

The Crystal Chemistry of Complex Niobium and Tantalum Oxides I. Structural Classification of MO_2 Phases

J. GRAHAM, AND M. R. THORNER

Division of Mineralogy, CSIRO, Floreat Park,
Western Australia, 6014

Abstract

Despite complications due to isomorphous substitution, polymorphism and metamictization, many of the mineralogically significant complex oxides of tantalum and niobium can be classified according to the size of the A cation and the linking of coordination polyhedra. The scheme has led to a reappraisal of the structures of M' fergusonite and thoreaulite. Interrelationships between the various structures are discussed.

Introduction

The complex oxides of niobium and tantalum with other metals (and in particular the transition and rare earth metals) are notable for the variety of structural modifications and the extent of the isomorphous replacements that are possible within them. At least 80 named varieties occur as minerals, many of these being disguised in their natural state by the fact that they are disordered. Synthesis studies have increased the number of known structures by a large factor.

The disordered state may be completely amorphous by X-ray diffraction criteria, and is usually ascribed to "metamictization," a disordering process presumed to be due to radiation damage. The α -particles normally responsible have such a short range in the solid state that, to do appreciable damage, they must have their origin within the crystal itself. Metamictization provides one of nature's apparent paradoxes. Metamict disorder is characterized by an apparently irreversible ordering of metal atoms when the disordered minerals are heated.

The type localities for a number of varieties—formanite, $Y(Ta,Nb)O_4$; simpsonite, $Al_4Ta_3O_{13}(F,OH)$; and wodginite, $MnTa(Ta,Nb,Sn,Fe)_2O_8$ —are in Western Australia, and the present work commenced as a study of some columbite-tantalite minerals from throughout the State¹, but because the structural principles differentiating one mineral from

another were not clear, it became necessary to review a wider range of the niobium-tantalum oxides.

A helpful review was published by the Academy of Sciences of the U.S.S.R. (Vlasov, 1964), and numerous papers on the rhombic titano-tantaloniobates by Ginsburg, Sidorenko, Gorzhevskaya, and others also appeared in 1964. This paper deals with the crystal chemical problems associated with these minerals, and makes use of recent ideas to understand the relationships among the wide variety of mineral forms.

General Discussion of Structure and Stoichiometry

In these minerals, tantalum, niobium, and titanium are usually grouped together as group B metals, and all other metals as group A , resulting in ideal formulae of the form ABO_4 , AB_2O_6 , etc. There are exceptions, however, and in some circumstances it is convenient to separate the cations on the basis of valence. The known structures are dominated by 5-valent B atoms (Ta and Nb) in octahedral coordination. Fergusonite and $H-Nb_2O_5$ ² are the only known exceptions, and in the latter only a small fraction of the niobium atoms are tetrahedrally coordinated. Because of this, Ginsburg (1964) recommended a return to the old description as acidocomplex compounds, rather than as complex oxides. The details of the structure are determined largely by the coordination requirements, mainly ionic size, of the A cation, and the resultant configuration is a compromise between the preferred coordination of

¹We are grateful to the Government Chemical Laboratories for the samples and for the helpful cooperation of their staff.

²The notation of Schäfer, Gruehn, and Schulte (1966) is followed for the different modifications of Nb_2O_5 .

the *A* cation and the strongly favored octahedral coordination of the *B* cations.

The number of basic structures involved in the oxide systems is very limited; where the stoichiometry is close to M_2O_5 , and with certain extensions to about M_3O_5 , complicated "Magneli phases" occur, some of which correspond to the tungsten bronzes with their unusual electrical properties. Phases of composition MO_2 are most often related to one of the structures of TiO_2 (rutile or α - PbO_2 structure types), while the M_4O_7 stoichiometry is usually represented by the pyrochlore structure. The composition M_2O_3 usually occurs as a modification of the perovskite structure, or in synthetic compositions the structure is sometimes related to that of corundum. The monoxides (with reduced Nb,Ta) are related to the NaCl structure.

This simple picture is, however, distorted almost beyond recognition by three features which are strongly marked in a great many of the phases.

(1) Variation of Stoichiometry due to Substitution

The true stoichiometry is difficult to recognize because of the wide range of substitutions that occur. In addition to substitutions between similarly charged ions (*e.g.*, Nb-Ta, Mn-Fe, Ti-Sn, *etc.*), coupled substitutions occur on both *A* and *B* sites. It is not necessary to preserve the charge on a particular site, so that the inclusion of a 3-valent cation in the *A* site, for example, may be compensated by a 4-valent ion in the *B* site. Titanium on the *B* site is usually dependent on this mechanism. These substitutions commonly occur between ions of roughly equivalent radius (see for example Komkov, 1970), but quite large radius changes can be accommodated. We shall see later how the α - PbO_2 structure, with comparatively minor modifications, can accommodate *A* cations ranging in radius from about 0.55 Å to 1.18 Å. The anion lattice may take part in other types of coupled substitutions involving the replacement of an oxygen ion by OH^- or F^- .

It is not uncommon to find minerals with a deficit of metals compared to the ideal formula, and it appears that metal vacancies may take part in coupled substitutions, a single 4-valent ion replacing two divalent ions, for example. To be specific, the oxide $Fe_2Nb_6O_{18}$ has a structure typical of the compounds AB_2O_6 . Here two-thirds of the *A* sites are occupied by $2Fe^{3+}$ without disturbing the structure (Gorzhevskaya, Grekulova, and Sidorenko, 1967).

Often, all these mechanisms operate together, and

the resulting list of metals taking part in the structure enable the niobo-tantalates to act as the "rubbish basket" of the pegmatite minerals. It will be evident that an understanding of the phase relationships and detailed compositions depends critically upon a knowledge of the ideal structure, which in turn depends on the ratios of ions of different charges and radii. Because of this, it would seem unwise to use Schröcke's method (1966) of dividing up a solid solution into its component oxides on the basis of MO_2 stoichiometry, and assuming that any iron present beyond that required to satisfy the (Fe,Mn) $(Nb,Ta)_2O_6$ component is ferric.

(2) Poorly Defined Structures

The structures may be poorly defined, despite the fact that these pegmatite minerals may have crystallized originally as large single crystals. The cryptocrystalline nature of many of these minerals, particularly in the euxenite, aeschynite, and pyrochlore groups (which are characterized by the larger *A* cations) has been ascribed to metamictization. The history of this subject has been well summarized by Pabst (1952). All of the above groups could contain radioactive elements such as uranium and thorium in their structure, but in other groups such as tapiolite and columbite-tantalite, the origin of the room-temperature disorder is more obscure. In all cases, the X-ray diffraction maxima of the natural mineral are broadened and weakened, and reflections due to cation ordering may be weak or absent. Crystallinity or order may be restored by heating in air in the temperature range 600°–1000°C, but it is not certain whether this restores the original crystalline phase, or produces a new non-equilibrium variety. Oxidation may also occur. In some cases, two phases are formed on heating, one of which often has a cubic cell corresponding to pyrochlore or sometimes to fluorite (Lima de Faria, 1958; Komkov, 1965, 1970). Where the natural material is amorphous to X-rays, the heating procedure cannot be proven to give correct results, but it is the best method available to characterize these poorly crystallized samples. Some confidence may be derived from the fact that there are usually some occurrences which are partially crystalline, and their diffraction patterns are consistent with those of material "restored" by heat treatment.

(3) Polymorphism

Many of the tantaloniobate minerals are subject to polymorphic transformations, which may or may

not be the result of cation ordering. Some appear to be irreversible (Borisenko, Maksimova, and Kazakova, 1969; Wolten and Chase, 1967), but it is possible that this is due to some minor "metamict" character in the natural minerals, or to oxidation of one or more of the component elements on heating.

A straightforward type of polymorphism is that shown by FeNbO_4 (Roth and Waring, 1964). This has a monoclinic wolframite-type³ cell at room temperature which disorders in a straightforward way to the orthorhombic $\alpha\text{-PbO}_2$ cell of very similar dimensions at about 1085°C. This in turn transforms to the tetragonal rutile cell at 1380°C. The structural rearrangements in the equivalent titanium oxides have been described by Simons and Dachille (1970). Since these two structures are among the most common for MO_2 compounds in the niobium and tantalum oxide systems, this polymorphic change should occur for many compositions, but it has not yet been thoroughly documented.

More complicated polymorphic relationships occur in other phases such as the fergusonites, and the aeschynite/euxenite groups (Komkov, 1963). Small structural distortions are very common among the niobo-tantalates, and are probably due to the high charge on the niobium and tantalum ions; the dis-

tortions allow Pauling's electrostatic valence rules to be better satisfied.

Classification of the Structures

Table 1 shows a grouping of the complex oxides of overall composition MO_2 that will be discussed in this section. Between groups II and III, in which the *A* and *B* cations are of comparable size, certain polymorphic transitions occur as a function of composition or temperature. Groups IVa and IVd are similarly inter-related.

We have assumed that the results of Roth and Waring (1964) for FeNbO_4 may be generalized to indicate that the rutile structure is favored at high temperature over the $\alpha\text{-PbO}_2$ structure, and this has recently been confirmed for the system $\text{NiNb}_2\text{O}_6\text{-NiF}_2$ (Senegas and Galy, 1972). It is also consistent with the work of Schröcke (1966). Such a transformation is interesting in itself, because in the Ti-O system the transformation to the $\alpha\text{-PbO}_2$ form has only been effected at very high pressures (Bendeliani, Popova, and Vereschagin, 1966). From their result, the $\alpha\text{-PbO}_2$ structure should be stabilized by slightly larger cations, and hence the greater stability of the $\alpha\text{-PbO}_2$ -related Mn columbites and tantalites over the iron ones (Moreau and Tramasure, 1965). The disordered orthorhombic $\alpha\text{-PbO}_2$ -type phase has come to be known as ixiolite (sometimes pseudo-ixiolite, Nickel, Rowland, and McAdam, 1963), although there is still some confusion over these terms. Since this phase may order into several room temperature forms of as yet indefinite composition and

TABLE 1. Classification of the MO_2 Tantalum-Niobium Oxides

Group	Characteristics	Oxygen Packing	Metamictization	Preferred A radius	MO_2	ABO_4	AB_2O_6	ABCDO_8	Other ratio
I	Clusters of edge-sharing octahedra	hcp		.53					Simpsonite $\text{Al}_4\text{Ta}_3\text{O}_{13}(\text{OH},\text{F})$
II	Rows of edge-sharing octahedra (Rutile related)	hcp	(✓)	.61	<i>ilmenorutile</i> ¹ (Nb-rutile) <i>strüverite</i> ¹ (Ta-rutile)	<i>Synthetic</i> ¹ e.g. CrNbO_4	tapiolite FeTa_2O_6 mössite $\text{Fe}(\text{Ta},\text{Nb})_2\text{O}_6$		Staringite (FeMn) ₅ (Ti,Sn) _{4,5} (Ta,Nb) ₁₂
III	Zig-zag rows of edge-sharing octahedra ($\alpha\text{-PbO}_2$ -related)	hcp	(✓)	.67			<i>ixiolite</i> ¹		
						"Wolframite" e.g. FeNbO_4 Samarskite	columbite MnNb_2O_6 tantalite MnTa_2O_6	wodginite olovo- tantalite	
IV	Mixed co-ordination	not c.p.	✓	.80+			<i>metamict phases</i> ¹		
(a)	$\alpha\text{-PbO}_2$ and "fluorite" A cations	"	✓			M'fergusonite	euxenite group		
(b)	scheelite related (tetrahedral B)	"	✓			T and M(?) fergusonite			
(c)	$\alpha\text{-PbO}_2$ and asymmetric A (covalent character)	"				stibio-tantalite	thoreaulite		
(d)	Double chains of octahedra and 8-co-ordinated A	"	✓	-1.0			aeschynite group		

¹ disordered phases.

may even be a mixture of ordered forms (see part IV of this series), it would seem preferable to give it the name *ixiolite* regardless of composition, and we recommend after consultation with Dr. Nickel the deletion of the term "pseudo-ixiolite."

Detailed Discussion of Phases in Table 1

The phases presented in the table will now be discussed in some detail. Groups I–III are based on hexagonally close-packed oxygen layers with both *A* and *B* cations in octahedral coordination. The octahedra share edges and corners to give the overall MO_2 stoichiometry. The structures are arranged in order of increasing *A* cation radius. Although the groups will be considered in order, the discussion of particular minerals within the groups may deviate from the order in the table. For example *M'* fergusonite has been placed after the euxenites so that the discussion of all the fergusonites can be contiguous.

I. *Simpsonite*

Simpsonite has a composition close to $Al_4Ta_3O_{13}$ (F,OH), and its structure is determined by the ratio of *A* to *B* cations (4:3), and by the small size of the aluminum, which encourages segregation of the cations into separate layers (Borisov and Belov, 1962).

The structure is shown in Figure 1 as a projection on (001) with the hexagonally close packed oxygen layers arranged parallel to the paper. The groups of three tantalum octahedra in the top layer are shown in full lines and, in the layer beneath, the groups of four aluminum octahedra are shown in dotted lines. The hexagonal cell has dimensions $a = 7.38 \text{ \AA}$, $c = 4.51 \text{ \AA}$, compared to the ideal dimensions for close-packed oxygen ions of $a = 7.41 \text{ \AA}$, $c = 4.57 \text{ \AA}$, a reduction in volume of about 2 percent.

II. *Rutile-Related Structures*

Ilmenorutile and *strüverite* are rutiles of rather indefinite composition in which Nb, Ta, and Fe^{2+} replace Ti. Typically, the composition varies within wide limits even in a single specimen, and no definite stoichiometric relationships are noted between Ti, Nb, Ta, and Fe (Vlasov, 1964). In only one out of 20 analyses was the amount of Fe^{2+} just sufficient to compensate for the 5-valent Nb and Ta present. In at least some cases, the extra iron is present as a fine lamellar intergrowth of ilmenite. It is probable that the illustration in Ramdohr (1969, p. 922) shows such ilmenite lamellae, rather than the rutile stated

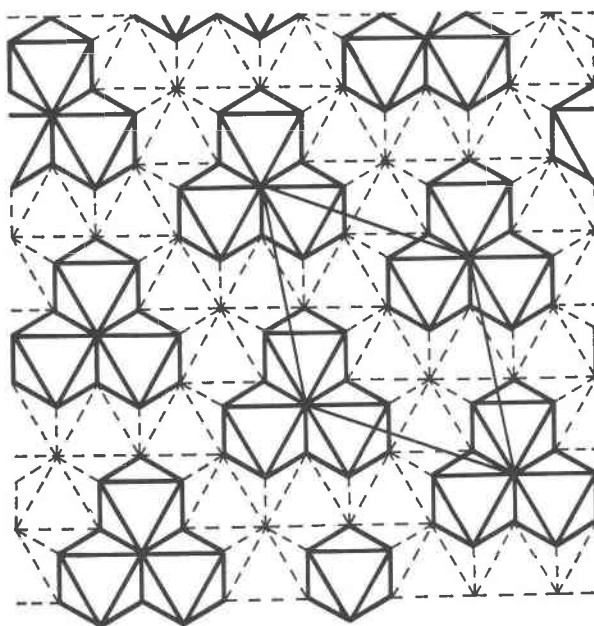


FIG. 1. Idealized section of the simpsonite structure parallel to the approximately close-packed layers along (001). Occupied octahedra in the upper level are shown in full lines, occupied octahedra in the next level down in broken lines. The upper layer contains only tantalum and the lower only aluminum. The hexagonal unit cell is one double layer deep.

in the caption. Electron probe analyses of similar rutiles substituted with tungsten and antimony suggest that there may still be deviations from MO_2 stoichiometry (Graham and Morris, 1973), and for smaller amounts of niobium and tantalum substitution there is often a metal deficiency (Deer, Howie, and Zussman, 1962). Flinter (1959) presented evidence of ordering in a Malayan ilmenorutile, but this has not been confirmed and is unlikely to be representative in view of the variability of composition.

A feature of the rutile-related structures which is at first sight surprising is the absence of ordered phases of composition ABO_4 . However, an examination of the space-group equivalent positions shows that such ordered phases are not possible in any tetragonal space-group with either two or four formula weights per unit cell. This suggests that the disordered ABO_4 rutile structures which have been synthesized (Brandt, 1943) may be metastable with respect to some other ordered structure, to some mixture of structures, or even to the separate oxides. They have not been observed in nature.

The only well-defined rutile phases in the niobium and tantalum oxide systems are the trirutile phases,

and the most common of these are found in the *tapiolite-mössite* series, $\text{Fe}(\text{Ta},\text{Nb})_2\text{O}_6$. These crystallize in the same space group as rutile, $P4_2/mnm$, and differ from it only because the *A* and *B* atoms are regularly arranged on the lattice, necessitating a unit cell having three times the height of the rutile cell. In the *A* positions, Fe^{2+} is always in considerable excess over Mn^{2+} , and in the *B* positions $\text{Ta} > \text{Nb}$. A manganese species of tapiolite reported recently (Khvostova and Arkhangel'skaya, 1970) contains Fe^{3+} which reduces the average size of the *A* cations, including manganese, to that of Fe^{2+} . Iron is still in excess over manganese.

The crystallization of the mineral *staringite* in the trirutile form (Burke *et al.*, 1969) is instructive. Since the trirutile form of ordering is the only simple ordering available, the cell contents, although far from ideal, distribute themselves accordingly, with Sn^{4+} playing the role of both *A* and *B* cations (the simplified formula is $\text{Fe}_{0.5}\text{Sn}_{4.5}\text{TaO}_{12}$).

A slightly idealized version of the rutile structure is shown in Figure 2. Filled octahedra in one layer share edges with one another to form continuous chains parallel to [001]. Similar chains of octahedra in the layer underneath share corners with the upper layer. This sequence repeats itself in a direction perpendicular to the paper.

There is some deviation of the oxygen positions from the close-packed planes, but the ideal structure represents the actual structure quite well, as can be

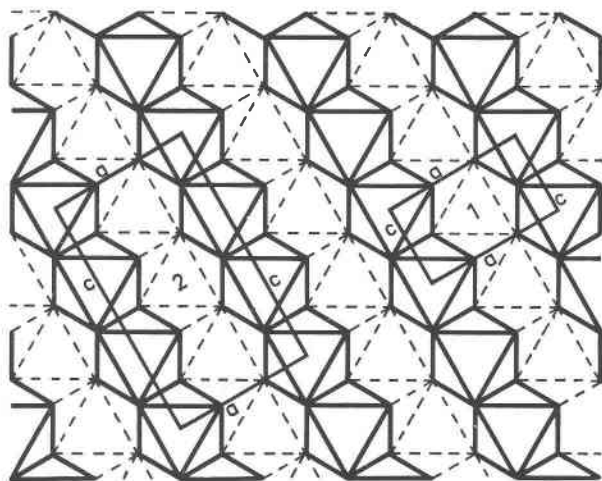


FIG. 2. Idealized section of the rutile structure parallel to (010). Representation of octahedra as for Figure 1. (1) is an outline of the rutile cell, and (2) of the trirutile cell. Both cells are one double layer deep into the paper.

TABLE 2. Rutile and $\alpha\text{-PbO}_2$ Structures Compared to Ideal Close-Packing (ideal lattice constants calculated for equal volumes)

	Rutile $\text{Fe}(\text{Nb},\text{Ta})_2\text{O}_6$		$\alpha\text{-PbO}_2$ $\text{Mn}(\text{Ta},\text{Nb})_2\text{O}_6$	
	Ideal	Tapiolite*	Ideal	Ixiolite**
a (Å)	4.67	4.67	4.79	4.79
b (Å)	4.95	4.67	5.86	5.76
c (Å)	2.86	3x3.05	5.08	5.16
u (metal)	—	—	.125	.168
x (oxygen)	.25	.30	.250	.278
y (oxygen)	.33	.30	.375	.378
z (oxygen)	0	0	.417	.416

* from Wyckoff (1965)

** from Grice (1972) using Wyckoff's origin

inferred from Table 2, where the parameters derived from an ideally close-packed lattice are compared with those observed. Cell volumes have been adjusted to give the best fit, and for tapiolite this represents a volume expansion of a close-packed oxygen lattice by 6.4 percent.

III. $\alpha\text{-PbO}_2$ -Related Structures

The same idealized oxygen arrangement characterizes ixiolite, columbite, tantalite, wolframite, olovo-tantalite, and wodginite, their structures being shown in Figure 3. The *ixiolite* cell is that of $\alpha\text{-PbO}_2$, as stated earlier, and the others are ordered structures based on it, which depend largely on the ratios of different kinds of atoms. The range of compositions embraced is extraordinarily wide, and includes the possibility of metal-deficient structures.

Despite the statement in Moreau and Tramasure (1965), these mineral structures are not derived from that of brookite, which has a double hexagonal oxygen packing; the packing in them is single hexagonal close-packed as in $\alpha\text{-PbO}_2$.

Table 2 shows the ideal parameters for ixiolite compared with those measured by Grice (1972) for an ixiolite containing largely Ta, Mn, and Nb. It will be noted that the main distortion from an ideal structure is the displacement of the metal atom from the center of the octahedron. We have chosen Wyckoff's (1965) settings for the unit cells, as these are in the correct orientation to apply the equivalent positions as given in the *International Tables* (Henry and Lonsdale, 1952) for the monoclinic cells. In each case, the *a* axis is perpendicular to the close-packed oxygen layers. In the case of ixiolite, the displacement of the oxygen *x* parameter results in a slight rumpling of the close-packed oxygen planes, but the projection of these planes is nearly ideal.

The volume expansion from the oxygen lattice is 14.8 percent.

Ordering of ixiolite into one of the supercells is governed largely by the atomic ratios. If the cation radii are similar, compounds of stoichiometry near $A^{3+}BO_4$ take the *wolframite structure*, and those near $A^{2+}B_2O_6$ the *columbite structure*.

The *samaraskites* have a general formula $(Y, Fe, Ti, U \dots)(Nb, Ta, Ti \dots)_2O_4$. Although they contain an appreciable amount of the large yttrium and rare earth ions, the average *A* cation radius is apparently reduced sufficiently by a large proportion of iron and titanium to enable them to crystallize in the wolframite structure. In the material studied by Komkov (1965), the average *A* radius was 0.77 Å. Samaraskites are almost always metamict, and may be attempting to precipitate fergusonite which would form in the absence of the iron.

The ideal composition of *olovotantalite* and *wodginite* (which may be approximately isostructural, with slightly different β angles) is not quite as clear. Both contain 32 oxygen atoms in the unit cell, and cannot be described by the formula AB_2O_6 , as attempted by early workers. Only two occurrences of olovotantalite have been described (Matias, 1963; Khvostova and Maksimova, 1962). The composition is characterized by high Nb_2O_5 (12–13 percent) compared to wodginite, and is very close to that of the Skogböle ixiolite which Nickel *et al* (1963) showed ordered to the olovotantalite structure. On the assumption of centrosymmetry, Grice (1972) derived a structural formula ACB_2O_8 for wodginite, in which *A* was largely Mn^{2+} , and *B* Ta^{5+} . He showed, however, that this structure did not obey Pauling's electrostatic valency rule well, and suggested that it would need to be partly disordered. The present authors independently determined the structure of wodginite (Part II) and showed it to be probably non-centrosymmetric. This allows a structural formula $ABCD_2O_8$, although the contents of sites *C* and *D* could barely be distinguished ($A = Mn^{2+}$ and $B = Ta^{5+}$ as before). Calculation showed (Part V) that the removal of the symmetry center allowed an improvement in the electrostatic energy of the lattice, a result which Grice attempted to reach in another way. The *C* and *D* sites have an average valence of 4.5 and may contain tantalum, niobium, tin, titanium, iron, and manganese.

Turnock (1966) showed that wodginite formed over a small composition range in the system $MnTa_2O_6$ - $FeTaO_4$ (while there was approximately

sufficient Mn to fill the *A* site of the above formula) but did not form in the absence of Fe^{3+} . This has led to the assumption that compositions in the Mn, Fe, Ta, Nb, and O system will form wodginite rather than columbo-tantalites in an oxidizing atmosphere. Thus Gouder de Beauregard, Dubois, and Bourguignon (1967) found that X-ray powder diffraction lines of columbo-tantalites split when heated in an oxidizing atmosphere, but were unaffected in an inert atmosphere. They took the splitting to be evidence of a monoclinic distortion. However, Komkov (1970) has shown that in the presence of SnO_2 , wodginite can form in the absence of Fe^{3+} , and Grice, Černý, and Ferguson (1972) have shown the cell to retain its monoclinic symmetry after strong reduction. By single-crystal methods we have examined a *columbite* with a high Fe/Mn ratio, MDC 3139. The size of its subcell before heating is $a = 4.73$ Å, $b = 5.74$ Å, $c = 5.12$ Å. A second columbite phase forms on oxidation, with the same orientation as the first, but with a unit cell smaller than the original ($a = 4.65$ Å, $b = 5.67$ Å, $c = 5.12$ Å). Its axial ratios indicate slightly less ideal oxygen packing. The oxidation occurs quite rapidly to form

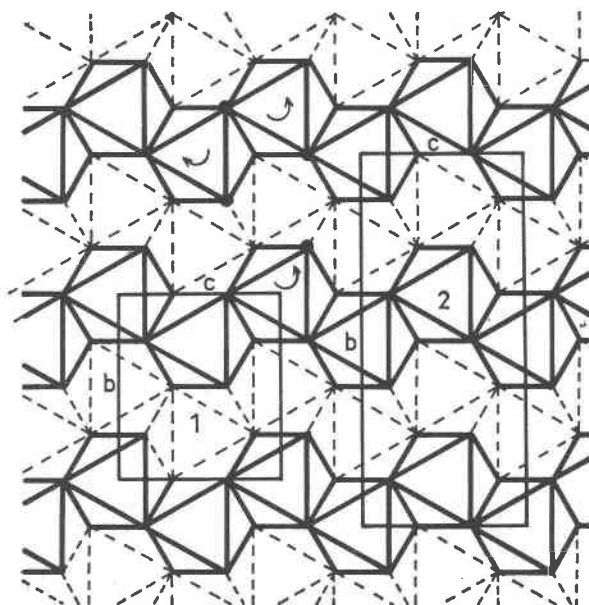


FIG. 3. Idealized section of the α - PbO_2 structure along (001). Representation as for Figure 1. (1) is an outline of the ixiolite and the columbite-tantalite cell; the former is one double layer deep, the latter three. (2) is an outline of the wodginite and olovotantalite cells, which are both two double layers deep. The arrows show rotations needed to convert the top oxygen layer into the euxenite/*M'* fergusonite configuration (Fig. 4).

a two-phase mixture, which thereafter appears to be stable, possibly through segregation into iron-rich and iron-poor regions. The coexistence of the two cells may be an alternative explanation for Gouder de Beauregard's results. The fact that wodginite did not form in our experiment could perhaps be due to a high niobium content (Komkov, 1970). All wodginite analyses so far have had a large excess of tantalum over niobium (Grice, 1972; Nickel, Rowland, and McAdam, 1963b; Vorma and Siivola, 1967). The resulting columbite must be metal-deficient; as mentioned in the introduction, in an extreme case all the iron in a columbite may be ferric, and $\frac{1}{3}$ of the A sites may be vacant (Gorzhevskaya, *et al*, 1967).

Wodginite is much more common than supposed until recently. Thus it is the most common tantalum mineral in the Tanco pegmatite (Grice *et al*, 1972). In addition to the three known West Australian localities in the Pilbara region (Pryce, 1970), we have identified wodginite from Mt. Matthew and Greenbushes, separated from the Pilbara occurrences by 650 and 1450 km respectively. In each of the latter two cases, the occurrence is a recrystallized intimate mixture containing ~ 20 percent wodginite and 80 percent tapiolite, suggesting perhaps that this mix-

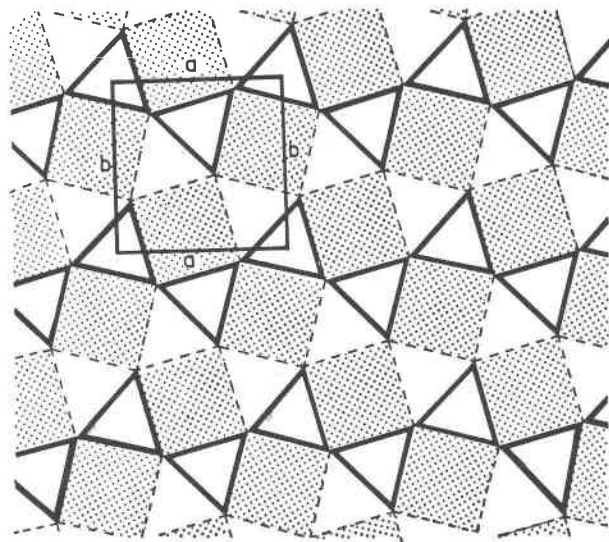


FIG. 4. Idealized section of the euxenite/ M' fergusonite configuration parallel to (001). The heavy triangles are the tops of occupied Ta/Nb octahedra (compare Fig. 2) and the squares are the bottoms of (rare earth, *etc*) coordination polyhedra (approximately cubes). In M' fergusonite, the unit cell is one double layer deep. In the euxenite series, it is two triple layers deep (one triple layer is two octahedral layers and one cubic).

ture recrystallized from a common pre-existing phase. This is an important piece of evidence in favor of a new interpretation of metamictization in the niobium and tantalum complex oxide systems and will be referred to again later.

IV. Structures with Mixed Coordination

As the A cation becomes larger (*e.g.*, in the rare earth series) or prefers an asymmetric environment (*e.g.*, Sb^{3+} , As^{3+} , Sn^{2+}), the α - PbO_2 structure is modified to accommodate it.

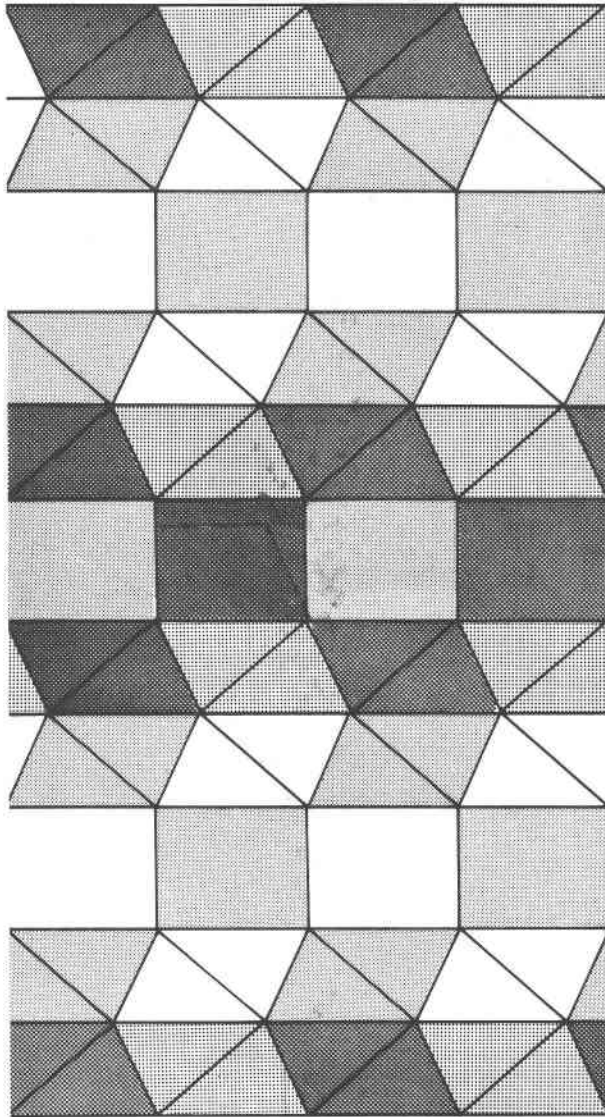
(a) Interlayered α - PbO_2 Structures (Large A Cations)

In the case of large A ions, the modifications may be viewed in two ways, either as a distorted α - PbO_2 structure, or as an interlayering of discrete sections of the α - PbO_2 and fluorite structures.

Thus the *euxenite* group, of ideal composition AB_2O_6 , has a columbite-like layer structure in which the A cations constitute every third layer (Alexandrov, 1960; Cummings and Simonsen, 1970). The layering is parallel to the "close-packed" planes depicted in Figure 3, so that the zig-zag chains of octahedra are still apparent. Slight movements, particularly of the oxygen atoms, adjust the coordination number of the A ions to eight.

We have indicated in Figure 3 the groups of four oxygen atoms at the top of the octahedral layer which are coordinated to the A cations in this structure. It will be obvious by comparison with Figure 4 that 15° rotations of the oxygen triangles in opposite directions as indicated by the arrows will result in these diamond shapes becoming square. Distortion of the adjacent oxygen layer in the opposite sense allows near cubic coordination of the A cations, and since the cubes are joined by edges, this represents a collapsed section of the fluorite structure. (Actually the top and bottom of the cube are rotated with respect to one another by about 30° .)

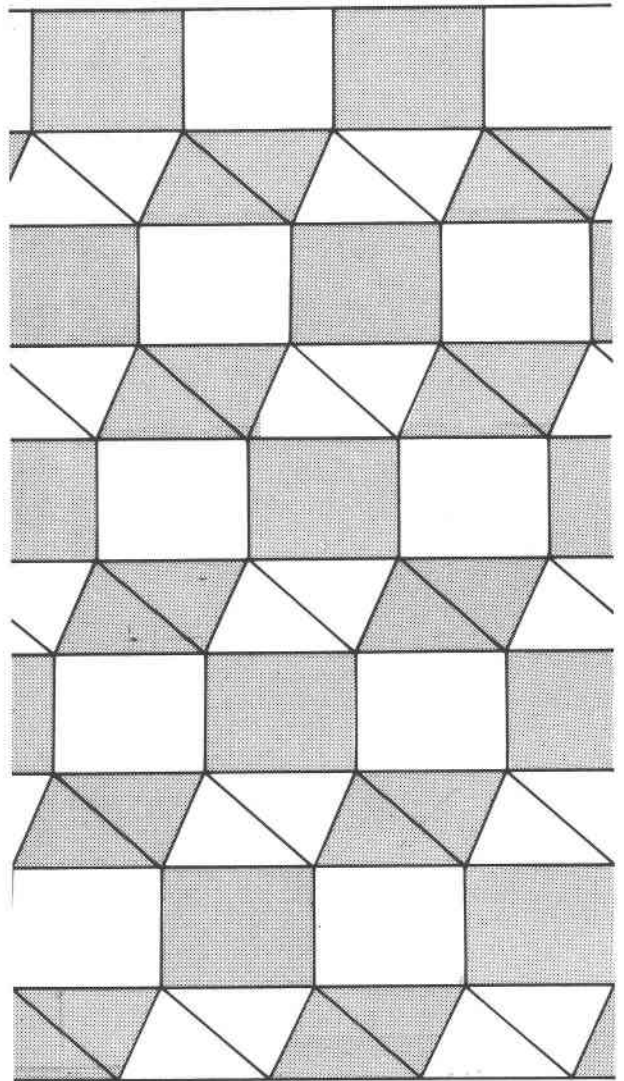
Figure 5a shows a section of the euxenite structure perpendicular to the layering, showing how the A and B cations are interleaved. The α - PbO_2 chains are viewed from the side, and because the octahedra of the two chains are pointing in opposite directions, the resulting structure is orthorhombic. The ideal dimensions of the unit cell of fergusonite, a member of the euxenite group, are shown in Table 3. The cell volume is expanded by 3.4 percent with respect to an oxygen lattice alone, or by 20 percent with respect to ideal close-packed oxygens.



(a)

The naturally occurring *fergusonite* modification (composition ABO_4) is usually "metamict," and requires heating to about 800°C in order to produce a tetragonal "scheelite" form. An occasional crystal is found naturally exhibiting this crystal structure, and one of these was studied by Komkov (1959). Formed as described, above, the tetragonal modification is stable at room temperature; on further heating, however, it becomes unstable at room temperature, and transforms reversibly on cooling to a low-temperature monoclinic form *M* (Wolten and Chase, 1967), the structure of which was also studied by Komkov (1959). The difference between the natural tetragonal form *T* (which is probably the same

as that formed by moderate heating of metamict material) and the high-temperature tetragonal form *T'* is not known. For CeNbO_4 , the stable phase is critically dependent on the atmosphere over the sample on heating, as the cerium is easily oxidizable (Gingerich and Bair, 1964). Two other monoclinic forms of *fergusonite* labelled β and *M'* respectively have been discussed (Gorzhevskaya *et al*, 1961; Wolten, 1967), and both transform irreversibly on



(b)

FIG. 5. Sections of the euxenite (a) and *M'* fergusonite (b) structures parallel to (010) and thus perpendicular to the (001) layering. The "fluorite" (rectangles) layer is schematic only, as the cubes are in fact significantly tilted about a vertical axis (Fig. 4). Intensity of shading increases with height perpendicular to the paper.

heating above 1000°C to the normal T' modification (high temperature) which cools to form M . The $T' - M$ transition temperature decreases as the radius of the A cation increases, so the T' form is preferred by the larger A cations, which is consistent with the 1 percent increase in volume in transforming to this phase (Gingerich and Bair, 1964). Although all other phases transform irreversibly to the M form after strong heating, this is not necessarily the equilibrium modification at room temperature.

The structures of M , M' , and T fergusonites as described in the literature constitute one of the enigmas of crystal chemistry for the following reasons:

(i) They are the only known phases in which Nb^{5+} and Ta^{5+} take on solely tetrahedral coordination with oxygen.

(ii) There is little volume change associated with the change in coordination from octahedral to tetrahedral coordination [vol. of $M' = \frac{1}{2} \times 293.0 \text{ \AA}^3$ (Wolten, 1967); vol. of $M = 292.4 \text{ \AA}^3$ (McCarthy, 1971) for $YNbO_4$].

(iii) The observed Nb-O interatomic distance of about 1.9 Å (Komkov, 1959; Wolten, 1967) is much greater than the tetrahedral distance of 1.66 Å in $H-Nb_2O_5$ (Gatehouse and Wadsley, 1964).

(iv) Since the metal lattice of these forms is fluorite-related, 4–8 coordination seems unnecessary; structures are known in which the Nb could have 6- or 7-coordination, and which would suit these compositions well.

(v) If there is an appreciable ionic component in the bonding, tetrahedral coordination is very unlikely for such a highly charged ion.

A strong contender for the position of most stable room-temperature phase is the M' monoclinic form, synthesized at temperatures below the stability range of the high-temperature T' form (Wolten and Chase, 1967). The structure of this M' modification (Wol-

TABLE 3. Lattice Spacings of Fersmite and M' Fergusonite Compared to Ideal Values (adjusted to equal volumes)

	M' fergusonite YTaO ₄		fersmite CaNb ₂ O ₆	
	ideal	actual*	ideal	actual**
a (Å)	5.39	5.29	5.47	5.20
b (Å)	5.39	5.45	5.47	5.75
c (Å)	5.07	5.11	7.46	2x7.46
β	<98.7°	96.4°	90°	90°

* from Wolten (1967)

** from Cummings and Simonsen (1970)

TABLE 4. Lattice Parameters of the Four Modifications of Fergusonite and of Aeschynite

	a	b	c	β	vol Å ³	Nb-O distances about each Nb atom Nb (I)	Nb atom Nb (II)
a. Yttrium niobates and tantalates (fergusonite structures)							
Tetragonal T*	5.16	2x5.45	5.16	-	145.1	4x1.89 4x2.35	-
Monoclinic M*	5.24	2x5.45	5.06	95.5°	143.8	or 4x2.69**	2x1.82
						2x1.74 2x2.05 2x2.59 2x2.85	2x1.94 2x2.70 2x2.73
M'***	5.29	5.45	5.11	96.4°	146.4	2x1.94 2x2.03 2x2.13	-
β†	5.20	2x5.45	5.12	91.8°	145.0	2x3.04	-
corresponding M†	5.30	2x5.45	5.06	94.2°	146.0	-	-
b. Gadolinium niobate							
M fergusonite††	5.38	11.08	½x7.65	94.4°	454.9		
GdNbO ₄ †††							
aeschynite†††	5.27	10.98	7.47	90.0°	432.3		
GdNbTiO ₆ †††							
euxenite†††	5.24	½x11.18	2x7.34	90.0°	430.0		
GdNbTiO ₆ †††							

* Komkov (1959)

** Wyckoff (1965)

*** Wolten (1967)

† Gorzhevskaya et al (1961)

†† Gingerich and Bair (1964); McCarthy (1971)

††† Aleksandrov (1963)

ten, 1967) is directly related to that of euxenite, although Wolten did not recognize the importance of the indisputably octahedral nature of the B cations (Table 4, a and b). Figure 5 also represents a section of the M' fergusonite lattice, but because of its ABO_4 composition, single layers of $\alpha-PbO_2$ and "fluorite" are interleaved (Fig. 5b). Evidently a single $\alpha-PbO_2$ octahedral layer is more susceptible to in-plane distortions than a double layer, which is self-reinforcing, and this is reflected in the deviations of a and b from their ideal values (Table 3). The actual cell is just 1 percent smaller in volume than the ideal oxygen arrangement, but is 18 percent greater than the corresponding volume of close-packed oxygen ions.

(b) Scheelite-Related Structures

In the scheelite structure, 8-coordinated A cations and 4-coordinated B cations are arranged in 3-dimensional packing rather than a layer structure.

The beautiful way in which the M' structure fits into the crystallochemical scheme suggests that the M and T fergusonite structures may not represent the stable form at room temperature. A detailed study of the coordination of the B atoms in these structures is hampered by inconsistencies between the quoted parameters, the diagrams, and the table of interatomic distances in the original paper (Komkov, 1959). In the case of M fergusonite, Wolten (1967) has given another interpretation with the x

TABLE 5. Lattice Spacings of Thoreaulite and Stibiocolumbite Compared to Ideal Values

	Stibiocolumbite SbNbO ₄			Thoreaulite SnTa ₂ O ₆		
	ideal	actual*	% increase	ideal	actual**	% increase
a (Å)	5.6	5.56	-	5.6	5.55	-
b (Å)	4.57	4.94	8	4.57	4.87	6.5
c (Å)	11.32	11.81	4.3	16.17	17.14	6.1
β				90°	91.0°	

* Skapski and Rogers (1965)
** Mumme (1970)

and z parameters transposed. A summary of the fergusonites using simple assumptions has been given by Muller and Roy (1974).

Considering first *T fergusonite*, if we assume (as Wyckoff, 1965) that Komkov has transposed x and y for the oxygen atoms, the niobium has 4 oxygens at 1.89 Å and 4 at 2.69 Å (Table 4), while the next nearest neighbors are 4.3 Å away. The second nearest neighbors are somewhat closer than in most typical scheelite structures, so that niobium is tending to 8-coordination. The use of Komkov's parameters as published results in much less distorted 8-coordination for both cations (Table 4), but anion-anion distances are impossibly short.

The case of *M fergusonite* is again not straightforward because of uncertainty in the original data. The interatomic distances in Table 5 are derived on the assumption that Komkov (1959) has used a β angle of 85.5° as quoted in the paper, rather than the standard setting with β obtuse. Whatever assumption is made, the coordination of both niobiums as derived by averaging the four shortest and the four next nearest bonds is remarkably similar, and the second nearest distorted tetrahedron may again be regarded as a part of the coordination figure. The nearest Nb-O distances average about 1.89 Å and the next 2.71 Å; the next nearest distance after that is about 4.0 Å. We propose to investigate an *M fergusonite* by neutron diffraction in order to verify the oxygen positions derived by Komkov (1959). The close relationship between the polymorphic forms (Part III) is indicated by the lattice spacings (shown in Table 4) and by the interesting stability relations.⁴

⁴ However, the dangers of an argument by analogy are illustrated by Wolten's interpretation of the *M'* structure. A case can also be made on the same grounds for a close relationship between the structures of *M fergusonite*, aeschynite, and euxenite. The lattice spacings are included in Table 4, and the uncanny relationship is discussed further when the aeschynite structure is described.

Evidently the large *A* cations in these structures are difficult to accommodate without some distortion of the octahedral coordination around the *B* cations. It is also evident that distortions introduced in different ways result in a large number of possible structures, many of which appear to be approximately equally stable. We think that it is significant that most minerals with group IV structures are particularly prone to metamictization.

(c) Interlayered α-PbO₂ Structures (Asymmetric *A* Environments)

The stibiotantalite and thoreaulite structures are built up on similar principles to those of *M'* fergusonite and fersmite, although because of the asymmetric environment favored by the *A* cations, the close-packing of oxygen is interrupted rather than merely distorted. In addition, the layers of α-PbO₂ structure occupied by the *B* cations are perpendicular to the close-packed planes instead of parallel with them. The resulting single or double layer segments could equally be regarded as segments of the rutile structure.

Stibiotantalite, SbTaO₄, has the same structure as SbNbO₄, Bi(Ta, Nb)O₄, and Sb³⁺Sb⁵⁺O₄ (Skapski and Rogers, 1965). The octahedral layers are linked by Sb or Bi, coordinated so that each metal atom is the apex of a pyramid with rhombic base (Fig. 6). Because alternate rows of Sb pyramids are opposed in direction, the unit cell is accurately orthorhombic in shape. This is not true of the *thoreaulite* structure

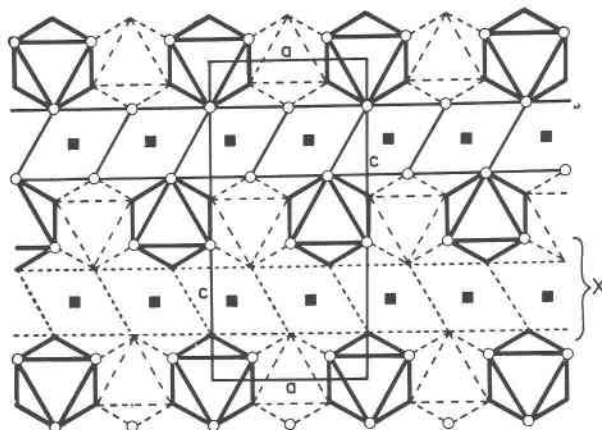


FIG. 6. Idealized section parallel to (010) of the stibiotantalite structure. The Sb or Bi atoms are shown as squares. Oxygens on a single level are marked with circles so that the interruption to the close-packing can be seen (X). The layering of *A* and *B* cations is now perpendicular to the paper, and the unit cell is just two octahedra deep.

(Fig. 7) where slight deviations from the ideal orthorhombic symmetry can occur. In the figures, all oxygen atoms in a single layer have been circled; it will be observed that at the position of the row of Sb pyramids, one close-packed oxygen layer continues across the gap in almost ideal packing, while the other has a larger than usual O-O distance here. This results in close-packed oxygen layers which extend indefinitely along a , but which are a little less than the c dimension in width. On one side of the gap, the oxygen slabs are packed $ABAB \dots$, and on the other, $ACAC \dots$, using the usual nomenclature for close-packed layers.

It is necessary to justify the choice of SnTa_2O_6 as the ideal composition of thoreaulite, since the ideal formula is usually given as SnTa_2O_7 (Mumme, 1970; Maksimova and Ilyukhin, 1967; Strunz, 1970). Bodiott (1968) observed a phase undoubtedly containing Sn^{2+} , of composition SnNb_2O_6 , which gave an X-ray pattern identical to that of thoreaulite, and lattice spacings $a = 17.07$, $b = 4.89$, $c = 5.57$ ($\beta = 91.1^\circ$) calculated from his published data. Oxidation of this phase resulted in an increase of weight corresponding to the transition $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$, and a dissociation into the component oxides. It can be confidently predicted that Bodiott's

phase has the structure shown in Figure 7. A difficulty with the published structures of SnTa_2O_7 is the placing of the seventh oxygen (Mumme, 1970; Maksimova and Ilyukhin, 1967), which even in the most favorable position has four short coplanar O-O contacts, two at 2.11 Å and two at 2.33 Å, in addition to a shorter than usual $\text{Sn}^{4+} - \text{O}$ distance of 1.82 Å. These difficulties disappear if the oxygen atom is not present; we then have Sn^{2+} in pyramidal coordination with two contacts of 2.21 Å and two of 2.39 Å, which is consistent with the coordination in SnO .

The thoreaulite and stibiocolumbite lattice spacings are compared with the ideal values based on close-packed partial layers of oxygen in Table 5. Relative to the ideal oxygen lattice, the structure has expanded by several percent in the two directions at right angles to the close-packed segments; the third direction, along the length of the segments, is ideal in both structures. The minerals in this group are commonly well crystallized, and it would seem that the bonding of the A cation in its asymmetric site is so energetic that alternative structures are comparatively unstable, and there is no tendency for metamictization.

(d) Structures with Double Chains of Octahedra

One group of MO_2 minerals remains which is polymorphic with the euxenite group, namely the *aeschnites*. The general formula is again AB_2O_6 ; there is usually a considerable Ti content in the B group, and a corresponding rare earth component in the A group, as in the euxenites, although CaTa_2O_6 itself takes this structure (Jahnberg, 1963). The only consistent feature which seems characteristic of the *aeschnites* compared with the euxenites is that the rare earths in the former are the earlier lanthanides, which have larger ionic radii, and in the latter, yttrium and the later lanthanides (with smaller radii). While the coordination is similar, the structures are different (Aleksandrov, 1962) and *aeschnite* consists of double chains of B octahedra linked in pairs by sharing edges, and extending indefinitely along b by sharing corners. The large A cations are accommodated in 8-coordinated sites in channels between the chains of octahedra, and the size of the site can be adjusted by rotating the octahedral chains about their common corners. This slightly alters a . Titanium and niobium are apparently not ordered on the octahedral sites (Fauquier and Gasperin, 1970). A section parallel to (010) is shown in Fig-

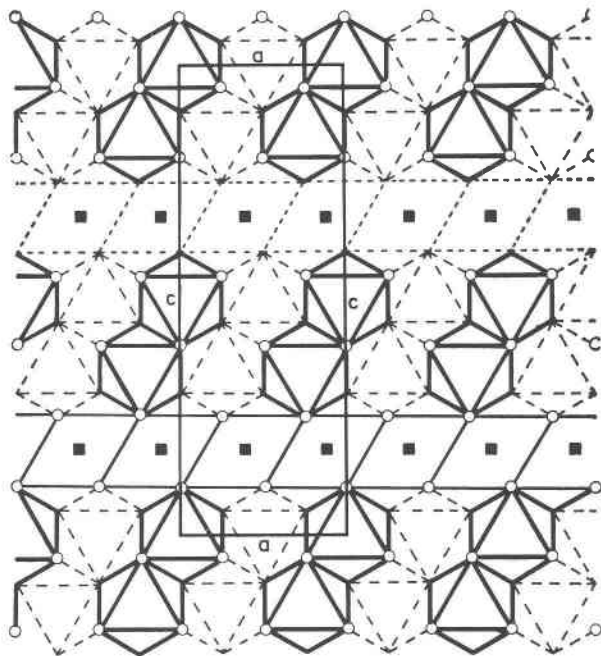


Fig. 7. Idealized section of the thoreaulite structure (see text) corresponding to Figure 6. The tin atoms are shown as squares.

ure 8a. The chains (perpendicular to the projection) are somewhat folded, the octahedra being tilted as shown.

Since many aeschynites and euxenites are metamict and do not give a recognizable diffraction pattern until ignited, it is not possible to be definite about their original structures. Even the crystal morphology may be confusing, since this will probably be determined by the higher temperature form. For some ideal compositions, it is known that the high temperature form is of the euxenite type and the low temperature form of the aeschynite type (Komkov, 1963, 1966; Aleksandrov, 1963; Seifert and Beck, 1965). The apparently contrary results of Pyatenko (1970) are probably due to the same kind of "metamictization" effects which render the fergusonite problem so intractable, and are due to the non-reversible nature of the transformation in natural minerals (Part IV). Aeschynite also seems to be favored by high pressure (Komkov, 1966).

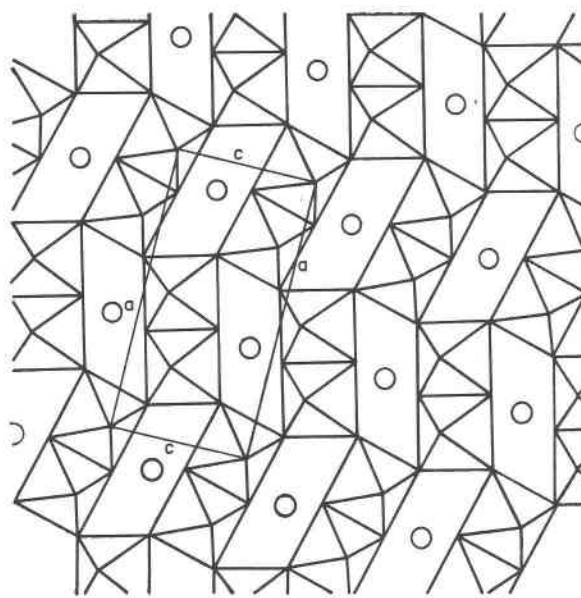
Figure 8b shows a single-layer oxygen-net from the Komkov (1959) structure of *M* fergusonite, discussed earlier. It is identical with the corresponding layer from aeschynite, but because the adjacent oxygen layers differ in the two structures, the coordination of both the *A* and *B* cations is different. The closeness of the lattice spacings (Table 4) and the similarity of the oxygen net in the same orientation do not accord with the different coordination, nor with the fact that the densest oxygen packing in aeschynite is parallel to (021) and similar planes, while in *M* fergusonite it is parallel to (001), (010), and (100). Similarly the densest packing of oxygens in *T* fergusonite is on {112} planes.

The three cells compared in Table 5b are fundamentally dissimilar structurally. It thus appears that structural arguments based on similarities of the unit cell size and shape may be misleading, or alternatively that the details of one or more of the structures concerned are still inadequately resolved.

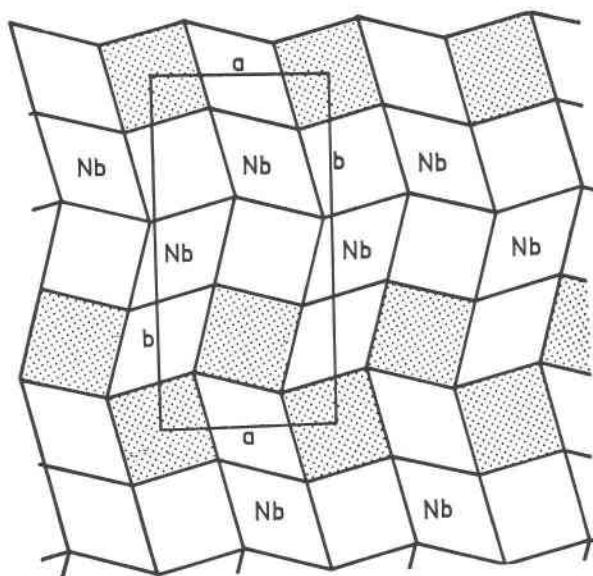
General

We do not propose to discuss in any detail the structures whose ideal compositions are not represented by the overall formula MO_2 . The natural minerals falling in this category are in fact restricted in number, although an enormous variety of synthetic phases is known.

The pyrochlores already mentioned take the ideal composition $A_2B_2O_6X$, where *X* is OH, F, or sometimes O. Metal-deficient phases are fairly common,



(a)



(b)

FIG. 8. (a) Idealized section parallel to (010) of the aeschynite structure showing the *B*-centered octahedra and the 8-coordinated rare earths. The double octahedra are tilted alternately in opposite directions along the chain length, *b*, and the *b* axis is two octahedra long. (b) Single layer oxygen net parallel to (001) from Komkov's (1959) structure of *M* fergusonite, for comparison with (a). The rare earths are now situated above the squares, and the niobiums in tetrahedral positions.

but anion deficient phases are also possible, especially with tin and lead as the *A* cation. For the naturally occurring niobium-tantalum pyrochlores, the average valence for occupants of the *A* site is between 1½ and 2, and of the *B* site between 5 and 4½. This is by no means the limit of stability of the structure (Barker *et al.*, 1970). The structure is cubic, and the *A* cation is usually large and 8-coordinated; the *B* cation is 6-coordinated. Structures closely related to pyrochlore but with slight cell distortions occur in rhombohedral, tetragonal, and orthorhombic forms.

Compounds of composition ABX_3 , where *X* is O or OH, usually adopt the perovskite structure or a modification of it. The *A* radius is about 1 Å, and the *B* group includes elements like Mg and Zr in addition to the usual *B* group ions. As in the pyrochlores, there is often a deficiency of *A* cations, which is correlated with the substitution of OH for O. Both of these phases when they occur naturally are commonly metamict.

Acknowledgment

We are indebted to Mrs. Wendy Gorton for her careful preparation of the diagrams.

References

- ALEKSANDROV, V. B. (1960) Crystal structure of fersmite. *Dokl. Akad. Nauk SSSR. Earth Sci.* **132**, 597–600.
- (1962) Crystal structure of aeschynite. *Dokl. Akad. Nauk SSSR Earth Sci.* **142**, 107–108.
- (1963) Isomorphism of cations in titaniferous tantalum-niobates of composition AB_2X_6 . *Dokl. Akad. Nauk SSSR Earth Sci.* **153**, 129–131.
- BARKER, W. W., J. GRAHAM, O. KNOP, AND F. BRISSE (1970) Crystal chemistry of oxide pyrochlores. *The Chemistry of Extended Defects in Solids*, L. Eyring and M. O'Keefe, Eds. North Holland, Amsterdam, p. 198–206.
- BENDELIANI, N. A., S. V. POPOVA, AND L. F. VERESCHAGIN (1966) New modification of titanium dioxide obtained at high pressures. *Geochem. Int.* **3**, 387–390.
- BODIOT, D. (1968) Comparison of niobium and tantalum compounds between their pentoxides and the oxides SnO , CeO_2 , UO_2 and M_2O_3 . *Rev. Chim. Mineral.* **5**, 569–607.
- BORISENKO, L. F., N. V. MAKSIMOVA, AND M. YE KAZAKOVA (1969) Scandium ixiolite—a new variety of tantaloniobates of the composition $(A,B)_2O_{2n}$. *Dokl. Akad. Nauk SSSR Earth Sci.* **189**, 148–150.
- BORISOV, S. V., AND N. V. BELOV (1962) Crystal structure of simpsonite $Al_4Ta_3O_{13}(F,OH)$. *Dokl. Akad. Nauk SSSR Earth Sci.* **147**, 147–150.
- BRANDT, K. (1943) X-ray studies on ABO_4 compounds of rutile type and AB_2O_6 compounds of columbite type. *Arkiv Kemi, Mineral. Geol.* **17A**, 8 pp.
- BURKE, E. A. J., C. KIEFT, R. O. FELIUS, AND M. S. ADUSMILLI (1969) Staringite, a new tin-tantalum mineral from north eastern Brazil. *Mineral. Mag.* **37**, 447–452.
- CUMMINGS, J. P., AND S. H. SIMONSEN (1970) The crystal structure of calcium niobate. *Am. Mineral.* **55**, 90–97.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock-Forming Minerals*. Longmans, London.
- DEM'YANETS, L. N., V. V. ILYUKHIN, A. V. CHICHAGOV, AND N. V. BELOV (1967) Crystal chemistry of isomorphic substitutions in molybdates and tungstates of divalent metals. *Izv. Akad. Nauk SSSR Neorg. Mat.* **3**, 2221.
- FAUQUIER, D., AND M. GASPERIN (1970) Synthesis of monocystals and structural study of $LaNbTiO_6$. *Bull. Soc. franc. Mineral. Crystallogr.* **93**, 258–259.
- FLINTER, B. H. (1959) Re-examination of "struverite" from Malaya. *Am. Mineral.* **44**, 620–632.
- GATEHOUSE, B., AND A. D. WADSLY (1964) The crystal structure of the high temperature form of niobium pentoxide. *Acta Crystallogr.* **17**, 1545–1560.
- GINGERICH, K. A., AND H. E. BAIR (1964) Relation between ionic radii and transformation temperature in rare earth niobates. *Advances in X-ray Analysis*, **7**, 22–30.
- GINSBURG, A. I. (1964) Rhombic titano-tantaloniobates. *Vsesoyuznyi Nauchno-Issledovatel'skii Institut Mineralogicheskaya Seria*, **23**, 4–7.
- , G. A. SIDORENKO, S. A. GORZHEVSKAYA, and others (1964) Various titles. *Vsesoyuznyi Nauchno-Issledovatel'skii Institut Mineralogicheskaya Seria*. (Entire Issue).
- GORZHEVSKAYA, S. A., G. A. SIDORENKO, AND I. E. SMORCHKOV (1961) (Translated 1963). A new modification of fergusonite: β -fergusonite. *New Data on Rare Element Mineralogy*, A. I. Ginzburg, Ed. Consultants Bureau, New York, pp. 16–17.
- , L. A. GREKULOVA, AND G. A. SIDORENKO (1967) Synthetic columbite and tantalite of binary composition. *Dokl. Akad. Nauk SSSR Earth Sciences*, **173**, 104.
- GOUDER DE BEAUREGARD, C., J. DUBOIS, AND P. BOURGUIGNON (1967) Thermal behaviour of columbo-tantalites. *Ann. Soc. Geol. Belgique*, **90**, 501–518.
- GRAHAM, J., AND R. C. MORRIS (1973) Tungsten- and antimony-substituted rutile. *Mineral. Mag.* **39**, 470–473.
- GRICE, J. D. (1972) *Crystal Structures of the Tantalum Oxide Minerals Tantalite and Wodginite, and of Millerite NiS*. Ph.D. Thesis, University of Manitoba.
- , P. ČERNÝ, AND R. B. FERGUSON (1972) The Tanco pegmatite at Bernic Lake, Manitoba. II. Wodginite, tantalite, pseudoixiolite, and related minerals. *Can. Mineral.* **11**, 609–642.
- HENRY, N. F. M., AND K. LONSDALE (1952) *International Tables for X-ray Crystallography*, Vol. I. Birmingham, The Kynoch Press.
- JAHNBERG, L. (1963) Crystal structure of orthorhombic $CaTa_2O_6$. *Acta Chem. Scand.* **17**, 2548–2559.
- KHVOSTOVA, V. A., AND V. N. ARKHANGEL'SKAYA (1970) A find of a manganese species of tapiolite. *Dokl. Akad. Nauk SSSR Earth Sci.* **194**, 128–129.
- , AND N. V. MAKSIMOVA (1962) New discovery of ixiolite. *Dokl. Akad. Nauk SSSR Earth Sci.* **148**, 101–103.
- KOMKOV, A. I. (1959) Structure of native fergusonite and of its polymorphic modification. *Kristallografiya*, **4**, 836–841.
- (1963) Euxenite and priorite-polymorphous varieties

- of YNbTiO_6 . *Dokl. Akad. Nauk SSSR Earth Sci.* **148**, 103–104.
- (1965) Structure and composition of samarskite. *Dokl. Akad. Nauk SSSR Earth Sci.* **160**, 693–696.
- (1966) Genetic relationships of euxenite and priorite. *Dokl. Akad. Nauk SSSR Earth Sci.* **171**, 145–146.
- (1970) Relationship between the X-ray constants of columbites and composition. *Dokl. Akad. Nauk SSSR, Earth Sci.* **195**, 117.
- LIMA DE FARIA, J. (1958) Heat treatment of metamict euxenites, polymignites, yttriotantalites, samarskites, pyrochlores, and allanite. *Mineral. Mag.* **31**, 937–942.
- MAKSIMOVA, N. V., AND V. V. ILYUKHIN (1967) Mineralogy. *Sov. Phys. Crystallogr.* **12**, 105–106.
- MATIAS, V. V. (1963) (Originally 1961) Stannotantalite—A new variety of tantalite. *New Data on Rare Element Mineralogy*, A. I. Ginzburg, Ed., p. 18–26. Consultants Bureau, New York.
- MCCARTHY, G. J. (1971) X-ray studies of rare earth niobate compounds. *Acta Crystallogr.* **B27**, 2285–2287.
- MOREAU, J., AND G. TRAMASURE (1965) Contribution to the series columbite-tantalite and tapiolite-mossite. *Ann. Soc. Geol. Belgique*, **88**, 301–390.
- MULLER, O., AND R. ROY (1974) The major ternary structure families. *Minerals, Rocks and Inorganic Materials*, Vol. 10. Springer Verlag. To be published.
- MUMME, W. G. (1970) The crystal structure of SnTa_2O_7 , thoreaulite, an example of tin in five-fold coordination. *Am. Mineral.* **55**, 367–377.
- NICKEL, E. H., J. F. ROWLAND, AND R. C. MCADAM (1963) Ixiolite—a columbite substructure. *Am. Mineral.* **48**, 961–979.
- PABST, A. (1952) The metamict state. *Am. Mineral.* **37**, 137–157.
- PRYCE, M. W. (1970) Identification of Western Australian columbite-tantalite, ixiolite, and wodginite. *J. Roy. Soc. West. Aust.* **53**, 65–68.
- PYATENKO, YU. A. (1970) Behaviour of metamict minerals on heating, and the general problem of metamictization. *Geochem. Int.*, p. 758–763.
- RAMDOHR, P. (1969) *The Ore Minerals and Their Inter-growths*. Pergamon, London.
- ROTH, R. S., AND J. L. WARING (1964) Ixiolite and other polymorphic types of FeNbO_4 . *Am. Mineral.* **49**, 242–246.
- SCHÄFER, H., R. GRUEHN, AND F. SCHULTE (1966) Chemistry of niobium and tantalum. XLIX. Modifications of niobium pentoxide. *Angew. Chem Intern. Ed. Engl.* **5**, 40–52. *Angew. Chem.* **78**, 28.
- SCHRÖCKE, H. (1966) On solid state equilibria within the columbite-tapiolite groups, and also of the columbite-tapiolite groups with $\text{YTi}(\text{Nb},\text{Ta})\text{O}_6$, euxenite, and with FeNbO_4 . *Neues Jahrb. Mineral. Abh.* **106**, 1–54.
- SEIFERT, H., AND H. BECK (1965) Crystal chemistry and geochemistry of metamict materials of the euxenite-aeschynite group I. *Neues Jahrb. Mineral. Abh.* **103**, 1–20.
- SENEGAS, J., AND J. GALY (1972) On the transformations of the columbite and trirutile structures. Study of the system $\text{NiNb}_2\text{O}_6\text{-NiF}_2$. *J. Solid State Chem.* **5**, 481–486.
- SIMONS, P. Y., AND F. DACHILLE (1970) Possible topotaxy in the TiO_2 system. *Amer. Mineral.* **55**, 403.
- SKAPSKI, A. C., AND D. ROGERS (1965) The structure of SbNbO_4 , $\alpha\text{-Sb}_2\text{O}_4$, and SbTaO_4 . *Chem. Commun.*, p. 611–613.
- SLEIGHT, A. W. (1972) Accurate cell dimensions for ABO_3 , molybdates and tungstates. *Acta Crystallogr.* **B28**, 2899–3003.
- STRUNZ, M. (1970) *Mineralogische Tabellen*. Akademische Verlagsgesellschaft, Geest and Portig K-G, Leipzig.
- TURNOCK, A. C. (1966) Synthetic wodginite, tapiolite, and tantalite. *Can. Mineral.* **8**, 461–470.
- VLAŠOV, K. A., Ed. (1964) *Geochemistry and Mineralogy of Rare Elements and Genetic Types of Their Deposits*, Vol. II. *Mineralogy of Rare Elements*, Section Eleven, *Minerals of Niobium and Tantalum*. English Translation by Israel Program for Scientific Translation, Jerusalem, 1966, pp. 397–567.
- VORMA, I. A., AND J. SIIVOLA (1967) Sukulaite ($\text{Ta}_2\text{Sn}_2\text{O}_7$) and wodginite as inclusions in cassiterite in the granite pegmatite in Sukula, Tammela, in south western Finland. *Bull. Comm. Geol. Finlande*, **229**, 173–187.
- WOLTEN, G. M. (1967) The structure of the M' -phase of YTaO_4 , a third fergusonite polymorph. *Acta Crystallogr.* **23**, 939–944.
- , AND A. B. CHASE (1967) Synthetic fergusonites and a new polymorph of yttrium tantalate. *Am. Mineral.* **52**, 1536–1541.
- WYCKOFF, R. W. G. (1965) *Crystal Structures*, Second Edition, Wiley, New York.

Manuscript received, November 7, 1973; accepted for publication, May 16, 1974