Canadian Mineralogist
Vol. 14, pp. 550-560 (1976)

THE CRYSTAL STRUCTURES OF TANTALITE, IXIOLITE AND WODGINITE FROM BERNIC LAKE, MANITOBA
II. WODGINITE

R. B. FERGUSON, F. C. HAWTHORNE AND J. D. GRICE*

Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ABSTRACT

The crystal structure of wodginite from the Tanco pegmatite, Bernic Lake, Manitoba has been analyzed using Mo$K\alpha$ radiation and 3-dimensional 4-circle diffractometer data. Monoclinic, *a* 9.489(5), *b* 11.429(7), *c* 5.105(3)Å, β 91.10(5)°. Symmetrically it is possible to choose any one of four possible positions in the parent ixiolite structure as an origin for wodginite, and these possible origins combined with the two possible space groups, centric *C2/c* and acentric *Cc*, result in eight closely related but different possible structures for wodginite. Refinement was carried out for all eight using a procedure that assumed no particular cation ordering scheme. The wodginite structure based on an origin in ixiolite at $(0,0,0)_i$ and space group *C2/c* refined to $R=6.1\%$ with reasonable anisotropic temperature factors for all atoms and is clearly the correct structure. The cations are essentially ordered: $Z=4[ACB_2O_8]=4[Mn_{1.00}(Sn_{0.567}Ta_{0.250}Ti_{0.113}Fe^{3+}_{0.070})(Ta_{0.891}Nb_{0.109})_2O_8]$. Mean octahedral cation-oxygen distances and radii sums are $A=2.185(8)$, 2.19; $B=2.003(8)$, 2.00; $C=2.027(8)$, 2.04Å. Bond strengths distributed inversely as the 4th power of the cation-oxygen distances yielded 2.020, 2.008, 1.978, 1.984 v.u. to O(1), O(2), O(3), O(4) respectively. Two previously described wodginite structures, one by Grice (1973) and Grice & Ferguson (1974), and the other by Graham & Thornber (1974) are based on ixiolite origins $(0,\frac{1}{2},0)_i$ and $(0,0,0)_i$ and on space groups *C2/c* and *Cc* respectively. Both have higher *R* factors (~12%) and different cation ordering patterns from ours, and show poor agreement between mean octahedral cation-oxygen distances and calculated radii sums.

SOMMAIRE

La structure cristalline de la wodginite a été analysée, sur un cristal provenant de la pegmatite de Tanco, Bernic Lake, Manitoba, à l'aide de données tridimensionnelles obtenues en rayonnement Mo$K\alpha$ au diffractomètre à 4 cercles. La wodginite est monoclinique, *a* 9.489(5), *b* 11.429(7), *c* 5.105(3)Å, β 91.10(5)°. Au point de vue symétrie, on peut trouver, dans la structure type de l'ixiolite, quatre origines possibles pour la wodginite; combinées aux deux groupes spatiaux possibles centré *C2/c* et non-centré *Cc*, ces quatre origines conduisent à huit structures possibles, différentes quoique apparentées, pour la wodginite. L'affinement des huit structures a été conduit à l'aide d'une méthode qui ne fait aucune hypothèse sur la mise en ordre des cations. La structure de la wodginite fondée sur une origine de l'ixiolite à $(0,0,0)_i$ et groupe spatial *C2/c*, affinée jusqu'au résidu $R=6.1\%$ avec des coefficients d'agitation thermique anisotrope raisonnables pour tous les atomes, est évidemment la bonne. Essentiellement, les cations sont ordonnés: $Z=4[ACB_2O_8]=4[Mn_{1.00}(Sn_{0.567}Ta_{0.250}Ti_{0.113}Fe^{3+}_{0.070})(Ta_{0.891}Nb_{0.109})_2O_8]$. Les longueurs moyennes les liaisons octaédriques cation-oxygène et les sommes des rayons sont: $A=2.185(8)$, 2.19; $B=2.003(8)$, 2.00; $C=2.027(8)$, 2.04Å. La valence de liaison étant prise inversement proportionnelle à la quatrième puissance de la distance cation-oxygène, on obtient les sommes 2.020, 2.008, 1.978, 1.984 u.v. à O(1), O(2), O(3), O(4) respectivement. Deux structures antérieures de la wodginite, l'une par Grice (1973) et Grice & Ferguson (1974), l'autre par Graham & Thornber (1974), sont fondées sur les origines $(0,\frac{1}{2},0)_i$ et $(0,0,0)_i$ de l'ixiolite et sur les groupes spatiaux *C2/c* et *Cc* respectivement. Elles possèdent chacune un résidu *R* ~12% plus élevé que le nôtre et une ordonnance des cations différente de la nôtre; de plus, l'accord entre les longueurs moyennes des liaisons octaédriques cation-oxygène et les sommes calculées des rayons laisse à désirer dans ces deux structures.

(Traduit par la Rédaction)

INTRODUCTION

In Part I of this pair of papers on the structures of the three principal tantalum ore minerals from the Tanco pegmatite, Bernic Lake, Manitoba, the Introduction gives a general description of the occurrence, nature and interrelationship of the tantalite and ixiolite and, in a general way, of the wodginite. The Introduction, Table 1, and Figure 1 in that paper provide a background to the more detailed description of the nature of wodginite that follows here.

Wodginite was first characterized as a distinct mineral phase by Nickel *et al.* (1963a),

---

*Present address: Mineral Sciences Division, National Museum of Natural Sciences, Ottawa, Ontario, K1A 0M8.

who showed that it occurred at Wodgina, Australia (the type locality) and Bernic Lake, Manitoba. Detailed descriptions of the chemistry and mineralogy of wodginite and its associated minerals are given by Černý & Turnock (1971) and Grice *et al.* (1972). Turnock (1966) showed that wodginite forms over a small compositional range in the system $MnTa_2O_6$–$FeTaO_4$, and he found that it could not be synthesized in the absence of Fe^{3+}. However, Komkov (1970) showed that wodginite can be formed in the absence of Fe^{3+} if Sn^{4+} is present in the system. These experimental results are supported by the chemical variation exhibited by natural wodginites (Grice *et al.* 1972; Graham & Thornber 1974), and suggest that polyvalent cation substitution and ordering play an important part in controlling the stability of this phase. Two different structures have been reported for wodginite, one by Grice (1972) and Grice *et al.* (1974), and the other by Graham & Thornber (1974); the structure reported in the present study is significantly different from either of these. Although all three structures are topologically equivalent, the cation distribution pattern is significantly different in each. As it appears that wodginite forms a distinct phase because of polyvalent cation ordering, it is important to the understanding of the stability of this phase that its cation ordering pattern be correctly characterized. Consequently, the various ordering schemes possible have been extensively investigated in this study, and are reported in detail.

The following conclusions may be drawn from the cell geometry presented in Table 1 and Figure 1 of the Part I paper as well as Figure 1 of this paper:

(1) monoclinic wodginite with $\beta \sim 91°$ has a strong subcell corresponding to the cell of ixiolite (α–PbO_2 structure type); as the symmetry of the subcell is $P2/c$ (Elphick 1972), there are two cation sites rather than one as in ixiolite and thus even the subcell of wodginite could

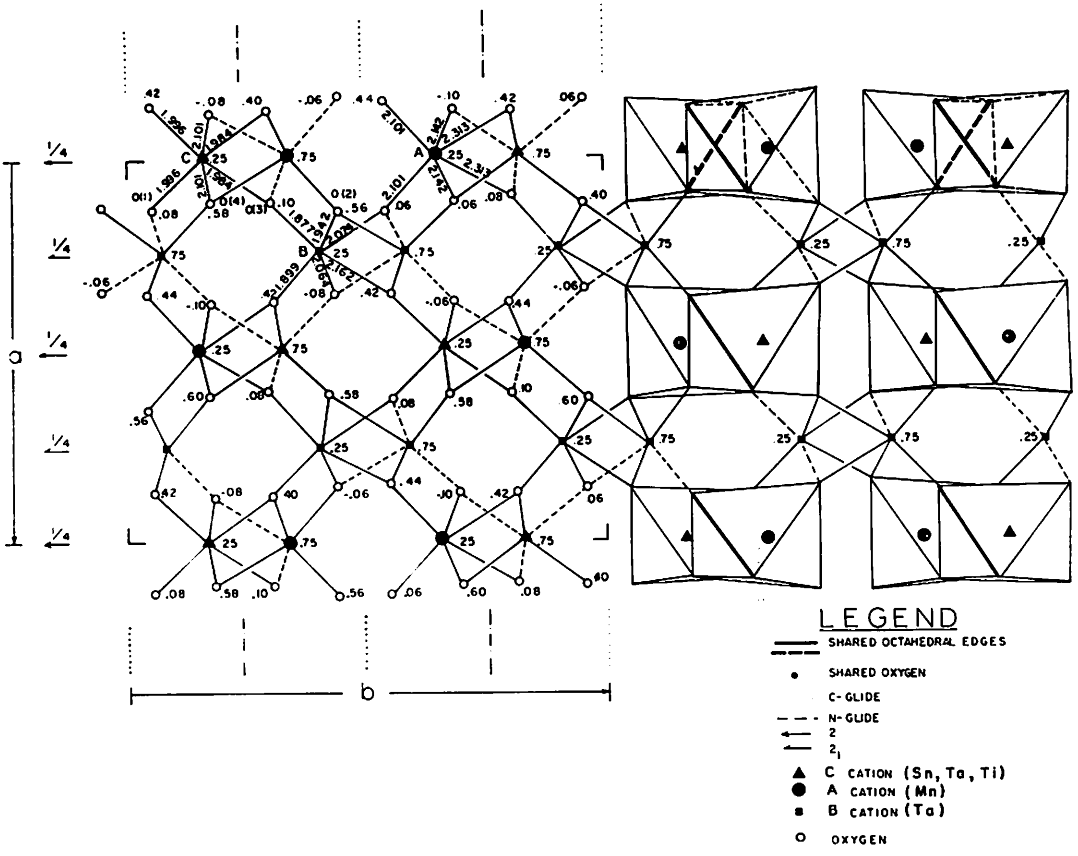

FIG. 1. Projection of the structure of wodginite along *z*. Prototype atoms are labelled A(=Mn), B(=Ta,Nb), C(=Sn,Ta,Ti), O(1), O(2), O(3), O(4). Shown are chains of staggered $(A_{1/2}C_{1/2})$–O octahedra parallel to *z* seen end-on; *B*-O octahedral chains are not shown.

be more cation-ordered than the cell of ixiolite;

(2) relative to the subcell, the true cell of wodginite has doubled *a* and *b* dimensions, but the same *c* dimension, and it has three ($C2/c$) or four (Cc) cation sites; it is therefore possible for wodginite to be much more ordered than either ixiolite or tantalite;

(3) the true cell of wodginite has the following relation to the true cell of tantalite: $a_w \sim 9.5\text{Å} \sim \frac{2}{3}a_t$; $b_w \sim 11.5\text{Å} \sim 2b_t$; $c_w \sim 5.1\text{Å} \sim c_t$. Thus the cell content of wodginite is 4/3 that of tantalite, namely 4/3 $[(A,B)_{12}O_{24}] = (A,B)_{16}O_{32}$.

EXPERIMENTAL

The quality of the wodginite crystals was generally poor, but because specimen G69-17 (Grice *et al.* 1972) is relatively well-crystallized, it was chosen for the single-crystal study. The chemical, physical and crystallographic data for this specimen, including a new electron microprobe analysis of the crystal used for the structure analysis, are given in Table 1.

Because the reflections that differentiate the true cell from the subcell (see Introduction) are weak, a fairly large crystal was used initially to collect the intensities, namely a sphere of ~0.45mm diameter. However, the quality of this crystal was poor and the intensities were not satisfactory. A second data set was collected on a second smaller sphere of ~0.35mm diameter using a Syntex P$\bar{1}$ automatic diffractometer. The cell dimensions given in Table 1 were derived during the automatic orientation procedure; they are slightly different than those derived earlier by Grice *et al.* (1972). Intensities were collected over two asymmetric units out to $2\theta(\text{Mo}K\alpha)$ 60°. For a few of the symmetry-equivalent pairs of reflections, the agreement was poor; the reason for this was not apparent, but where it occurred the larger value was used. The data were corrected for absorption, Lorentz, polarization and background effects and averaged to produce an asymmetric set. A reflection was considered as observed if its magnitude exceeded 3 standard deviations based on counting statistics; this resulted in 814 reflections of which 718 were considered as observed.

TABLE 1. CHEMICAL, PHYSICAL AND CRYSTALLOGRAPHIC DATA FOR WODGINITE

Specimen no. (Grice *et al.* 1972) G69-17

Crystal diameter	~0.35mm	a	9.489(5)Å
Radiation/Mon.	Mo/C	b	11.429(7)
No. of equiv. $\lvert F_{obs}\rvert > 3\sigma$	718	c	5.105(3)
R (observed)	6.1	β	91.10(5)°
R (all data)	6.6	V	553.5Å^3
R_w(observed)	7.5	Space Group	$C2/c$ (No.15)
R_w(all data)	7.6	D(obs)	7.19[5] g/cc
		D(calc.)	7.80
		μ	491 cm^{-1}

Chemical analysis[1]		Cell content Z[2]		Formula used in refinement[3]		Simplest structural formula[4] (Z=4)	
				species	content	site	content
Ta_2O_5	68.64 wt.%	Ta	8.20		Mn 3.98		
Nb_2O_5	3.96	Nb	0.79	Mn*4.74	Fe 0.29	A	Mn 1.00
TiO_2	1.44	Ti	0.47		Ti 0.47		
SnO_2	13.00	Sn	2.27				
Fe_2O_3	0.79	Fe^{3+}	0.29	Ta 8.20	Ta 8.20	2B	Ta 0.891 Nb 0.109
MnO	10.74	Mn	3.98				
Total	98.57	(O	32)		Sn 2.27	C	Sn 0.567
				Sn*3.06	Nb 0.79		Ta 0.250
							Ti 0.113
							Fe^{3+} 0.070
					O 32		O 8

$R(\%) = \Sigma(|F_{obs}| - |F_{calc}|)/\Sigma|F_{obs}|$;

$R_w = [\Sigma w(|F_{obs}| - |F_{calc}|)^2/\Sigma w F_{obs}^2]^{\frac{1}{2}}$, $w=1$

Temperature factor form used: $\exp\left[-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right]$

---

[1] Electron microprobe analysis by E.E. Foord (private comm. to P. Cerny, 1975). [2] Based on 16 cations per formula unit. [3] See text for further details. [4] From the present structure analysis. [5] From Nickel *et al.* (1963a).

Preliminary considerations: possible origins for the wodginite unit cell in the ixiolite cell, and possible cation distributions in wodginite

Nickel *et al.* (1963a) concluded that wodginite, because of the general similarity of its chemistry, powder pattern and unit-cell characteristics to those of tantalite (as described in the Introduction), must have a closely related structure. They pointed out that, for the two possible space groups for wodginite, $C2/c$ and Cc, and with $Z = M_{16}O_{32}$ (Table 1 in Part I), the 16 cations could occupy either two 4-fold positions and one 8-fold position in $C2/c$, or four 4-fold positions in Cc. From their chemical analyses, they were unable to group the metallic elements to give whole numbers of particular cations in one site, and they thus concluded that the 16 cations may be randomly distributed in the 16 available sites in either space group.

In a detailed analysis of the structure of wodginite, an obvious starting-point is the structure of tantalite. However, as we describe in the Part I paper, the cation-ordered tantalite structure is based on a supercell of the cation-disordered ixiolite structure whose structure type is that of α-PbO_2 (Wyckoff 1963). The wodginite structure is based on another and different supercell of ixiolite, and so it is more appropriate to relate the structure of wodginite to that of ixiolite than to that of tantalite. Starting with the known ixiolite structure, it is necessary to make two initial decisions: first, which of the two possible space groups to assume for wodginite, and second, which of several possible origins in the ixiolite unit cell should be chosen as origin for the wodginite structure.

Regarding possible origins for the wodginite structure in the ixiolite structure, we consider first the more restricted case of the centric space group $C2/c$ for wodginite. The symmetry characteristics of $C2/c$ (No. 15) are given in the *International Tables*, Vol. *I* (1952) and most are shown in Figure 1 (of the final structure). From these it may be seen that $\bar{1}$'s occur at (0,0,0), (½,0,0), etc., 2-fold axes at (0,*y*,¼), (½,*y*,¼), and *c*-glide and *n*-glide planes at (*x*,0,*z*),(*x*,½,*z*) and (*x*,¼,*z*), (*x*,¾,*z*) respectively. The relevant symmetry elements in the parent ixiolite structure with space group symmetry *Pbcn* (No. 60) (*International Tables*, Vol. *I*, and Fig. 2c in Part I) are $\bar{1}$'s at (0,0,0), (½,0,0), etc., 2-fold axes at (0,*y*,¼), (½,*y*,¼), and *c*-glide planes at (*x*,0,*z*), (*x*,½,*z*). Further consideration of the structure of ixiolite shows that, in relation to $2a_i \sim a_w$, planes which are *c*-glides in ixiolite become *n*-glides in the doubled cell. A careful comparison of the symmetry requirements for wodginite (*C*2/*c*) with the symmetry characteristics of ixiolite, considered in the light of the relative cell dimensions of the two structures ($a_w \sim 2a_i$, $b_w \sim 2b_i$, $c_w \sim c_i$), reveals that the symmetry requirements for wodginite would be satisfied if an origin for wodginite were chosen at any of *four* different positions in the ixiolite structure, namely: $(0,0,0)_i$, $(\frac{1}{2},0,0)_i$, $(0,\frac{1}{2},0)_i$, $(\frac{1}{2},\frac{1}{2},0)_i$. By comparing the structure of tantalite with that of ixiolite (Figs. 1a and 1c respectively in Part I) and taking account of the fact that certain symmetry elements in cation-disordered ixiolite degenerate to only pseudo-symmetry elements in cation-ordered tantalite, it may be seen that the four possible origins for wodginite in ixiolite have their equivalent in the tantalite structure at, respectively, $(0,0,0)_t$, $(1/6,0,0)_t$, $(0,\frac{1}{2},0)_t$, $(1/6,\frac{1}{2},0)_t$.

Wodginite structures whose origins are taken at these four different positions in the ixiolite (tantalite) structure would be similar topologically but slightly different structurally, and in particular the four different structures would each be compatible with a different kind of cation distribution scheme as described below. *The conclusion may be drawn that one must refine wodginite structures based on all four possible origins* in order to be sure that one of these is more satisfactory than the other three.

In addition to taking account of the four possible origins, one must also consider that the space group may be *Cc* rather than *C*2/*c*. Because *Cc* is acentric, the constraint that the origin of wodginite must be at a $\bar{1}$ in ixiolite no longer holds, and furthermore, the 2-fold axes no longer exist; however, the *c*– and *n*–glides do remain in *Cc*, and they must coincide with equivalent or pseudo-equivalent glide planes in ixiolite. In this case the wodginite origin could be taken, from a symmetry point of view, at *any* position in either of planes $(x,0,z)_i$ or $(x,\frac{1}{2},z)_i$. In these circumstances, it would be necessary to arbitrarily define the origin in the *xz* plane by fixing one atom, and for wodginite, the most appropriate atom would be the heavy Ta (or the cation site that contains the most Ta). Although for *Cc*, the wodginite origin could be chosen at any position in $(x,0,z)_i$ or $(x,\frac{1}{2},z)_i$, in practice because of the closeness of the symmetry to *C*2/*c* even if it really were *Cc*, one would choose the origin at a $\bar{1}$ in the ixiolite structure, that is, at one of the four origins possible for *C*2/*c*. Because of the lower symmetry of *Cc* in relation to *C*2/*c*, the cation distribution schemes possible for wodginite in *Cc* are different from those in *C*2/*c*, and we may therefore draw a *second conclusion, namely that one must refine wodginite structures for both possible space groups, C2/c and Cc.*

We now consider possible cation distribution schemes for wodginite. As described below, our results indicate that the most satisfactory structure is one based on space group *C*2/*c* rather than *Cc*, and on ixiolite origin $(0,0,0)_i$, rather than one of the other three. For this reason, we consider here mainly the distribution schemes for *C*2/*c*, and our particular interest is in the relationship between the cation distribution scheme for the correct structure based on origin at $(0,0,0)_i$ and such schemes for structures based on the other three possible origins. The possible cation distribution schemes for wodginite in *C*2/*c* for the four possible origins in ixiolite are given in Table 2 where it may be seen that two of the possible origins, $(\frac{1}{2},0,0)_i$ and $(\frac{1}{2},\frac{1}{2},0)_i$, lead to the same cation distribution scheme ($4R'=4R''=4P$, $4R'=4R''=4Q$, $(4P'+4Q')=(4P''+4Q'')=8R$. However, the three cation sites for one of these origins have different parameters from those of the other, and thus the two distribution schemes, although the same, correspond to different structures.

For the acentric space group *Cc*, the cation distribution schemes (which are not included in the Table) differ from those for centric *C*2/*c* for any given origin by the fact that the one $8R$-type site in *C*2/*c* degenerates to two $4R$-type sites in *Cc*. This increases the number of possible cation distribution schemes in *Cc* over those possible in *C*2/*c*.

A relevant question is whether the known cation-ordering scheme in the tantalite structure (Part I) can give any clue to the likely cation distribution scheme in wodginite. It may be shown that, regardless of which of the four possible origins is chosen for wodginite and using the symbols of Table 2, for space group

TABLE 2. POSSIBLE ORIGINS FOR WODGINITE IN IXIOLITE AND POSSIBLE CATION DISTRIBUTION SCHEMES IN WODGINITE FOR SPACE GROUP *C2/c*

Parameters (x,y,z) given here are approximate.

ixiolite origin	$(0,0,0)_i^*$	$(1/2,1/2,0)_i$	$(1/2,0,0)_i$	$(0,1/2,0)_i$
wodginite origin	$(0,0,0)_w$	$(1/4,1/4,0)_w$	$(1/4,0,0)_w$	$(0,1/4,0)_w$
1st cation				
symbol	4P	4P'	4P''	4P'''
$(x,y,z)_w$	0,0.17,1/4		0,0.09,3/4	
2nd cation				
symbol	4Q	4Q'	4Q''	4Q'''
$(x,y,z)_w$	0,0.66,1/4		0,0.58,3/4	
3rd cation				
symbol	8R	8R'	8R''	8R'''
$(x,y,z)_w$	0.25,0.41,0.25		0.25,0.16,0.25	
Equivalent sites*:				
4P	-	4R'	4R''	2P'''+2Q'''
4Q	-	4R'	4R''	2P'''+2Q'''
8R	-	4P'+4Q'	4P''+4Q''	4R'''
4P'	4R			
4Q'	4R			
8R'	4P+4Q			
4P''	4R			
4Q''	4R			
8R''	4P+4Q			
4P''	2P+2Q			
4Q''	2P+2Q			
8R''	8R			

* The origin for wodginite at $(0,0,0)_i$ proved to be the correct one, and therefore the equivalent positions for the other origins are given only relative to this and not to each other.

For "Equivalent sites", last three entries should have triple primes.

$C2/c$ $4P_w = 4Q_w = (1\text{-}1/3\text{Mn} + 2\text{-}2/3\text{Ta})_t$ and $8R_w = (2\text{-}2/3\text{Mn} + 5\text{-}1/3\text{Ta})_t$. The known cation ordering in tantalite can give therefore no clue to the likely cation distribution in wodginite.

We may now draw a *third conclusion namely, that in analyzing the structure of wodginite, allowance must be made for all reasonable cation distribution schemes.*

The consequence of the these three conclusions is that, in order to arrive at the correct wodginite structure, analyses would have to be carried out for both the space groups *C2/c* and *Cc* in relation to all four possible origins, $(0,0,0)_i$, $(½,0,0)_i$, $(0,½,0)_i$, $(½,½,0)_i$, that is, for *eight* different structures, and the analytical procedure for any one would have to be such as to allow for all reasonable cation distribution schemes. We have followed this procedure in our analysis of the wodginite structure.

REFINEMENTS OF THE POSSIBLE STRUCTURES

Effective scattering factors. Scattering curves for neutral atoms were taken from Cromer & Mann (1968) with anomalous dispersion corrections from Cromer & Liberman (1970). The refinements were carried out using the least-squares program RFINE (Finger 1969a) using the bulk composition as a linear constraint in the refinement of site-populations (Finger 1969b). Because of the similarity in scattering powers between Mn, Fe and Ti, these three species were combined and expressed as Mn*; similarly, Sn and Nb were combined and expressed as Sn*. The chemical formula used for constraining the site-populations is given in Table 1 in terms of Mn*, Sn* and Ta. *R*-factors quoted below are of the forms given in Table 1, expressed as percentages.

Provision for all possible cation distributions. In order to fulfill the requirement described earlier that the solution for the possible site-ordering schemes for the various possible structures be the most general, the site occupancy refinements were handled in the following manner. In *C2/c*, one 4-fold cation site was designated *A*, the other *C*, and the 8-fold site *B*[1]. For origins $(0,0,0)_i$ and $(½,½,0)_i$, site *A* corresponded to *P* and *P′* and site *C* to *Q* and *Q′* respectively in Table 2, and the two sites were assigned parameters close to those given in Table 2. For origins $(½,0,0)_i$ and $(0,½,0)_i$, *A* corresponded to *Q″* and *Q‴* and *C* to *P″* and *P‴* respectively in Table 2 and were also assigned parameters close to those in the Table. For all four origins, site *B* corresponded to the *R*-type sites (*R*,*R′*,*R″*,*R‴*) and was given parameters close to those in the Table for the particular origin. For all four origins, appropriate approximate parameters were deduced for each of the four oxygen sites from the known tantalite structure.

Regarding assumed occupancies for the cation sites, the 4-fold *A* site was assumed to be occupied by Mn* and Sn* with the initial occupancies set at 1.0Mn* and 0.0Sn*. The 8-fold *B* site was assumed to be occupied by Ta and Sn* with initial occupancies of 1.0Ta and 0.0Sn*. The other 4-fold site, *C*, was split into two half-occupied sites with the positional parameters and temperature factors of the second site constrained to be equal to those of the first site, and with the two half-occupied sites combined constrained to be occupied by the cations not already occupying the other two sites, that is initially by ¼(0.74Mn*+3.06Sn*+0.20Ta) (Table 1). With this arrangement of sites, it was possible to refine the Mn* occupancy (with constraints) over the *A* and *C* sites, and the Ta occupancy over the *B* and *C* sites (with constraints). In this manner, all possible ordering

---

[1] These designations were adopted after the completion of the refinements so that they would conform to those given for these tantalum oxide minerals in Table 1 of Part 1.

schemes (with the exception of Mn^{2+} substituting for Ta^{5+} and vice versa, which may be considered as extremely improbable on crystallochemical grounds) were encompassed, and the total composition of the cation sites was constrained to the bulk composition of the crystal.

For refinement in space group *Cc*, all the structural sites that are in 8-fold general equivalent positions in *C*2/*c*, namely cation *B* and the four oxygens, will occupy pairs of 4-fold equivalent positions, and so positional parameters had to be chosen for one additional of each of these five atoms (sites) that were no longer equivalent to the prototypes. The same kind of occupancy, Ta+Sn*, was assumed for the two 4-fold *B*-type sites in *Cc* as for the one 8-fold *B* site in *C*2/*c*, but the occupancies of these two 4-fold sites were now free to vary independently. All other cation occupancy conditions were kept the same as for *C*2/*c*.

(1) *Origin at* $(0,0,0)_{ii}$; *space group C2/c.* Using positional parameters close to those given in Table 2, full-matrix refinement of all possible variables for an isotropic thermal model resulted in convergence at an *R*-factor of 7.2%. The isotropic temperature factors were completely satisfactory at this stage; all the temperature factors for the oxygens were statistically equal (~1.0Å²) reflecting the similarity in their environments, as were the temperature factors for the cation sites. The occupancy refinement showed that the *A* site was completely occupied by Mn*; however, the *B* site was found to be occupied by 0.89(1) Ta+0.11Sn*. Because it is possible that anisotropic vibration of the Ta atom could significantly affect the parameters of the much lighter oxygen atoms, the cation sites were allowed to vibrate anisotropically. Refinement of all variables for this model resulted in convergence at an *R*-factor of 6.6%. Subsequent conversion of the temperature factors of the remaining atoms to anisotropic, followed by full-matrix refinement of all variables resulted in convergence at an *R*-factor of 6.1%.

(2) *Origin at* $(0,0,0)_{ii}$; *space group Cc.* For an isotropic thermal model, initial attempts to refine this structural variant were not successful, as wild oscillations occurred in the temperature factors of the anions related by a pseudo-centre of symmetry. This problem was overcome by constraining all oxygen temperature factors to be equal. With this constraint applied, refinement of all variables resulted in convergence at an *R*-factor of 7.1%. Because of the extreme correlations between anion temperature factors that necessitated the use of the constraints described above, an anisotropic thermal model was not attempted.

(3) *Origin at* $(\frac{1}{2},0,0)_{ii}$; *space group C2/c.* Full-matrix refinement of all variables for an isotropic thermal model resulted in convergence at an *R*-factor of 20.2%. The following occupancies were obtained: *A*=0.77(7)Mn*+0.23Sn*; *B*=0.82(3)Ta*+0.18Sn*; *C*=0.50Sn*+0.41(7)Mn*+0.09(3)Ta. As with most of the previous refinements, the oxygen temperature factors were extremely large, all being between 7 and 9Å², although reasonable temperature factors were obtained for the metal sites. In view of the high *R*-factor and the large anion temperature factors, this model cannot be considered as satisfactory.

(4) *Origin at* $(\frac{1}{2},0,0)_{ii}$; *space group Cc.* Full-matrix refinement of all variables for an isotropic thermal model with the constraints that the cation temperature factors were equal and the anion temperature factors were equal resulted in the matrix becoming singular.

(5) *Origin at* $(0,\frac{1}{2},0)_{ii}$; *space group C2/c.* Full-matrix refinement of all possible variables for an isotropic thermal model converged at an *R*-factor of 13.1%. At this stage, the occupancy refinement showed that the *A* and *B* sites were completely occupied by Mn* and Ta respectively within one standard deviation. However, there were several unsatisfactory features to the refinement. The isotropic temperature factors of the *A* and *B* sites were both zero (within one standard deviation). In addition, one of the oxygen isotropic temperature factors was three times as large as the other three. It was possible that some of these features arose from a strongly anisotropic vibration of the Ta atom, and thus the *B*=Ta and *C* sites were converted to anisotropic temperature factors. Upon refinement, one of the diagonal temperature factor coefficients of Ta became negative, and the anisotropic model was abandoned. Because of the poor temperature factors, the refinement of this model cannot be considered as satisfactory.

(6) *Origin at* $(0,\frac{1}{2},0)_{ii}$; *space group Cc.* All attempts to refine in the space group *Cc* were unsuccessful, all refinements leading to a dramatic increase in the *R*-factor. Parameters oscillated wildly and there was extreme correlation between pseudo-centrically related variables.

(7) *Origin at* $(\frac{1}{2},\frac{1}{2},0)_{ii}$; *space group C2/c.* Full-matrix refinement of all possible variables for an isotropic thermal model resulted in convergence at an *R*-factor of 11.6%. The occupancy refinement showed that the *A* site was fully occupied by Mn*; the occupancies of the *B* and *C* sites were 0.89(2)Ta*+0.11Sn* and 0.54Sn*+0.28Ta*+0.18Mn* respectively. The isotropic temperature factors for all three ca-

tion sites were satisfactory; however, the oxygen temperature factors were very large, all being equal to 8.0Å^2 within one standard deviation. In view of this, the refinement cannot be considered as satisfactory.

(8) *Origin at $(\frac{1}{2},\frac{1}{2},0)_i$; space group Cc.* Full-matrix refinement of all variables for an isotropic thermal model with the constraints that the cation temperature factors were equal and the anion temperature factors were equal resulted in the matrix becoming singular.

Conclusion: the most satisfactory structure. Table 3 gives a summary of the *R*-factors for the eight different possible structures, and these *R*-factors as well as the temperature factors given in the descriptions of the results indicate that model (1) based on origin $(0,0,0)_i$ and space group *C2/c* is clearly the most satisfactory in every respect, and we thus consider it to be the correct structure. In terms of the joint scattering species Mn*, Sn* and Ta, the following cation site occupancies were obtained:

TABLE 3. LOWEST R FACTORS FOR THE EIGHT POSSIBLE WODGINITE STRUCTURES.

Details are given in the text.

Origin in ixiolite	$(0,0,0)_i$		$(1/2,0,0)_i$		$(0,1/2,0)_i$		$(1/2,1/2,0)_i$	
Space group	C2/c	Cc	C2/c	Cc	C2/c	Cc	C2/c	Cc
R(%)	6.1	7.1	20.2	*	12.1	*	11.6	*

*designates non-convergence.

$A = 1.0Mn^*$
$B = 0.891(9)Ta + 0.109Sn^*$
$C = 0.565Sn^* + 0.250Ta + 0.185Mn^*$

On the basis of ionic radius and ionic charge, the minor constituents were assigned as follows: Nb was assigned to the *B* site, the amount of Nb available being almost exactly equal to the Sn* occupancy of that site; all the remaining minor cations were assigned to the *C* site. The resulting site-populations are given in Table 1 and may be expressed by writing the chemical formula as $ACB_2O_8 = Mn_{1.00}(Sn_{0.567}Ta_{0.250}Ti_{0.113}Fe^{3+}_{0.070})(Ta_{0.891}Nb_{0.109})_2O_8$. Final positional parameters and equivalent isotropic temperature factors are given in Table 4 and anisotropic temperature factor coefficients in Table 5.* Interatomic distances and angles were calculated with the program ERRORS (L. W. Finger, pers. comm.) and are listed in Table 6. A projection of the structure is shown in Figure 1.

TABLE 4. POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR WODGINITE

Site	x	y	z	$B_{equiv.}$ (Å^2)
C	0	0.1689(2)	1/4	0.52(6)
A	0	0.6575(4)	1/4	0.63(7)
B	0.2498(1)	0.4131(1)	0.2472(2)	0.61(3)
01	0.1334(20)	0.0577(15)	0.0833(37)	0.89(27)
02	0.1453(19)	0.4504(17)	0.5597(39)	1.12(28)
03	0.1215(19)	0.3060(16)	0.0984(38)	1.01(27)
04	0.1161(19)	0.1834(17)	0.5758(37)	1.09(27)

TABLE 5. ANISOTROPIC TEMPERATURE COEFFICIENTS FOR WODGINITE ($\beta_{ij} \times 10^4$).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	13(2)	10(2)	53(8)	0	16(3)	0
A	12(4)	13(3)	73(15)	0	21(7)	0
B	15(1)	12(1)	64(4)	-1(1)	13(1)	1(1)
01	31(20)	13(11)	85(62)	0(12)	19(27)	1(21)
02	21(19)	22(13)	139(70)	4(12)	21(28)	-5(24)
03	20(16)	16(12)	141(65)	-15(11)	23(27)	-2(23)
04	23(16)	19(13)	142(66)	3(12)	33(27)	5(24)

DISCUSSION

Comparison of models (1) and (7).

For space group *C2/c*, structures based on origins $(0,0,0)_i$ and $(\frac{1}{2},\frac{1}{2},0)_i$ would have cations in the same relation to the origin (Table 2) but oxygens that differ by $\sim(\frac{1}{2}-z)$. The results bear out the nature of the difference between these two structures (models (1) and (7) respectively): model (7) has cation site occupancies which are essentially the same as those of model (1), the most satisfactory structure, but the oxygens of model (7) show very high isotropic temperature factors (~8.0Å^2) whereas for the correct structure represented by model (1), the isotropic temperature factors of the oxygens are reasonable (Table 4: $B \sim 1.0$Å^2).

Comparison to the tantalite structure. The cation ordering scheme in wodginite is different from that in tantalite; the latter has one 4-fold cation (*A*) site occupied by Mn and one 8-fold cation site (*B*) occupied by Ta whereas wodginite with a cell of different symmetry, cell dimensions and volume, has one 4-fold cation site (*A*) occupied by Mn and one 8-fold cation site (*B*) occupied by Ta but another 4-fold site (*C*) occupied by (Sn+Ta+Ti); furthermore, the *A* and *B* sites in wodginite do not correspond structurally to the *A* and *B* sites in tantalite. The chains formed by the linking of staggered cation-oxygen octahedra running parallel to *z*

---

*Complete set of structure factor tables is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

TABLE 6. SELECTED INTERATOMIC DISTANCES AND ANGLES IN WODGINITE.

Ba -O(1)c	2.064(18)Å	
-O(1)d	2.162(18)	
-O(2)a	1.942(19)	
-O(2)e	2.074(19)	
-O(3)a	1.877(17)	
-O(4)f	1.899(19)	
	2.003(8)	
Ca-O(1)a,b	1.996(18)	x 2
-O(3)a,b	2.101(17)	x 2
-O(4)a,b	1.984(19)	x 2
	2.027(8)	
Aa-O(2)e,g	2.101(19)	x 2
-O(3)h,i	2.142(19)	x 2
-O(4)e,g	2.313(18)	x 2
	2.185(8)	

Equivalent Positions

a	x	y	z
b	-x	y	½-z
c	½-x	½-y	-z
d	½-x	½+y	½-z
e	x	1-y	z-½
f	½-x	½-y	1-z
g	-x	1-y	1-z
h	x	1-y	½+z
i	-x	1-y	-z

B Octahedron

O(1)c-O(1)d	2.875(15)	O(1)c-Ta-O(1)d	85.7(6)°	
*O(1)c-O(2)e	2.659(24)	*O(1)c-Ta-O(2)e	76.1(7)	
O(1)c-O(3)a	2.963(26)	O(1)c-Ta-O(3)a	97.4(8)	
O(1)c-O(4)f	2.966(25)	O(1)c-Ta-O(4)f	96.8(7)	
*O(1)d-O(2)a	2.551(26)	*O(1)d-Ta-O(2)a	76.7(8)	
O(1)d-O(2)e	2.757(24)	O(1)d-Ta-O(2)e	81.2(7)	
O(1)d-O(4)f	2.761(25)	O(1)d-Ta-O(4)f	85.4(8)	
O(2)a-O(2)e	2.793(16)	O(2)a-Ta-O(2)e	88.1(6)	
O(2)a-O(3)a	2.880(24)	O(2)a-Ta-O(3)a	97.9(8)	
O(2)a-O(4)f	2.830(25)	O(2)a-Ta-O(4)f	94.9(8)	
O(2)e-O(3)a	2.721(27)	O(2)e-Ta-O(3)a	90.2(8)	
O(3)a-O(4)f	2.969(26)	O(3)a-Ta-O(4)f	103.7(8)	
⟨O-O⟩	2.810	⟨O-Ta-O⟩	89.5	

C Octahedron

O(1)a-O(1)b	3.078(15)	O(1)a-C-O(1)b	100.9(10)	
O(1)a,b-O(4)a,b	2.904(27)	O(1)a,b-C-O(4)a,b	93.7(8)	x 2
O(1)a,b-O(4)b,a	2.873(26)	O(1)a,b-C-O(4)b,a	92.4(8)	x 2
O(1)a,b-O(3)a,b	2.842(25)	O(1)a,b-C-O(3)a,b	87.8(7)	x 2
O(3)a-O(3)b	2.801(17)	O(3)a-C-O(3)b	83.6(10)	
O(3)a,b-O(4)a,b	2.813(25)	O(3)a,b-C-O(4)a,b	87.0(8)	x 2
*O(3)a,b-O(4)b,a	2.786(24)	*O(3)a,b-C-O(4)b,a	85.9(7)	x 2
⟨O-O⟩	2.860	⟨O-C-O⟩	89.8	

A Octahedron

O(2)e-O(2)g	3.404(15)	O(2)e-A-O(2)g	108.2(10)	
O(2)e,g-O(3)h,i	3.219(25)	O(2)e,g-A-O(2)g,i	98.7(7)	x 2
O(2)e,g-O(3)i,h	3.116(27)	O(2)e,g-A-O(3)h,i	94.5(7)	x 2
O(2)e,g-O(4)i,g	3.064(25)	O(2)e,g-A-O(4)i,g	87.8(7)	x 2
O(3)h,i-O(4)e,g	3.012(25)	O(3)h,i-A-O(4)e,g	85.0(7)	x 2
*O(3)h,i-O(4)g,e	2.786(24)	*O(3)h,i-A-O(4)g,e	77.3(7)	x 2
O(4)e-O(4)g	2.858(15)	O(4)e-A-O(4)g	76.3(9)	
⟨O-O⟩	3.055	⟨O-A-O⟩	89.3	

*shared edges

that characterize tantalite are present in wodginite, but whereas in tantalite one layer of *A*=Mn chains is followed by two layers of *B*=Ta chains (Fig. 2a in Part I), in wodginite layers of *A*(=Mn) + *C*(=Sn,Ta) chains alternate with layers of *B*(=Ta) chains (Fig. 1).

Bond lengths. Table 6 shows the following variation and mean bond lengths (Å) for the three cation-oxygen octahedra: *A*(=Mn), 2.101(19)-2.313(18), 2.185(8); *B*(=Ta), 1.877 (17)-2.162(18), 2.003(8); *C*(~Sn,Ta), 1.984(19) -2.101(17), 2.027(8). Using the derived cation site contents (Table 1) and the ionic radii of Shannon & Prewitt (1969, 1970), the mean cation-oxygen radii sums are for site *A*=Mn, 2.19Å; for *B*=(Ta,Nb), 2.00Å; and for *C*=(Sn,Ta,Ti,Fe^{3+}), 2.04Å (Table 7). The observed values agree well with these calculated values. In addition, the mean octahedral bond lengths observed for the Mn-rich *A* sites in tantalite and in wodginite, 2.18(2) and 2.185(8)Å respectively, agree well with each other as do the Ta-rich *B* sites in both minerals with respective values of 2.01(1) and 2.003(8)Å.

Both the individual cation-oxygen distances and the oxygen-cation-oxygen angles in Table 6 for the three octahedra reveal that all three are appreciably distorted from ideal octahedral configurations with the *C* octahedron showing the least distortion. The Table also shows that the oxygen-oxygen distances for the shared octahedral edges are the shortest for all three octahedra, and that the oxygen-cation-oxygen angles for the shared edges are the second smallest, the smallest and the second smallest for the *A*, *B* and *C* octahedra respectively, so it may be said that the wodginite structure conforms well to Pauling's third rule regarding the linking of coordination polyhedra.

Comparison with previous wodginite structures. Two previous structure analyses of wodginite have been described, one by Grice (1973) and Grice & Ferguson (1974), and the other by Graham & Thornber (1974). In neither case were refinements carried out for all four of the structures it is possible to derive from ixiolite

TABLE 7. COMPARISON OF CATION SITE DATA BY GRAHAM & THORNBER (1974) (GT) WITH THAT OF PRESENT AUTHORS (FHG)

Transformation: $x_{GT}-0.125 = x_{FHG}$, $y_{GT} = y_{FHG}$, $z_{GT} = z_{FHG}$

	site	content	obs. size Å	calc. size Å	site	content	obs. size Å	calc. size Å	site	content	obs. size Å	calc. size Å	site	content	obs. size Å	calc. size Å
GT	Mn	Mn$_{1.0}$	2.13	2.19	X2	Ta$_{0.7}$Nb$_{0.3}$	1.97	2.00	X1	Sn$_{0.47}$Ta$_{0.42}^{*}$	2.08	1.95	Ta	Ta$_{1.0}$	2.09	2.00
									site	content	obs. size Å	calc. size Å				
mean GT									X1/Ta	Ta$_{0.71}$Sn$_{0.24}^{*}$	2.08	1.98				
FHG	C	Sn$_{0.57}$Ta$_{0.25}^{**}$	2.03	2.04	A	Mn$_{1.00}$	2.19	2.19	B	Ta$_{0.89}$Nb$_{0.11}$	2.00	2.00				

*plus Fe$_{0.01}$ $\square_{0.1}$ for X1 and plus $\square_{0.05}$ for X1/Ta.

**plus Ti$_{0.11}$Fe$_{0.070}$.

combined with both possible space groups as we have now done.

The Grice & Ferguson structure is based on ixiolite origin $(0,\frac{1}{2},0)_i$ and space group *C*2/*c*, and thus it corresponds to our model (5). Both the earlier and the present analysis of this model met with serious problems with the temperature factors of most of the atoms, and both refined to $R \sim 12\%$. Furthermore, it can be shown that the mean cation-oxygen distances observed for the octahedra of the two cations in 4-fold sites (*A* and *B* in Grice 1973), agree poorly with the weighted mean cation-oxygen distances calculated for the deduced site occupancies from the ionic radii. We now reject that structure in favor of the one described here.

The structure described by Graham & Thornber (1974) was carried out on a crystal from the type locality, Wodgina, Australia using Cu*K*α radiation and photographic intensity data. They refined their structure in both space groups *C*2/*c* and *Cc* and concluded on the basis of a slightly better *R*-factor (13.1% over 14.3%) and of electrostatic calculations that *Cc* is to be preferred.

A comparison of their cation parameters with those relative to the possible origins in *C*2/*c* in our Table 2 and also taking account of their oxygen parameters in relation to ours shows that a change of their *x* by –0.125 will transform their origin to one of ours, and the particular one is that for the correct structure, $(0,0,0)_i$. It is then possible to equate their cation sites with ours, and this is done in Table 7 where the contents and the observed and calculated mean cation-oxygen octahedral distances (sizes) are also given for both structures for comparative purposes.

Table 7 shows that the two structure analyses result in somewhat different cation ordering schemes: their Mn site containing $Mn_{1.0}$ is structurally equivalent to our *C* site containing $Sn_{0.57}Ta_{0.25}Ti_{0.11}Fe_{0.07}$ rather than to our Mn-rich site, *A*, to which their site *X*2 containing $Ta_{0.7}Nb_{0.3}$ is equivalent. Their other two 4-fold sites in *Cc*, *X*1 and Ta are together equivalent to our 8-fold site *B* in *C*2/*c*, and in this case there is better agreement than in the other two cases of their combined cation contents with our single content, both being Ta-rich. We cannot explain why the two different structure analyses resulted in two different ordering schemes.

Graham & Thornber (1974) note that the accuracy of their individual *M*-O bond lengths is probably no better than 0.12Å which corresponds to a σ of the mean octahedral cation-oxygen distances of 0.05Å whereas our σ's for the mean octahedral cation-oxygen distances are 0.008Å (Table 6). Nevertheless, one may still compare their observed mean octahedral cation-oxygen distances with those calculated from the ionic radii of Shannon & Prewitt (1969, 1970), and this we have done in Table 7. The agreement is generally poor, especially compared with the agreement between the observed and calculated values for our structure which are also given in the Table.

Because of the lower *R*-factor and the better agreement between observed and calculated mean octahedral cation-oxygen distances of our structure relative to those derived by Graham & Thornber (1974), we conclude that ours is the preferred structure for wodginite.

Bond strengths. Table 8 gives the bond strengths to the oxygens from the cations, evaluated in the same general ways as was done for tantalite (see Discussion in Part I). In wodginite the non-distance-dependent Pauling values to the oxygens are fairly poor but somewhat better than the corresponding values for tantalite (Table 6 of Part I). The distance-dependent method of Ferguson (1974) in which the bond strengths from the cations to the anions are distributed in amounts that are inversely proportional to the cation-oxygen distances, that is, using an exponent of 1, yielded bond strengths (not reproduced here) that were more satisfactory than the Pauling values but were such that a higher exponent was indicated. We accordingly carried out calculations using the method of Pyatenko (1973) for which different exponents are in general used for chemically different cations; for wodginite an exponent of 5.0 was applicable to all the elements. Bond strengths calculated in this way are given in Table 8, and although they are fairly satisfactory, they suggested that a somewhat smaller exponent would give better results, particularly for O(1). The exponent was then changed arbitrarily to 4.0, and the bond strengths to both the individual oxygens and to the oxygens taken in octahedral groups of six are better than those for the exponent of 5.0 and in fact they may be regarded as reasonably satisfactory. It is possible that still further modifications of the exponent embodying different values for the different cations might improve the bond strengths still further.

Barker & Graham (1974) have calculated lattice energies and site potentials for the wodginite structures described by Graham & Thornber (1974) and by Grice (1973) as well as for other related compounds, and their results were important in the choice of space group *Cc* over *C*2/*c* for the wodginite structure of Graham & Thornber. We have not attempted to assess our tantalite or wodginite structures in this way al-

TABLE 8. BOND STRENGTHS IN THE WODGINITE STRUCTURE

See Figure 1 and Table 7. All bond strengths (v_{ij}) are in valence units (v.u.)

method of evaluation			Pauling (1929)			Modified Pyatenko (1973)/ Ferguson (1974)			Pyatenko (1973)**		
cation A=$Mn^{2+}_{1.00}$											
assumed charge				2+			2+			2+	
assumed A-O exponent				0*			4.0			5.0	
cation B=$Ta^{5+}_{0.891}Nb^{5+}_{0.109}$											
assumed charge				5+			5+			5+	
assumed B-O exponent				0*			4.0			5.0	
cation C=$Sn^{4+}_{0.567}Ta^{5+}_{0.250}Ti^{4+}_{0.113}Fe^{3+}_{0.07}$											
assumed charge				4+			3.98+			3.98+	
assumed C-O exponent				0*			4.0			5.0	
anion	cation	anion-cation distance	v_{ij}	Σ	$\|\Delta\|^{\dagger}$	v_{ij}	Σ	$\|\Delta\|^{\dagger}$	v_{ij}	Σ	$\|\Delta\|^{\dagger}$
$^{III}O(1)$	B	2.064(18)Å	5/6	2 1/3	1/3	0.721	2.020(257)	0.020	0.691	1.947(339)	0.053
	B'	2.162(18)	5/6			0.598			0.547		
	C	1.996(18)	2/3			0.701			0.710		
$^{III}O(2)$	A	2.101(19)	1/3	2	0	0.384	2.008(231)	0.008	0.396	2.004(309)	0.004
	B	1.942(19)	5/6			0.918			0.935		
	B'	2.074(19)	5/6			0.706			0.673		
$^{III}O(3)$	A	2.142(19)	1/3	1 5/6	1/6	0.355	1.978(184)	0.022	0.359	2.017(241)	0.017
	B	1.877(17)	5/6			1.052			1.108		
	C	2.101(17)	2/3			0.571			0.549		
$^{III}O(4)$	A	2.313(18)	1/3	1 5/6	1/6	0.261	1.984(198)	0.016	0.245	2.022(262)	0.022
	B	1.899(19)	5/6			1.004			1.046		
	C	1.984(19)	2/3			0.718			0.731		
$\Sigma\|\Delta\|$					2/3			0.066			0.096
Total bond strengths (v.u.) to octahedral groups of 6 oxygens:											
Around A											
Σ				11 1/3			11.940			12.086	
$\|\Delta\|'^{\dagger\dagger}$				2/3			0.060			0.086	
Around B											
Σ				12 1/3			12.018			11.941	
$\|\Delta\|'^{\dagger\dagger}$				1/3			0.018			0.059	
Around C											
Σ				12			11.964			11.972	
$\|\Delta\|'^{\dagger\dagger}$				0			0.036			0.028	
$\Sigma\|\Delta\|'$(1A+2B+1C)				1 1/3			0.132			0.232	

*Implying a non-distance dependent relationship.

**Pyatenko (1973) gives no exponent for Mn; we have assumed the value of 5.0.

† $|\Delta| = |2 - \Delta|$ v.u.

†† $|\Delta|' = |12 - \Delta|$ v.u.

though it would perhaps be a valuable approach. Because of the satisfactory bond strengths derived for our tantalite and wodginite structures when evaluated according to the Pyatenko (1973) or the modified Pyatenko method, and especially in view of the high degree of distance distortion in at least one of the cation octahedra in each of these structures, we feel that this procedure provides a reasonably satisfactory crystal-chemical interpretation of these structures. Implicit in this interpretation is the concept that, in structures such as these, the differently-charged cations tend to order themselves into particular sites — which is largely the case with our wodginite — and at the same time the cation-oxygen bond lengths within one polyhedron are able to vary to a fairly high degree in order to maintain close to ideal bond strengths to each oxygen anion. Because wodginite contains an appreciable proportion of cations that are other than divalent or pentavalent, it requires an additional cation site over the two sites in tantalite to accommodate them; the result is a structure that is topologically similar to that of tantalite although lower in symmetry but still one in which the particular cations are largely ordered and the oxygens are essentially satisfied with respect to bond strengths.

ACKNOWLEDGMENTS

We express our thanks to the following for 4-circle diffractometer data collections: C. Calvo and R. Faggiani, McMaster University; M.N.G. James, University of Alberta; and V. Kocman, formerly of the University of Toronto. E. E. Foord of Stanford University kindly carried out an electron microprobe analysis of our wodginite specimen. Financial assistance was provided by the National Research Council.

REFERENCES

BARKER, W. W. & GRAHAM, J. (1974): The crystal chemistry of complex niobium and tantalum oxides: V. Electrostatic energy calculations. *Amer. Mineral.* **59**, 1051-1054.

BROWN I. D. & SHANNON, R. D. (1973): Empirical bond-strength-bond-length curves for oxides. *Acta Cryst.* **A29**, 266-282.

ČERNÝ, P. & TURNOCK, A. C. (1971): Niobium-tantalum minerals from granitic pegmatites at Greer Lake, southeastern Manitoba. *Can. Mineral.* **10**, 755-772.

CROMER, D. T. & MANN, J. B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Cryst.* **A24**, 321-324.

——— & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys.* **53**, 1891-1898.

ELPHICK, M. (1972): *Crystal Structure Analysis of Wodginite from Bernic Lake, Manitoba.* M.Sc. thesis, Univ. Manitoba, Winnipeg, Canada.

FERGUSON R. B. (1974): A cation-anion distance dependent method for evaluating valence-bond distributions in ionic structures and results for some olivines and pyroxenes. *Acta Cryst.* **B30**, 2527-2539.

FINGER, L. W. (1969a): RFINE. A Fortran IV computer program for structure factor calculation and least squares refinement of crystal structures. *Geophys. Lab., Carnegie Inst. Wash.* (unpubl. manuscript).

——— (1969b): Determination of cation distributions by least squares refinement. *Carnegie Inst. Wash. Year Book* **67**, 216-217.

GAIT, R. I., FERGUSON, R. B. & COISH, H. R. (1970): Electrostatic charge distributions in the structure of low albite, $NaAlSi_3O_8$. *Acta Cryst.* **B26**, 68-77.

GRAHAM, J. & THORNBER, M. R. (1974): The crystal chemistry of complex niobium and tantalum oxides II. Composition and structure of wodginite. *Amer. Mineral.* **59**, 1040-1044.

GRICE, J. D. (1970): *The Nature and Distribution of the Tantalum Minerals in the Tanco (Chemalloy) Mine Pegmatite at Bernic Lake, Manitoba.* M.Sc. thesis, Univ. Manitoba, Winnipeg, Canada.

——— (1973): *Crystal Structures of the Tantalum Oxide Minerals Tantalite and Wodginite, and of Millerite NiS.* Ph.D. thesis, Univ. Manitoba, Winnipeg, Canada.

——— & FERGUSON, R. B. (1974): The crystal structures of manganotantalite, pseudo-ixiolite and wodginite from the Tanco pegmatite, Bernic Lake, Manitoba. *Program Abstr. 1974 Meet. Geol./Mineral. Assoc. Canada*, 40.

———, ČERNÝ, P. & FERGUSON, R. B. (1972): The Tanco pegmatite at Bernic Lake, Manitoba. II. Wodginite, tantalite, pseudo-ixiolite and related minerals. *Can. Mineral.* **11**, 609-642.

HAWTHORNE, F. C. & FERGUSON, R. B. (1975): Notes on VLBDDB ("Valence Bond Distribution"), a computer program to calculate distance-dependent bond strengths. *Univ. Manitoba*, Winnipeg. (Unpublished).

INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY I. SYMMETRY GROUPS (1952): N. F. M. Henry & K. Lonsdale, eds. Kynoch Press, Birmingham, England.

KHVOSTOVA, V. A. & MAXIMOVA, N. V. (1969): On the minerals of the tantalite-columbite group. *Mineral. Sbornik State Univ. Lvov* **23**, 38-52.

KOMKOV, A. I. (1970): Relationship between the X-ray constants of columbites and composition. *Dokl. Akad. Nauk SSR, Earth Sci.* **19**, 117.

LARSON, A. C. (1971): The LASL crystal structure program library, Los Alamos Scientific Laboratory. *Univ. California*, Los Alamos, New Mexico.

NICKEL, E. H., ROWLAND, J. F., & MCADAM, R. C. (1963a): Wodginite, a new tin-manganese tantalite from Wodgina Australia and Bernic Lake, Manitoba. *Can. Mineral.* **7**, 390-402.

———, ——— & ——— (1963b): Ixiolite — a columbite substructure. *Amer. Mineral.* **48**, 961-979.

PAULING, L. (1929): The principles determining the structures of complex ionic crystals. *J. Amer. Chem. Soc.* **51**, 1010-1026.

PYATENKO, YU. A. (1973): Unified approach to analysis of the local balance of valences in inorganic structures. *Soviet Phys. Cryst.* **17**, 677-682.

SHANNON, R. D. & PREWITT, C. T. (1969): Effective ionic radii in oxides and fluorides. *Acta Cryst.* **B25**, 925-946.

——— & ——— (1970): Revised values of effective ionic radii. *Acta Cryst.* **B26**, 1046-1048.

SIDORENKO, G. A., SOLNTSEVA, L. S. & GORZHEVSKAYA, S. A. (1971): Crystallochemical study of minerals of the columbite-tantalite series. *Trudy Mineral. Museum Acad. Sci. U.S.S.R.* **20**, 140-154.

STRUNZ, H. & TENNYSON, C. (1970): *Mineralogische Tabellen.* 5th ed. Akademische Verlagsgesellschaft, Leipzig.

STURDIVANT, J. H. (1930): The crystal structure of columbite. *Z. Krist.* **75**, 88-108.

TURNOCK, A. C. (1966): Synthetic wodginite, tapiolite and tantalite. *Can. Mineral.* **8**, 461-470.

WYCKOFF, R. W. G. (1963): *Crystal Structures* **1**, 2nd ed. Interscience Publishers, New York.

——— (1965): *Crystal Structures* **3**, 2nd ed. Interscience Publishers, New York.

Manuscript received April 1976, emended June 1976.