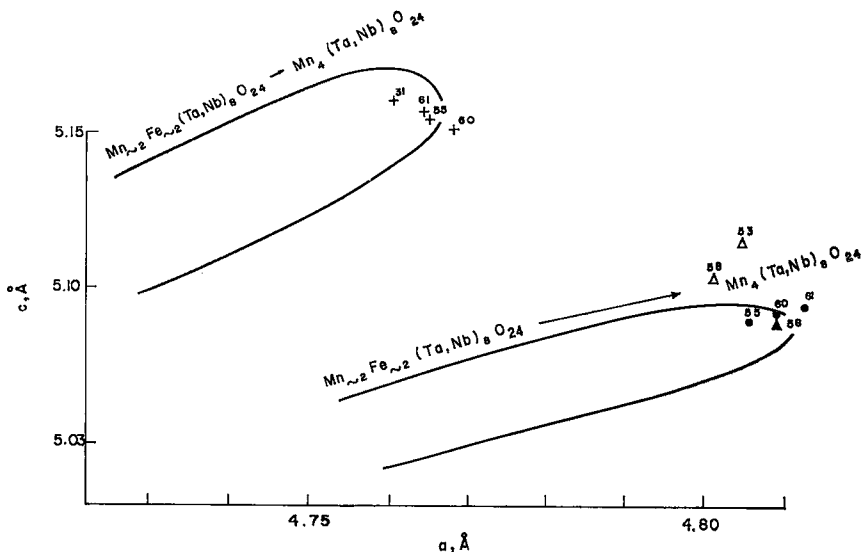

Fig. 8. Plots of *a* versus *c* for natural and heated tantalites (empty and solid triangles respectively), and for natural and heated pseudo-ixiolites (crosses and solid circles respectively). The *a* period relates to the true small cell of natural pseudo-ixiolites and to the corresponding sub-cell of all the tantalite-type phases. The fields of the compositional range Mn$\sim_2$Fe$\sim_2$(Ta,Nb)$_8$O$_{24}$–Mn$_4$(Ta,Nb)$_8$O$_{24}$ for columbite-tantalite (lower right) and pseudo-ixiolite (upper left) are derived from Černý & Turnock (1971).

In addition to the changes in cell dimensions after heating described in the preceding section, other observations we made were : (1) the ordering of pseudo-ixiolite to tantalite at 1000°C is apparently independent of fO_2 ; and (2) the colour of both granular and powdered samples does seem to depend upon fO_2, the more reducing the atmosphere the darker the colour. The unheated specimens were brownish-black ; on heating in an oxidizing atmosphere, they turned ochre yellow, and in a reducing atmosphere they turned back. We noted earlier that wodginite too darkens in a reducing atmosphere. On the basis of colour changes, our tantalites and pseudo-ixiolites appear to have formed in an atmosphere with fO_2 slightly less then the magnetite-wustite transition. At 1000°C and at a total pressure of 1 atm. this would correspond to $fO_2 \sim 10^{-14}$ atm. If we assume the pegmatite formed between 600°C and 400°C and at 2 Kb total pressure, these tantalites and pseudo-ixiolites would have formed in an atmosphere with fO_2 between 10^{-25} and 10^{-35} atm. respectively.

Chemistry

The results of the microprobe analyses of five tantalites are given in Table 3, and of six pseudo-ixiolites in Table 4. As in the case of the wodginite analyses in Table 2, Mn and Fe are arbitrarily reported as MnO and FeO.

The probe revealed that these minerals are homogeneous within grains, and that each of the two minerals is fairly consistent in composition in different grains throughout the mine ; notable exceptions to this second observation are tantalite specimen G69-52, and pseudo-ixiolite specimen G69-59, the compositions of both differing markedly from those of the other tantalites and pseudo-ixiolites respectively. Because of their differing compositions, these two specimens have been arbitrarily omitted from the mean compositions for the tantalites and the pseudo-ixiolites given in Tables 3 and 4 respectively. Comparisons of the compositions of the tantalites and the pseudo-ixiolites with each other and with the wodginites are given later.

The formula of tantalite is of the type $A_4B_8O_{24}$. Table 2 shows that for our specimens, Ta and Nb total close to 8 so that, on purely chemical grounds, the formula for our specimens may be written as $(Mn,Ti,Fe,Sn)_4$ $(Ta,Nb)_8O_{24}$. Nickel *et al.* (1963b) point out that ixiolite and pseudo-ixiolite probably have all cations disordered into one structural site, and that the formula would thus be of the type $A_{12}O_{24}$. In this interpretation our pseudo-ixiolites would have the formula $(Ta,Nb,Mn,Ti,Sn,Fe)_{12}O_{24}$. This matter is discussed further in relation to the crystal structures later in the paper.

TABLE 6. X-RAY POWDER DIFFRACTOMETER DATA FOR PSEUDO-IXIOLITE, TANTALITE, COLUMBITE AND IXIOLITE.

CuKα radiation for all minerals.

| Pseudo-ixiolite[1] | | | | Tantalite[2] | | | | Columbite-Tantalite[3] | | | Ixiolite[3] | | | |
| Tanco (G69-61) | | | | Tanco (G69-53) | | | | Tinton, S. D. (Nickel et al. 1963a) | | | Skogböle, Finland (Nickel et al. 1963a, b) | | | |
hkl	I	d(obs.),Å	d(calc.),Å	hkl	I	d(obs.),Å	d(calc.),Å	hkl	I	d(obs.),Å	hkl	I	d(obs.),Å	d(calc.),Å
				200	6	7.227	7.208	200	12	7.13				
				110	4	5.352	5.344	110	4	5.30				
110	30	3.673	3.669	310	35	3.687	3.688	310	48	3.66	110	32	3.65	3.653
				400	8	3.604	3.604	400	9	3.57				
111	100	2.991	2.990	311	100	2.991	2.992	311	100	2.96	111	100	2.98	2.980
020	10	2.877	2.877	020	10	2.877	2.877	020	10	2.86	020	5	2.87	2.866
002	11	2.579	2.579	002	11	2.560	2.558	002	6	2.53	002	13	2.57	2.576
021	19	2.512	2.513	021	16	2.508	2.508	021	12	2.49	021	20	2.51	2.504
200	6	2.381	2.381	600	15	2.404	2.403	600	12	2.38	200	5	2.37	2.371
								511	1	2.279				
											102	2	2.265	2.263
				420	2	2.247	2.248	302	3	2.236				
								321	4	2.207	121	4	2.213	2.214
112	6	2.110	2.110	312	2	2.102	2.102	312	5	2.084	112	9	2.104	2.105

hkl	I	d	d	hkl	I	d	hkl	I	d	d	hkl	I	d	d
421	3			421	3	2.043	421	3	2.059	2.058	211	1	2.017	2.016
022	8	1.9198	1.9204	022	5	1.898	022	8	1.9106	1.9116	022	4	1.915	1.916
220	5	1.8340	1.8344	620	9	1.831	620	6	1.8442	1.8404	220	6	1.826	1.826
512 711				512 711	4	1.796	512 711	8	1.8140	1.8132				
130	19	1.7792	1.7793	330	14	1.772	330	15	1.7812	1.7813	130	13	1.772	1.772
202	22	1.7490	1.7494	602	12	1.735	602	20	1.7500	1.7513	202	17	1.746	1.744
221	23	1.7288	1.7284	621	22	1.721	621	20	1.7333	1.7349	221	24	1.722	1.722
				331	2	1.672								
113	8	1.5578	1.5568	313	8	1.534	313	10	1.5421	1.5420	113	12	1.554	1.554
				910	1	1.516					310	1	1.521	1.524
222	6	1.4953	1.4948	622	4	1.484	622	5	1.4930	1.4932	222	1	1.490	1.490
911 802	20	1.4666	1.4670	023 911 332	14 12	1.465 1.454	911 802	15 3	1.4763 1.4708	1.4765 1.4712	023 311 132	29	1.459	1.473 1.461 1.460
332	15			040	1	1.432	332	15	1.4600	1.4596				
041	3	1.3861	1.3858	041	2	1.380					041	1	1.380	1.380

[1]For composition, cell dimensions, space group and specific gravity, see Table 4.

[2]For composition, cell dimensions and space group, see Table 3.

[3]The indexing of Nickel et al. (1963a) has been transformed to agree with our setting given in Table 4. In neither that paper nor their later one (1963b) do Nickel et al. give chemical data or cell dimensions for their columbite-tantalite, but for their ixiolite the latter give composition $(Ta_{1.75}Fe_{0.71}Sn_{0.73}Nb_{0.50}Mn_{0.48}Zr_{0.03}Ti_{0.03}W_{0.01})O_{7.98}$, (transformed) cell dimensions a 4.742, b 5.731, c 5.152 Å, calculated density 7.392.

OTHER MINERALS

Tapiolite

This mineral is rare in the Tanco pegmatite, and it may be seen only under the microscope as small anhedral blebs in wodginite or in tantalite from zone (6). It can be recognized in polished sections by its weak reflective pleochroism and strong anisotropism; its reflectivity is close to that of wodginite and tantalite, but its internal reflection is not nearly as marked.

The results of microprobe analyses of two grains are given in Table 7. These grains are from widely separated localities within the pegmatite, yet their compositions are very similar. The mean composition of these two tapiolites may be written, in conformity with the general formula $A_2B_4O_{12}$, as $Fe^{2+}_{1.86}Mn^{2+}_{0.29}Ti^{4+}_{0.02}Sn^{4+}_{0.01}(Ta^{5+}_{3.77}Nb^{5+}_{0.17}) \, O_{12}$.

TABLE 7. ANALYSES OF TAPIOLITE, MICROLITE AND ILMENITE

Analyses in Weight Percent	Tapiolite[1]		Microlite[1]		Ilmenite[2]	
Specimen No.	G69-21	G69-52	G69-30	G69-31		
FeO	13.5	14.0	0.5	0.5	FeO	36.0
MnO	2.1	2.2	0.8	0.7	TiO$_2$	51.0
SnO$_2$	0.2	0.2	0.5	0.2	MnO	9.1
TiO$_2$	0.2	0.1	1.0	1.0	MgO	0.5
Ta$_2$O$_5$	85.0	85.0	73.	74.	Al$_2$O$_3$	tr.
Nb$_2$O$_5$	2.4	2.2	6.0	5.5	SiO$_2$	0.0
Total	103.4	103.7	81.8	81.9		96.6

Numbers of Cations on the Basis of 12 (O)

Fe^{2+}	1.83 ⎫		1.90 ⎫	
Mn^{2+}	0.29 ⎬ 2.16		0.30 ⎬ 2.22	
Sn^{4+}	0.01 ⎪		0.01 ⎪	
Ti^{4+}	0.03 ⎭		0.01 ⎭	
Ta^{5+}	3.75 ⎫ 3.93		3.79 ⎫ 3.96	
Nb^{5+}	0.18 ⎭		0.17 ⎭	
Total	6.09		6.18	

[1] Analyzed by electron microprobe by Mr. S. Jones, Nuclear Research Establishment, Pinawa, Manitoba.

[2] Analyzed by atomic absorption and X-ray fluorescence by J. D. Grice.

Microlite

This mineral was identified in a small number of specimens by means of powder diffractograms or the probe, but was found later by x-ray diffraction to constitute a substantial portion of the tantalum ore concentrate from zone (6). Microlite is difficult to distinguish in the hand specimen or in reflected light under the microscope, but when it can be seen in the hand specimen, it resembles a highly lustrous yellowish quartz. Under the petrographic microscope it is colourless, isotropic and of high relief (Fig. 9). Most microlite is closely associated with wodginite, tantalite or pseudo-ixiolite. Granular microlite from zone (6) appears to be primary, but in zones (4) and (5) microlite clearly replaces pseudo-ixiolite.

Incomplete probe analyses on two specimens, one from each of zones (4) (G69-31) and (5) (G-69-30), are given in Table 7, the incompleteness arising from the fact that we were unable to analyze for Ca quantitatively. Calcium was identified qualitatively as a major element, and W, U, Si, Cs and Sb as minor or trace elements.
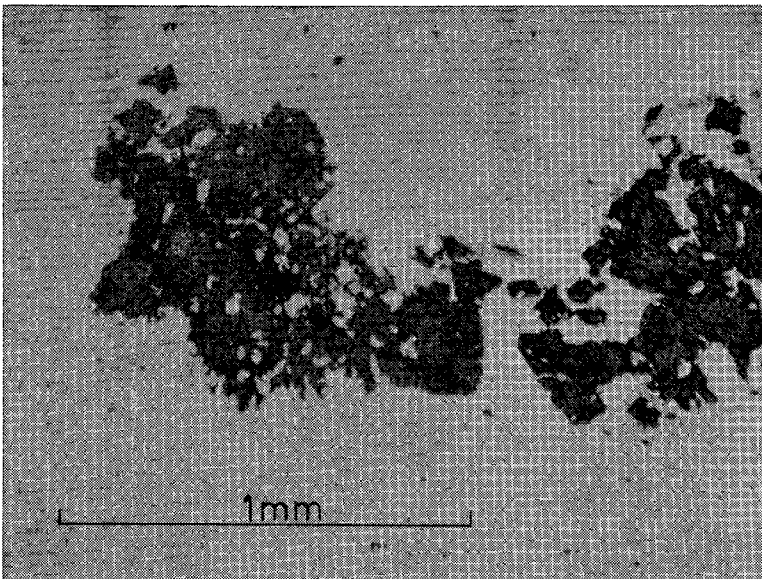
Fig. 9. Microlite grains (grey, high relief) with some wodginite (black) in altered microcline-perthite. Assemblage (a) of zone 6, polarized light.

Cassiterite

Although much of the Sn in the Tanco pegmatite occurs as a constituent of the three principal Ta minerals, especially wodginite, some is also present as cassiterite. As shown in Table 1, most cassiterite is concentrated in zone (6), commonly in association with tantalite; its occurrence in zones (4) and (5) is very subordinate, and little is known about its abundance in zone (9).

In reflected light cassiterite has a lower reflectivity and less marked internal reflections than tantalite. Under the electron beam of the probe it is luminescent.

Microprobe analyses indicate that the cassiterite contains up to 3% Ta_2O_5 or Nb_2O_5, as well as minor amounts of TiO_2 and FeO.

Ilmenite

No ilmenite has been found in hand specimens to date, but some was separated from shaker table concentrates from the mill using the Frantz Isodynamic Separator. We are indebted to A. C. Turnock for the separation and identification of the ilmenite.

The ilmenite concentrate was analyzed by atomic absorption and x-ray fluorescence, and the results are given in Table 7. The low total may result from the fact that we have expressed all Fe as FeO : commonly in ilmenites about one-half the Fe exists as Fe_2O_3, and if this were so in this specimen, the total would come much closer to 100%. Because of the high MnO in this ilmenite, it should strictly be termed manganilmenite.

RELATIONSHIPS BETWEEN THE TANTALUM OXIDE MINERALS
IN THE TANCO PEGMATITE

Chemistry

Some of the chemical relationships among the tantalum oxide minerals in the Tanco pegmatite are shown in the ternary plot of Fig. 10 prepared from the results given in Tables 2, 3, 4 and 7. Fig. 10 and these Tables show that the wodginites have on the average ~ 16½% more (SnO_2 + TiO_2), ~ 12½% less (Ta_2O_5 + Nb_2O_5), and ~ 1½% less (MnO + FeO) than the tantalites-pseudo-ixiolites. The chemical differences between the tantalites and the pseudo-ixiolites are much smaller than those between the wodginites and the tantalites-pseudo-ixiolites, but they are nevertheless real : most tantalites have on the average ~ ½% less (SnO_2 + TiO_2), ~ 1% more (Ta_2O_5 + Nb_2O_5), and ~½% less (MnO + FeO) than the pseudo-ixiolites. The two tapiolite specimens can be seen to have com-

positions that, with respect to the amounts of these pairs of oxides, are close to those of the tantalites but with, on the average, $\sim 1\%$ less $(SnO_2 + TiO_2)$, $\sim 2\%$ more $(Ta_2O_5 + Nb_2O_5)$, and $\sim 1\frac{1}{2}\%$ more $(MnO + FeO)$.

The ratio $FeO/(FeO + MnO)$ and $(Ta_2O_5)/(Ta_2O_5 + Nb_2O_5)$ for the three principal and the two minor Ta oxide minerals at Tanco are plotted in Fig. 11. The wodginites have generally higher Ta/Nb and Fe/Mn ratios than the tantalites-pseudo-ixiolites. The tantalites have, in general, slightly higher Fe/Mn and Ta/Nb ratios than the pseudo-ixiolites. The two tapiolite specimens have much higher Fe/Mn and Ta/Nb ratios than the tantalites-pseudo-ixiolites, and much higher Fe/Mn ratios than, and about equal Ta/Nb ratios as, the wodginites. No chemical data are available for the granular, primary microlite of zone (6) ; the two analyzed microlites have much higher Ta/Nb ratios than the pseudo-ixiolites replaced by them. Two specimens, tantalite G69-52 and pseudo-ixiolite G69-59, show marked deviations from these general relationships. Tantalite G69-52 is associated with tapiolite, and its environment may, therefore, have been such as to give it relatively high Fe/Mn and Ta/Nb ratios for a Tanco tantalite. Pseudo-ixiolite G69-59 is unique among our pseudo-ixiolite specimens in that it is associated with spodumene and cassiterite although it, like most of the others, is in zone (4).
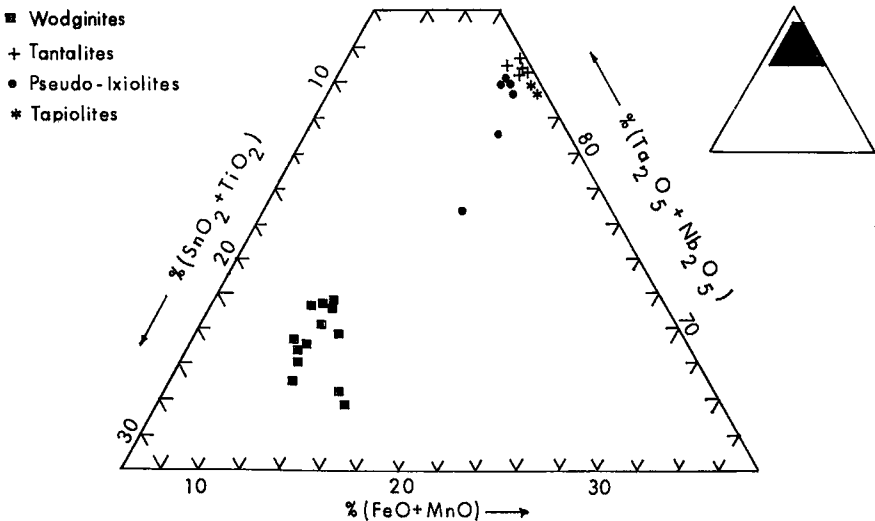
FIG. 10. Ternary plot of $(Ta_2O_5 + Nb_2O_5)$, $(SnO_2 + TiO_2)$, and $(FeO + MnO)$, in wt.%, for the Tanco wodginites, tantalites, pseudo-ixiolites, and tapiolites.

Unit cell dimensions

The mean unit cell dimensions for the unheated wodginites, tantalites and pseudo-ixiolites are given in Tables 2, 3 and 4. If these three sets of values are put into comparable terms by relating them all to the simplest cell, that of pseudo-ixiolite, using the relationships given in Table 5, they appear as follows :

	a or a' Å	b or b' Å	c Å	β	V Å³
wodginite	4.750	5.727	5.113	91°03′	139.21
tantalite	4.803	5.756	5.110	(90°)	141.15
pseudo-ixiolite	4.762	5.793	5.158	(90°)	141.30

These figures show that all corresponding cell dimensions and cell volumes differ by $< 1\frac{1}{2}\%$ from each other. The a and b dimensions for wodginite are smaller than those for tantalite and pseudo-ixiolite, with c of wodginite nearly equal to c of tantalite and smaller than c of pseudo-ixiolite. Com-paring the dimensions of closely similar tantalite and pseudo-ixiolite, a, b and c of tantalite are larger, smaller, and smaller respectively than a, b and c of pseudo-ixiolite.

Regarding cell volumes, that of wodginite is distinctly less than that of tantalite and pseudo-ixiolite which are nearly equal to each other. The relationships of the cell volumes to the ratio $MnO/(MnO + FeO + TiO_2 + SnO_2)$ using weight percentages, for all specimens of the three minerals are shown graphically in Fig. 12 where all are related to the simplest cell of pseudo-ixiolite ; the plot includes all of our Tanco specimens analyzed in detail, as well as three tantalites and five pseudo-ixiolites from other Manitoba pegmatites described by Černý & Turnock (1971a). The Figure shows that the volume increases with an increase in MnO. The probable explanation for this is that Mn^{+2} has an appreciably larger ionic radius than all the other ions involved as the following tabulation of Goldschmidt's radii in Å units shows : Fe^{2+} 0.82 Fe^{3+} 0.67 Mn^{2+} 0.91 Sn^{4+} 0.74 Ti^{4+} 0.64

Structural relationship between tantalite, pseudo-ixiolite and wodginite

Nickel *et al.* (1963a and b) showed that, on the basis of closely related cell dimensions and space groups, and colsely similar powder diffracto-grams, these three minerals must have closely related structures. We have referred to this earlier in the X-Ray Diffraction section under Wodginite, and we have summarized the crystallographic relationships in Table 5.

Only the structure of tantalite (columbite) has been published to date (Sturdivant 1930). In the true cell (as distinct from the pseudo-cell) in this structure, as Nickel *et al.* (1963b) have discussed, the 24 O atoms are in an approximately hexagonal close-packed arrangement parallel to (100)

(in our setting) with the 4(Fe,Mn) atoms occupying one set of octahedral sites and the 8(Nb,Ta) another set. The true structure is thus ordered with respect to (Fe,Mn) and (Nb,Ta), and this is implied in the conventional form of writing the cell content for columbite-tantalite, $(Fe,Mn)_4(Nb,Ta)_8O_{24}$ (Table 5).

In ixiolite, and hence presumably in pseudo-ixiolite which has the same cell dimensions, space group and cell content, as Nickel *et al.* (1963b)
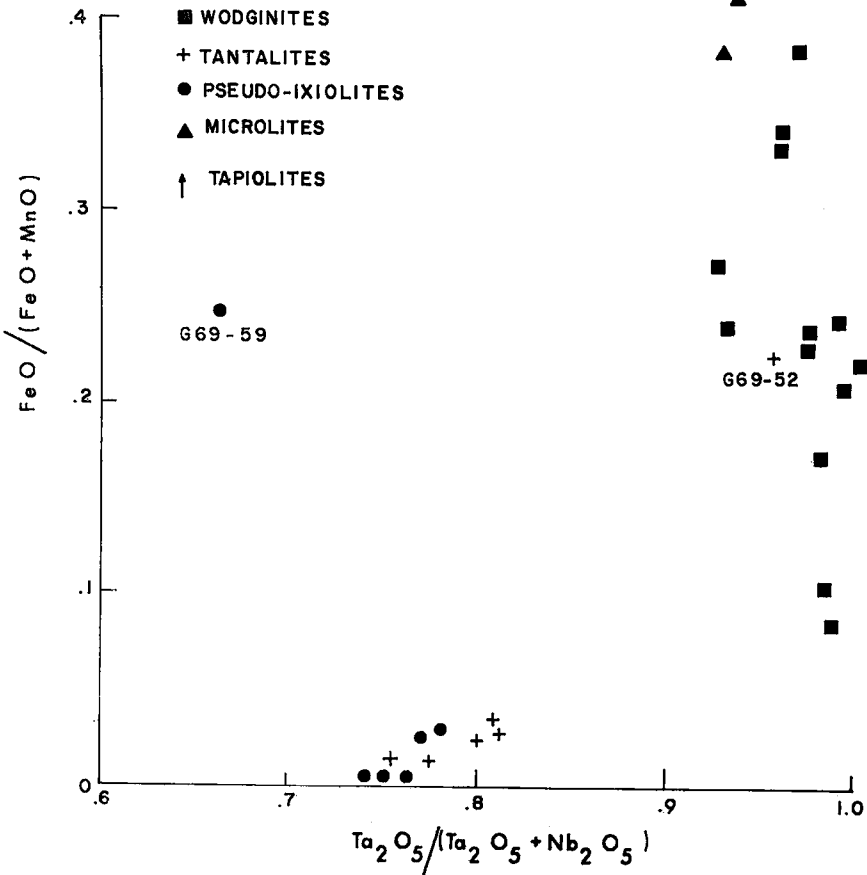

FIG. 11. The FeO/(FeO + MnO) ratio plotted against the $Ta_2O_5/(Ta_2O_5 + Nb_2O_5)$ ratio of the Tanco tantalites, pseudo-ixiolites, wodginites, tapiolites, and microlites. The arrows indicate the $Ta_2O_5/(Ta_2O_5 + Nb_2O_5)$ ratio of tapiolite, and the attached numbers show the FeO/(FeO + MnO) ratio.

describe, the a period is $a/3$ of the true cell of tantalite (with b and c the same) (our setting), and ixiolite has thus one-third the volume and cell content of tantalite. Thus it contains a total of only 4 metal atoms instead of 12, and the space group apparently requires that all 4 metal atoms in ixiolite occupy one 4-fold structural site. For this reason, Nickel *et al.* (1963a) concluded that the metal atoms in ixiolite are disordered into one site that, in the smaller ixiolite cell, is comparable to the two different metal sites in the larger columbite-tantalite cell. Powder intensities which they calculated for a cation-disordered ixiolite gave reasonable agreement with the observed values. A single-crystal structure analysis of ixiolite (or pseudo-ixiolite) is still desirable, but until this has been carried out, it is
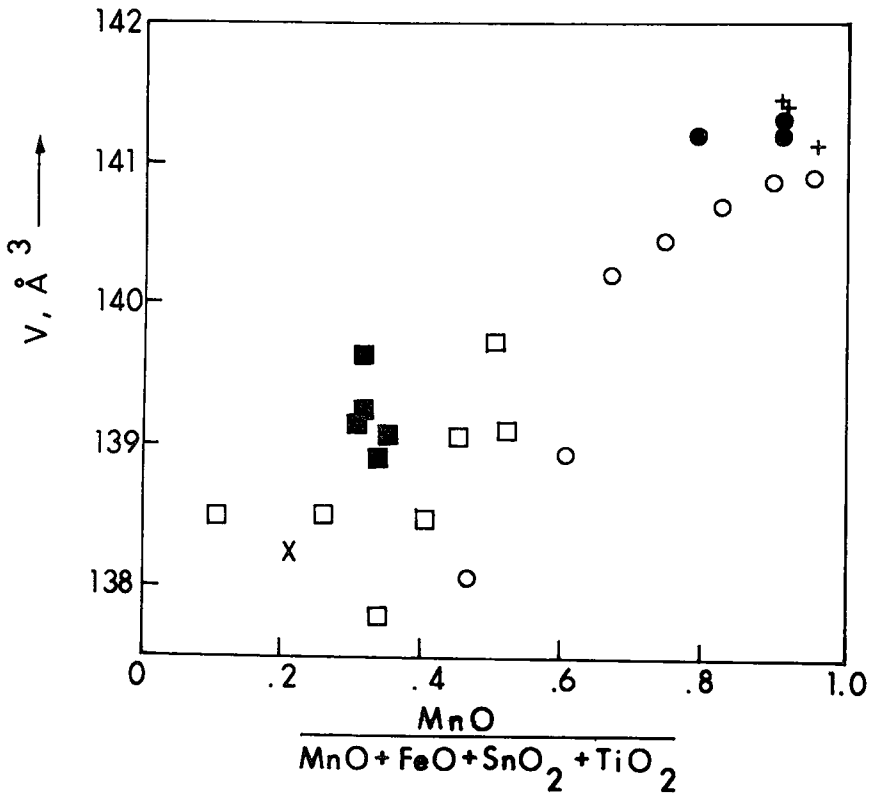

Fig. 12. The cell volumes of the Tanco wodginites (solid squares), tantalites (crosses), and pseudo-ixiolites (solid circles), and Greer Lake pseudo-ixiolites (empty circles) and tantalites-columbites (x) (after Černý & Turnock 1971a), plotted against the $MnO/(MnO + FeO + SnO_2 + TiO_2)$ ratio.

reasonable to accept the interpretation of Nickel *et al.* (1963b) that the metal atoms in ixiolite (and pseudo-ixiolite) are disordered, and that the cell content should be written as $(Ta,Nb,Mn,Ti,Sn,Fe)_4O_8$ for the Tanco pseudo-ixiolites. The strong pseudo-cell of tantalite has pseudo $a' =$ true $a/3$ like the true cell of pseudo-ixiolite ; this pseudo-cell is presumably an expression of the ordering of the metal atoms in tantalite in relation to those in pseudo-ixiolite.

No structure of wodginite has yet been published but, as we have noted earlier, a structure analysis of wodginite specimen G69-17 is at present nearing completion in our Laboratory by Elphick, Ferguson & Grice based on the smaller pseudo-cell which has one-quarter the volume of the true cell, and contains a total of 4 metal atoms and 8 oxygens (Table 5). Pending the final interpretation and publication of this analysis, it can be said at present that the pseudo-structure has the space group $P2/c$, not Pc, and that all the Ta atoms (1.98 from the probe analysis) occupy one 2-fold site, and all the other metal atoms (2.03 from the probe analysis) (Table 2) occupy another 2-fold site. Both the metal and the oxygen positions are comparable to the corresponding ones in the columbite structure of Sturdivant (1930).

We have at present no explanation for the monoclinic symmetry of wodginite in relation to the orthorhombic symmetry of the other two minerals, but it may be related to the valence states and the distribution of the cations. A modern, accurate refinement of Sturdivant's (1930) columbite structure using an analyzed columbite-tantalite should be carried out to aid in the interpretation of the crystal chemistry of these minerals, and the structure of Tanco tantalite specimen no. G69-58 is presently being refined in our Laboratory.

Because our structure analysis of wodginite was based only on the small pseudo-cell, we cannot answer definitely the question posed by Nickel *et al.* (1963a) whether, in the true cell of wodginite, the 16 cations occupy two sets of four, and one set of eight, equivalent positions in $C2/c$, or four sets of four equivalent positions in Cc. The fact that two of the four Ta atoms occupy one of the two 2-fold sites in the small cell suggests that all or most of the Ta atoms would occupy one 8-fold site in the large cell, in which case the true space group would be $C2/c$, and the structure would be to some degree ordered. Meanwhile, we suggest that the content of the small cell of the Tanco wodginite be written as $(Mn,Fe,Sn,Ti,Nb)_2Ta_2O_8$ to indicate the ordering of the Ta atoms (Table 5) ; the content of the large cell could probably be written with reasonable certainty as four times this, namely $(Mn,Fe,Sn,Ti,Nb)_8Ta_8O_{32}$.

GENETIC CONSIDERATIONS

The following conclusions can be drawn from the distribution and chemistry of the tantalum oxides and associated minerals in the Tanco pegmatite.

(i) These minerals are accumulated in the innermost portions of the pegmatite body, in the lower, upper, and central intermediate zones (4), (5), and particularly (6) (Table 1). These zones are among the latest primary units of the pegmatite, succeeded only by quartz and pollucite bodies (7) and (8), and by the metasomatic lepidolite zone (9) (see Crouse & Černý 1972).

This is the usual location of economic tantalum mineralization as known from other pegmatites (Ginzburg 1956, Kuzmenko 1960). Besides this, the muscovite + wodginite + microlite (+ tapiolite) association which replaces mainly the K-feldspar in assemblage (a) in zone (6) compares with the metasomatic character of Ta-mineralization, known from late assemblages in many pegmatites (Ginzburg 1956, Kuzmenko 1960, Beus & Sitnin 1961). It is quite possible that much of the pseudo-ixiolite in zones (4) and (5) is also of metasomatic origin, being closely associated with cleavelandite veinlets.

(ii) There is a general increase in the Ta/Nb ratio and a decrease in the Mn/Fe ratio in the Ta-oxide minerals during the crystallization of the pegmatite. The earliest pseudo-ixiolites of zones (4) and (5) are richest in Mn and Nb, the tantalites from the albitic aplite (b) of zone (6) are slightly richer in Fe and Ta, and the wodginites * associated with metasomatic muscovite in assemblage (a) of zone (6) are the richest in Fe and Ta ** (Fig. 11). The Fe-rich tapiolite and ilmenite also occur in zone (6).

The increase in the Ta/Nb ratio during evolution of a pegmatite is well known from many localities (Cameron et al. 1949, Heinrich 1953, Staatz & Trites 1955, Ginzburg 1956, Solodov 1959, Slepnev 1964, but compare Fersman 1940 and Kornetova 1961 for reverse trends). However, the decreasing Mn/Fe ratio in Ta-oxides is quite surprising; gradual increase

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* There is no direct information available about the chemistry of the granular microlite of zone (6), associated mainly with wodginite, but the analyses of commercial wodginite + microlite concentrates (courtesy Mr. C. T. Williams, Tanco) show no increase in Nb against wodginite concentrates with negligible microlite; thus the Ta/Nb ratio of this microlite should be about the same as for wodginite.

** The wodginite + microlite (+ tapiolite) association in assemblage (a) of zone (6) is mostly metasomatic, associated with muscovite replacing K-feldspar. This association is thus presumably later than wodginite + tantalite from the albitic aplite nodules (b) of the same zone (see also Crouse & Černý 1972).

in Mn is almost "mandatory" in similar sequences (Heinrich 1953, Ginzburg 1960).

It is possible, of course, that the most conspicuous increase in Fe between tantalite and wodginite is strongly influenced by the structural, crystallochemical difference between the two minerals. On the other hand, the presence of the Fe-rich ilmenite and tapiolite in association with wodginite and microlite in zone (6) suggests a general enrichment in Fe in the whole mineral assemblage.

(iii) The only reaction among the Tanco Ta-minerals observed to date is the replacement of pseudo-ixiolite by microlite in zones (4) and (5). The metasomatic microlite is considerably enriched in Ta, as is usual in similar occurrences (Ginzburg 1956).

(iv) Along with the increase in Ta and Fe, Sn and Ti were also accumulated in the late zones and assemblages that carry Ta-minerals. Wodginite from zone (6) is the main Sn, Ti-carrier among the Ta-oxides; cassiterite is much more abundant in zone (6) than in the earlier zones, and ilmenite occurs only in this zone.

The enrichment of the late zone (6) in Sn, due to a gradual accumulation of this element during the pegmatite crystallization, seems indisputable. The source and migration of Ti is, however, not clear at present. Ilmenite seems to occur mainly in the upper parts of zone (6), closely adjacent to the amphibolite in the roof of the pegmatite body. The Tanco pegmatite generally shows only negligible traces of reaction with the wallrock, but a Ti-contamination of zone (6) from the hanging-wall amphibolite could be considered a possibility. It should be noted that such a contamination would also explain the "anomalous" Fe-enrichment of zone (6), discussed in (ii).

(v) Despite the relative enrichment in Fe in the late assemblages of zone (6), the overall composition of the Ta-oxides and associated minerals is definitely Mn-rich. This is particularly well illustrated by the compositions of ilmenite and wodginite, the major Fe-bearing minerals (neglecting the trace amounts of Mn-poor tapiolite) : ilmenite is a Mn-rich variety, and wodginite is the Fe-poorest among all occurrences of this species. This strong predominance of Mn over Fe is evident also from the compositions of other Fe, Mn-bearing minerals, not affected by contamination from the wallrock (e.g., Mn-rich lithiophilite; unpublished data of P.Č.). A general enrichment in Mn and impoverishment in Fe is quite common in Li-rich pegmatites, compared to the less differentiated Li-poor types.

(vi) The position of wodginite in the crystallization sequence of the Tanco Ta-minerals is significant in terms of the oxygen fugacity. According to Turnock (1966), a high fO_2 is necessary for crystallization of wodginite

(the Fe-content of which is supposed to be always partly ferric). An increase in fO_2 can be expected during the late stages of pegmatite crystallization, due to a general increase of vapour pressure. Thus wodginite should originate in late assemblages that follow after those carrying tantalite and/or pseudo-ixiolite, and this is where wodginite actually occurs in the Tanco pegmatite (Table 1).

The albitic aplite (b) in zone (6) is particularly interesting in this respect since it carries both tantalite and wodginite ; this suggests an oxygen fugacity compatible with crystallization of both minerals.

In general, the world-wide scarcity of wodginite suggests that fO_2 values high enough for formation of this phase are seldom reached in pegmatite crystallization. The geological environments and paragenetic relations of the wodginite-bearing pegmatites should be examined for features suggestive of the conditions leading to exceptionally high fO_2 during their formation.

The preceding conclusions, and the data they are based on, should not be considered a final word on the tantalum mineralization of the Tanco pegmatite. These data and the derived genetic interpretations should be supplemented and checked, respectively, by a study of the chemical composition of the primary granular microlite of zone (6), of the distribution of ilmenite and microlite in this zone, of the overall mineralogy of the Ta-oxides and associated phases in the metasomatic lepidolite zone (9), and of spatial variations in the distribution of these minerals in all zones that carry them. On the other hand, an investigation of structure, crystal chemistry, stability, compatibility, and order/disorder relationships of all the Fe, Mn, Ta, Nb minerals is necessary to understand the strict separation of tantalite from pseudo-ixiolite, the chemistry of coexisting mineral pairs, and other characteristics of the tantalum mineralization. These presumably contain significant petrological information, but their meaning cannot be understood without extensive basic investigation of the minerals involved.