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IXIOLITE—A COLUMBITE SUBSTRUCTURE

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ABSTRACT

Ixiolite, first described in 1857 and mentioned in the literature only a few times since then, has generally been regarded as a discredited mineral species. A re-examination of samples from the type locality in Finland, however, has provided significant new information indicating that ixiolite is a valid species with distinctive characteristics. *X*-ray diffraction studies show that ixiolite is orthorhombic with $a=5.73$, $b=4.74$ and $c=5.16$A, space group *Pcan*. The unit-cell content is $(Ta, Fe, Sn, Nb, Mn)_4O_8$. The ixiolite unit-cell is a sub-cell of columbite, with similar parameters except for b, which is one-third of the columbite b parameter. Structurally, ixiolite can be regarded as a disordered form of columbite.

INTRODUCTION

The mineral name ixiolite first appeared in 1857 in a paper by Nordenskiöld in which he described two tantalite-like minerals from Skogböle in Kimito, Finland. He regarded one of these as a relatively normal tantalite, but the other, which was morphologically different and was extraordinarily high in manganese and tin, he regarded as a separate species. This mineral, which was previously called "Kimito-tantalite," was given the name ixiolite, from Ixion of Greek mythology.

The name ixiolite has been given also to minerals from two other localities. One of these is in the Ilmen Mountains in the Russian Urals (Vernadsky and Fersman, 1910). Since there is no record of a complete chemical analysis nor of *x*-ray diffraction analysis having been made, this occurrence cannot be considered authenticated. The other use of the name was made for a mineral found at Wodgina, Australia (Simpson, 1909), but this has recently been discredited (Nickel *et al.*, 1963).[1]

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[1] After completion of this paper, a new occurrence of ixiolite was reported from the Kalbin Ridge in the U.S.S.R. (V. A. Khvostova and N. V. Maximova, *Dokl. Akad. Nauk S.S.S.R.* 1963, **148**, 424–426; translation provided by M. Fleischer). However, evidently

Åmark (1941) and Quensel (1941) reviewed the status of ixiolite. Their work, which was based on a review of the literature as well as on x-ray powder diffraction studies on type material from Skogböle, failed to substantiate ixiolite as a separate species. Quensel concluded that:

"The name ixiolite, primarily defined by Nordenskiöld as representing a species of orthorhombic symmetry, consituting an isomorphous mixture of SnO_2 and Nb-Ta oxides, must for the present be regarded as problematic."

Mineralogical reference works, apparently drawing largely on the work of Åmark and Quensel, have tended to treat ixiolite as a discredited species. Palache *et al.* (1944) and Hey (1962) conclude that ixiolite is probably identical with tapiolite. Strunz (1957) states that ixiolite is probably a mixture of tantalite and cassiterite. Ramdohr (1960) does not mention it at all.

The authors became involved in the ixiolite problem during an investigation of a tin-manganese tantalate from Bernic Lake, Manitoba. This mineral, subsequently characterized as a new species and given the name wodginite (Nickel *et al.*, 1963), was found to be very similar to the mineral from Wodgina, Australia, to which Simpson (1909) had given the name ixiolite. This led the authors to investigate the ixiolite from the type locality. Since this ixiolite was found to be distinct from other species, it was decided that the mineral should be redefined.

The chemical analyses were made by R. C. McAdam of the Analytical Chemistry Subdivision. Responsibility for the remainder of the investigation, including interpretation, was shared by E. H. Nickel of the Mineralogy Section and J. F. Rowland of the Physical Chemistry Section.

Terminology

In this paper frequent reference will be made to minerals of the columbite-tantalite group and, in view of the confusion surrounding the nomenclature of these minerals, the terminology employed here will be clarified. In the mineralogical literature, minerals in the columbite-tantalite group are generally regarded as being orthorhombic and having a composition expressed by the formula $(Fe,Mn)(Nb,Ta)_2O_6$, with complete substitution of the cations within the brackets. The names columbite and tantalite are given to members predominating in niobium and

no samples of the type ixiolite were obtained for a direct comparison with the mineral from the new occurrence, and the single-crystal and power x-ray data reported are not in complete agreement with our data on the Skogböle ixiolite. No heating experiments were reported. It is therefore questionable whether Khvostova and Maximova are justified in calling their mineral ixiolite.

tantalum, respectively (Palache *et al.*, 1944). Other names, such as ferrocolumbite and manganotantalite have been used to denote iron- or manganese-rich end-members.

Minerals of the columbite-tantalite group, in addition to being regarded as forming continuous compositional series, have also been regarded as isostructural. In the light of the present investigation and from recent literature reports, the authors do not consider this to have been proven. In point of fact, there has only been one structural analysis of a mineral of the columbite-tantalite group (Sturdivant, 1930), and this was done on a specimen that has not been chemically analyzed, and whose composition is consequently uncertain. Sturdivant's structure has generally been taken to apply to all members of the columbite-tantalite group. Recent evidence, however, strongly suggests the existence of crystallographic variants. Donnay and Donnay (1961), for example, noted significant differences in morphology between members differing in Mn:Fe ratio, and Schröcke (1962) found $MnNb_2O_6$ to have a unit cell twice the size of the one reported by Sturdivant for his columbite-tantalite.

Since a firm relationship between composition, crystallography, and structure has not yet been established, the authors will employ the term columbite-tantalite with reference to those minerals having a composition expressed by $(Fe,Mn)(Nb,Ta)_2O_6$ and producing *x*-ray diffraction patterns corresponding to the mineral characterized by Sturdivant (1930). Following Sturdivant's usage, the structure will be referred to as the columbite structure.

General Description

Samples from the type locality at Skogböle, Kimito, Finland were obtained from collections at the Royal Ontario Museum, the University of Helsinki and the Geological Survey of Canada. All the samples were similar in appearance, consisting of different proportions of black minerals and pink feldspar. A preliminary series of *x*-ray powder diffraction patterns of the black grains in each of the samples demonstrated the presence of two distinct mineral species—tapiolite and the mineral that will henceforth be designated as ixiolite. As shown in Table 1, the sample labels do not, in general, conform to the *x*-ray identifications, nor is there any consistent relationship between them.

None of the powder patterns obtained represented more than one phase, which indicates the absence of fine-grained intergrowths between the two minerals. Sample M-11894 contained eight black grains, four of which proved to be ixiolite and four tapiolite. The remaining samples appeared to contain either one mineral or the other, but not both.

TABLE 1. IDENTIFICATION OF SKOGBÖLE SAMPLES BY X-RAY POWDER DIFFRACTION ANALYSIS

Source	Sample	Label	Mines Branch Identification
Royal Ontario Museum	M-6591	Skogbölite (=tapiolite)	Ixiolite (6)
Royal Ontario Museum	M-11606	Tapiolite	Tapiolite (4)
Royal Ontario Museum	M-11894	Ixiolite	Tapiolite (4) and Ixiolite (4)
Royal Ontario Museum	M-14653	Ixiolite	Tapiolite (4)
University of Helsinki	1014	Tapiolit (Tantalit)	Ixiolite (1)
University of Helsinki	1015	Tapiolit (Ixionolit)	Tapiolite (1)
Geological Survey of Canada	x-344	Ixiolite	Tapiolite (1)

(The number of x-ray powder diffraction patterns obtained from each sample is given in parentheses.)

MORPHOLOGY

Most of the ixiolite in the samples examined occurs as irregular grains with no discernible crystal faces. Sample M-6591, however, contained two relatively large ixiolite masses, one of which had three uneven crystal faces (Fig. 1b). Although the faces were too irregular for accurate measurement, approximate measurements of two interfacial angles could nevertheless be made with a contact goniometer. The results (Table 2) agree, within the errors of measurement, with two of the angles reported by Nordenskiöld, and with values of 100∧130 and 100∧112 calculated

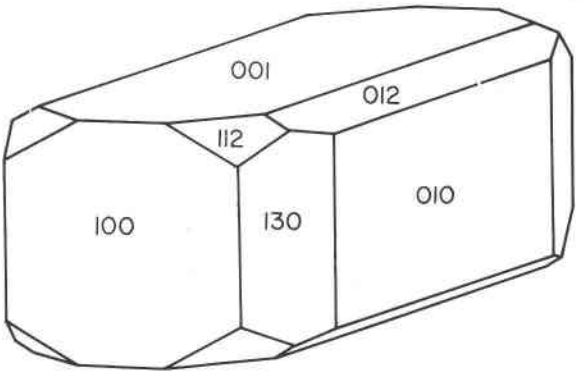

FIG. 1a. Crystal drawing of ixiolite, adapted from Nordenskiöld's Figure 3, and reoriented to conform to the setting used in this paper. Relationship to Nordenskiöld's symbols are as follows:

Nordenskiöld	a	b	c	m	l	p
This paper	{010}	{001}	{100}	{012}	{130}	{112}

TABLE 2. INTERFACIAL ANGLES OF IXIOLITE CRYSTALS FROM SKOGBÖLE, FINLAND

Indices[1]	M-6591 (This paper)	Nordenskiöld (1857)	Calculated Angles[2]
100∧130	75°	74°58′	74°35′
100∧112	67°	68°50′	68°26′
100∧110	—	51°15′	50°24′
110∧112	—	54°46′	54°47′

[1] Nordenskiöld's indices have been transformed to agree with the ixiolite unit cell parameters, as follows: h→k; k→l/2; l→h.

[2] Calculated values are derived from the following unit-cell parameters: $a=5.731$, $b=4.742$ and $c=5.152$ Å (see Table 3).

from the unit-cell parameters determined by single-crystal *x*-ray diffraction analysis. The other two angles reported by Nordenskiöld, but not observed by the authors, are also in good agreement with the calculated angles. For this reason, and because of other evidence given later, the authors believe that sample M-6591 corresponds to the material originally described by Nordenskiöld under the name of ixiolite.

Figures 1a and 1b show the relationship between one of the crystals described by Nordenskiöld and the partial crystal from sample M-6591.

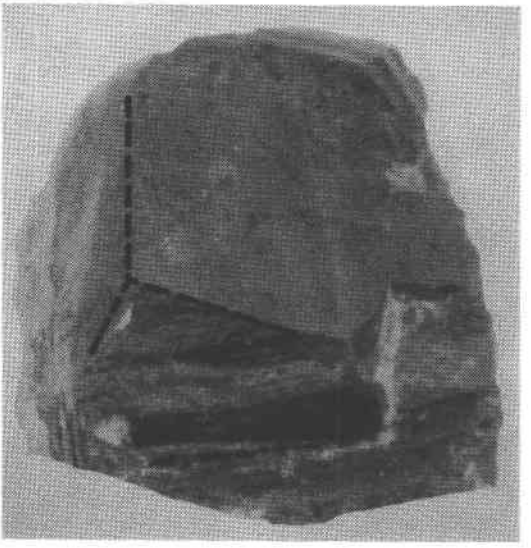

FIG. 1b. Photograph of ixiolite crystal from sample M-6591, in approximately the same orientation as Fig. 1a. Crystal faces (100), (130) and (112) are shown. Magnification approx. 3×.

Specific Gravity

Nordenskiöld determined the specific gravities of three separate crystals of ixiolite, obtaining values of 7.06, 7.08 and 7.17.

The specific gravities of seven small fragments of ixiolite from sample M-6591 and weighing from 10 to 20 mg were determined by means of a Berman balance. These fragments had been carefully examined under a stereomicroscope to make reasonably sure that they were free of externally attached impurities. Polished sections of apparently pure grains, however, showed that the ixiolite is penetrated by tiny irregular veinlets of a non-metallic mineral, thus making any determinations subject to a certain degree of error. The values obtained ranged from 7.03 to 7.23 and averaged 7.14, which agrees closely with those of Nordenskiöld, and provides further evidence for the identity of this sample with the originally described ixiolite. Nevertheless, these values are appreciably below the specific gravity calculated from the chemical analysis and unit cell (7.392), a discrepancy which may reasonably be attributed to the mineral forming the above-mentioned veinlets.

X-ray Crystallography

Buerger precession photographs of ixiolite single crystals indicate orthorhombic symmetry, with space group D_{2h}^{14}. Rather than adopt the

Table 3. Unit-Cell Parameters of Ixiolite
(Angstrom Units)

Sample No.	*a*	*b*	*c*
M-6591	5.731	4.742	5.152
M-11894	5.738	4.747	5.163

conventional setting of the unit cell ($c<a<b$), a setting was chosen that related the ixiolite parameters directly to those of columbite-tantalite as given by Strunz (1957). This led to the space group *Pcan*. The single-crystal and powder patterns are both consistent with the extinction rules required by this space group.

The unit-cell parameters derived from the precession photographs were refined by least-squares calculations from the powder diffraction data. The resulting parameters are given in Table 3.

Table 3 shows that the parameters of Sample M-11894 are slightly greater than those of sample M-6591. The reason for this difference has not been determined, since only the latter was analyzed chemically.

TABLE 4. RELATIONSHIP BETWEEN THE UNIT CELLS OF IXIOLITE, COLUMBITE-TANTALITE AND WODGINITE

	Ixiolite, Skogböle, Finland	Columbite-Tantalite Tinton, S. D.	Wodginite[1] Wodgina, Australia
Axial Lengths (Å)	a=5.73 b=4.74 c=5.16 90°	a=5.73 b=14.24 (3×4.75) c=5.08 90°	b=11.47 (2×5.73) a= 9.52 (2×4.76) c= 5.10 β=91°18
Cell vol. (Å^3)	140	414 (3×138)	557 (4×139)
Space group	*Pcan*	*Pcan*	C2/c or Cc

[1] From Nickel, *et al.*, 1963.

The unit-cell parameters of ixiolite are closely related to those of columbite-tantalite and of wodginite, the latter two being simple multiples of the ixiolite cell (Table 4).

The close relationship between these minerals is also evident in their powder diffraction patterns. As shown by diffractometer tracings (Fig. 2), the ixiolite pattern can be distinguished from that of the other two minerals by the absence of low-angle diffractions. The entire diffraction pattern of ixiolite is also more diffuse, the amplification having to be increased by a factor of two to produce peak heights comparable to those of columbite-tantalite and wodginite. This accounts for the higher background in the ixiolite tracing.

The measured powder diffraction data for ixiolite and an intermediate member of the columbite-tantalite series are shown in Table 5. The intensities given in this table are integrated peak intensities measured from the *x*-ray diffractometer tracings shown in Fig. 2, and recalculated to maximum intensities of 100. The lines that were visible on the powder films, but not resolved on the diffractometer tracings were arbitrarily assigned intensities of 1.

There is some uncertainty as to what indexing should be used for columbite-tantalite, since at least three axial settings are given in the literature. It was decided to adopt Strunz' setting of *Pcan* since it follows the generally accepted convention of $c<a<b$. As stated previously, the ixiolite setting was chosen so that its parameters could be directly related to those of columbite-tantalite.

CHEMICAL COMPOSITION

It was decided to obtain a new chemical analysis for ixiolite because all previous analyses had been done in the nineteenth century, and because

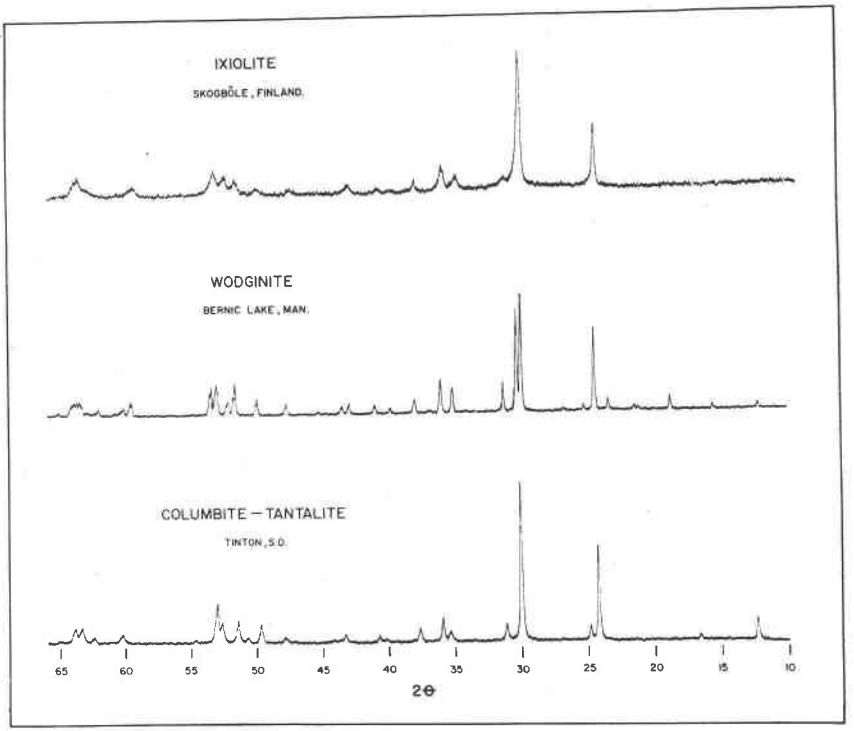

FIG. 2. Diffractometer tracings of ixiolite, wodginite, and columbite-tantalite. Copper radiation, nickel filter; scanning speed ¼ degree per minute.

of the uncertainty as to which of these were actually performed on ixiolite. The ixiolite in sample M-6591 was found to be suitable for analysis because the sample was large enough to provide sufficient material, and there was no evidence of any tapiolite being present in the sample.

The sample was prepared as follows: a portion of sample M-6591 was broken off and gently crushed; the crushed material was then hand-picked under a stereomicroscope, only grains free of detectable impurities being selected. Approximately three grams of hand-picked ixiolite were obtained in this way. Although an *x*-ray diffraction pattern of this sample exhibited no extraneous lines, a small amount of contamination was nevertheless unavoidable, as shown by a polished section prepared from one of the ixiolite fragments; this revealed the presence of microscopic veinlets of a mineral with low reflectivity. Although this mineral could not be isolated for identification, the chemical analysis indicated that it could be a hydrous calcium aluminosilicate.

The results of the chemical analyses are shown in Table 6, together with

TABLE 5. *X*-RAY POWDER DIFFRACTION PATTERNS OF COLUMBITE-TANTALITE AND IXIOLITE

Columbite-Tantalite, Tinton, S. D.			Ixiolite M-6591 Skogböle, Finland			Ixiolite (calc.)
Int.	d	hkl	Int.	d	hkl	d
12	7.13	020	—	—	—	—
4	5.30	110	—	—	—	—
48	3.66	130	32	3.65	110	3.653
9	3.57	040	—	—	—	—
100	2.96	131	100	2.98	111	2.980
10	2.86	200	5	2.87	200	2.866
6	2.53	002	13	2.57	002	2.576
12	2.49	201	20	2.51	201	2.504
12	2.38	060	5	2.37	020	2.371
1	2.279	151	—	—	—	—
3	2.236	032	2	2.265	012	2.263
4	2.207	231	4	2.213	211	2.214
5	2.084	132	9	2.104	112	2.105
3	2.043	241	—	—	—	—
—	—	—	1	2.017	121	2.016
5	1.898	202	4	1.915	202	1.916
9	1.831	260	6	1.826	220	1.826
4	1.796	152, 171	—	—	—	—
14	1.772	330	13	1.772	310	1.772
12	1.735	062	17	1.746	022	1.744
22	1.721	261	24	1.722	221	1.722
2	1.672	331	—	—	—	—
1	1.608	—	—	—	—	—
8	1.534	133	12	1.554	113	1.554
1	1.516	190	1	1.521	130	1.524
4	1.484	262	1	1.490	222	1.490
14	1.465	203	29	1.459	203	1.473
12	1.454	191, 332			131	1.461
					312	1.460
1	1.432	400	—	—	—	—
1	1.393	—	—	—	—	—
2	1.380	401	1	1.380	401	1.380

The d-values were measured from 114.6 mm Debye-Scherrer patterns. Intensities were measured from diffractometer tracings obtained with CuKα radiation. The calculated ixiolite spacings are from a unit cell with $a=5.731$, $b=4.742$ and $c=5.152$ Å.

the analytical data on other so-called ixiolite samples from Skogböle, taken from the literature.

Table 6 shows a considerable variation in analytical results. This may be attributable in part to shortcomings in early analytical techniques

TABLE 6. CHEMICAL ANALYSES OF IXIOLITE FROM SKOGBÖLE, FINLAND

	R. C. McAdam[1] (1962)	Norden-skiöld (1857)	Rose (1858)					Rammelsberg (1871)	
			1	2	3	4	5	1	2
Ta_2O_5	61.47%	72.51%	75.71%	76.81%	83.2%	85.85%	84.44%	69.97%	63.58%
Nb_2O_5	10.50							12.26	19.24
TiO_2	0.38	—	—	—	—	—	—		
FeO	8.08	7.38	9.80	9.49	7.2	12.94	13.41	14.83	9.19
MnO	5.40	7.32	4.32	4.27	7.4	1.60	0.96		5.97
SnO_2	12.27	12.79	9.67	9.14	0.6	0.80	1.26	2.94	1.70
CaO	0.11	—	—	0.41	—	0.56	0.15	—	—
Al_2O_3	0.16	—	—	—	—	—	—	—	—
ZrO_2	0.60	—	—	—	—	—	—	—	—
WO_3	0.30	—	—	—	—	—	—	—	—
CuO	—	—	—	0.07	—	—	0.14	—	—
SiO_2	0.12	—	—	—	—	0.72	—	—	—
H_2O^-	0.08	—	—	—	—	—	—	—	—
H_2O^+	0.16	—	—	—	—	—	—	—	0.23 (L.O.I.)
Totals	99.63	100.00	99.50	100.19	98.4	102.47	100.36	100.00	99.91

[1] This paper; sample no. M-6591.

and/or to lack of sample authenticity. It is quite possible, indeed likely, that some of the analyses may be of tapiolite or of tapiolite-ixiolite mixtures, as these minerals are indistinguishable by eye. Semi-quantitative spectrographic analyses of ixiolite and tapiolite picked from the same sample (M-11894) indicate that ixiolite contains more tin than does tapiolite (Table 7). Consequently, it seems likely that only the analyses high in tin, *i.e.*, those in the first four columns in Table 6, are of ixiolite. That some confusion exists regarding ixiolite and tapiolite is shown by the fact that the labels on the samples obtained from the various collections are not at all consistent with the minerals actually present, as was noted earlier.

The atomic proportions and unit-cell content calculated from the new ixiolite analysis are shown in Table 8. In these calculations the CaO, Al_2O_3, SiO_2 and H_2O have been disregarded, since these constituents are probably due to impurities. The atomic proportions were multiplied by a factor to yield 12 atoms per unit cell.

According to the data in Table 8, the formula for the ixiolite from sample M-6591 is $Ta_{1.75}Fe_{0.71}Sn_{0.51}Nb_{0.50}Mn_{0.48}Zr_{0.03}Ti_{0.03}W_{0.01}O_{7.98}$, or, in generalized form, X_4O_8. The specific gravity calculated from the unit-cell dimensions and the unit-cell content is 7.392.

TABLE 7. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSES OF IXIOLITE AND TAPIOLITE FROM SAMPLE M-11894 FROM SKOGBÖLE, FINLAND

(Figures indicate order of magnitude in per cent)

	Ixiolite	Tapiolite
Ta	PC	PC
Nb	2%	2%
Sn	5	2
Fe	4	8
Mn	3	0.6
Zr	0.6	0.2
Ti	0.3	0.4
Mg	0.4	0.03
Ca	tr	0.4
Si	0.2	0.4

PC = Principal Constituent
Analyst: Miss E. M. Kranck

STRUCTURE

The close crystallographic relationship between ixiolite and columbite-tantalite must be an expression of a structural similarity between the two minerals. In the structure of columbite (Sturdivant, 1930), the iron and niobium atoms lie within regular octahedra of oxygen atoms in close-packed arrangement. The octahedra share two edges to form staggered

TABLE 8. UNIT-CELL CONTENT OF IXIOLITE

	Weight Per Cent[1]	Atomic Proportions	Atoms per Unit Cell
Ta	50.85	0.2810	1.752
Fe	6.34	0.1136	0.708
Sn	9.76	0.0822	0.512
Nb	7.42	0.0798	0.497
Mn	4.23	0.0769	0.480
Zr	0.45	0.0049	0.031
Ti	0.23	0.0048	0.030
W	0.24	0.0013	0.008
O	20.48	1.2804	7.982
	100.00	1.9249	12.000

[1] From the oxide percentages given in Table 6, recalculated to 100% after the exclusion of CaO, Al_2O_3, SiO_2 and H_2O.

chains parallel to the *c*-axis, the chains being combined by shared corners. The metal atoms are in an ordered arrangement, any one chain consisting of Fe-O or Nb-O octahedra. The chains, themselves, are ordered, one chain of Fe-O octahedra alternating with two chains of Nb-O octahedra along the *b*-direction.

In ixiolite, which has only four metal atoms per unit cell, and a space

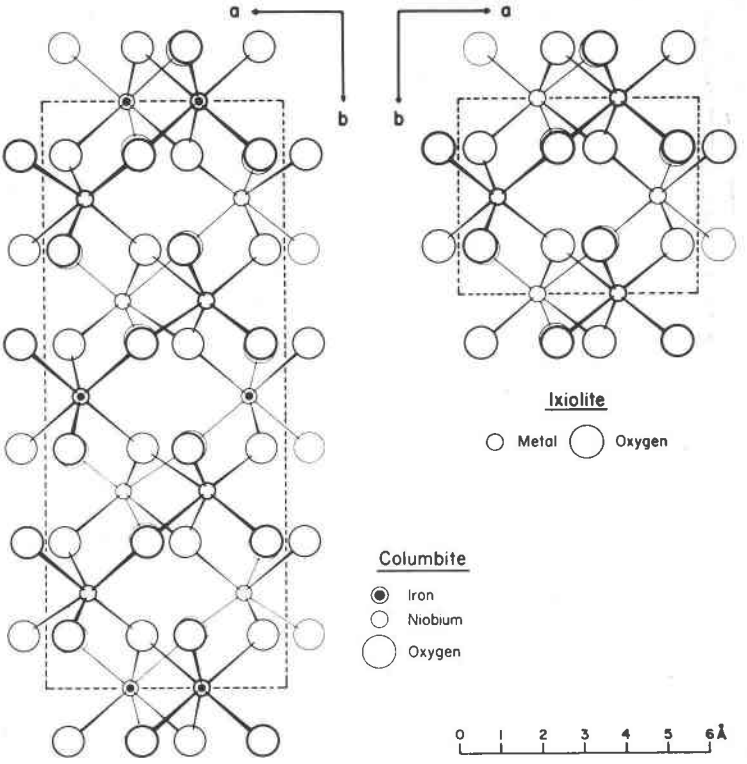

FIG. 3. Structures of columbite and ixiolite. (The columbite structure is taken from Sturdivant, 1930.)

group permitting only 4-fold and 8-fold positions, this 2:1 ordering is impossible. Consequently, the metal atoms in the ixiolite unit cell probably occupy equivalent positions and can therefore be regarded as disordered. If these atoms are placed in the (c) positions required by the space group *Pcan*, then they lie fairly close to the equivalent positions in the columbite structure occupied by niobium and iron. The relationship between the columbite structure and the proposed ixiolite structure can be clearly seen in Fig. 3, which is a projection of the two structures paral-

TABLE 9. COMPARISON BETWEEN CALCULATED AND OBSERVED POWDER PATTERN INTENSITIES OF IXIOLITE

hkl	Calculated Intensities		Measured Intensities
	Absolute	Calc. to 100	
110	144,500	23	32
111	633,500	100	100
200	29,600	5	5
002	118,500	19	13
201	174,400	27	20
020	78,000	12	5
012	11,400	2	2
211	19,600	3	4
112	110,600	17	9
121	0	0	1
202	55,600	9	4
220	57,000	9	6
212	1,700	0.3	0
310	150,800	24	13
020	183,200	29	17
221	259,100	41	24
113	8	0	0
122	0	0	0
113	160,200	25	12
130	25,400	4	1
222	41,300	6	1
203	103,200	16	
131	138,100	22	29
312	183,700	29	
400	17,200	3	0
321	0	0	0
213	16	0	0
401	70,760	11	1

lel to the ab plane. The chains are normal to the plane of projection.

Intensity calculations have been made to confirm this proposed ixiolite structure. The oxygen atoms were placed in the eight (d) positions with $x=0.250$, $y=0.092$ and $z=0.079$; these parameters correspond to the average oxygen positions in the columbite-tantalite structure. The metal atoms were placed in the four (c) positions with $y=0.333$, which corresponds to the average y parameter of the Fe and Nb atoms in columbite. The intensities calculated from this structure are in good qualitative agreement with the observed intensities (Table 9).

From a quantitative standpoint, the measured intensities are generally lower than the calculated values, which is to be expected in view of the

diffuseness of the diffraction pattern, as noted earlier. This diffuseness is probably due to structural irregularities resulting from ions of different size occupying equivalent positions in the structure. Taking this into account, the agreement between calculated and observed intensities is sufficiently good to confirm the general structural scheme proposed for ixiolite.

Like the structure of columbite, that of ixiolite can be described as consisting of chains of metal-oxygen octahedra formed by the sharing of two edges of each octahedron, with the chains connected by the sharing of one corner of each octahedron. This structure was first suggested as a hypothetical possibility by Pauling and Sturdivant (1928) in their discussion of the brookite structure. Actual examples of compounds with this structure are a-PbO_2 (Zaslavskij and Tolkačev, 1952), the orthorhombic form of ReO_2 (Magnéli, 1957,) and disordered $GaTaO_4$ (Bayer, 1962).

Nielsen (1956) appears to have been the first to suggest the existence of a disordered tantalite, although he provided only scant evidence to support his contention. Donnay and Donnay (1961) pointed out that some specimens of columbite-tantalite (with Mn>Fe) have a distinctive morphology, indicating the probability of a unit cell one-third the size of columbite-tantalite, which corresponds to ixiolite.

Response to Heating

When ixiolite is heated in air, several changes occur in the x-ray diffraction pattern. As shown by the diffraction data in Table 10, the d-values of the heated ixiolite are consistently lower than the corresponding d-values of the unheated sample, indicating a reduction in interatomic distances. In addition, a number of new lines appear at high d-values, suggesting an increase in the degree of atomic ordering. Several of the new lines correspond to olovotantalite (literally "tin tantalite") from the U.S.S.R., recently described by Matias (1961). Matias' x-ray diffraction data are included in Table 10 for purposes of comparison.

Unfortunately Matias was unable to obtain any single-crystal diffraction data. His powder data, however, as well as that of the heated ixiolite, can be indexed on an orthorhombic unit cell with the approximate dimensions of the wodginite unit cell, *i.e.*, a cell four times the size of ixiolite (Nickel *et al.*, 1963). Confirmation of this unit cell, however, must await the results of single-crystal work on olovotantalite.

The changes in the x-ray diffraction patterns were observed at temperatures of 700°C and over. The intensities of the extra lines were found to depend on the temperature, duration of heating time, and the cooling rate, as indicated in Table 11.

TABLE 10. *X*-RAY POWDER DIFFRACTION PATTERNS OF UNHEATED AND HEATED IXIOLITE, AND OF OLOVOTANTALITE

Line No.	Ixiolite No. M-6591				Olovotantalite	
	Unheated		Heated to 950° C.		(Matias, 1961)	
	I (meas.)	d (A)	I (est.)	d (A)	I[1]	d (A)
1	—	—	3	11.3	40	11.1
2	—	—	4	5.70	—	—
3	—	—	12	4.70	10	4.69
4	—	—	10	3.79	20	3.79
5	32	3.65	50	3.62	—	—
6	100	2.98	100	2.95	70	2.95
7	5	2.87	8	2.85	20	2.88
8	—	—	—	—	20	2.76
9	13	2.57	15	2.54	40	2.56
10	20	2.51	20	2.49	70	2.51
11	5	2.37	12	2.35	30	2.38
12	2	2.265	7	2.245	10	2.275
13	4	2.213	8	2.192	50	2.21
14	9	2.104	8	2.082	30	2.12
15	—	—	—	—	40	2.099
16	1	2.017	1	1.997	10	2.077
17	—	—	—	—	10	1.952
18	4	1.915	15	1.899	60	1.917
19	6	1.826	15	1.815	50	1.835
20	13	1.772	17	1.763	80	1.780
21	17	1.746	1	1.739	70	1.743
22	24	1.722	18	1.718	70	1.723
23	—	—	1	1.666	—	—
24	—	—	—	—	20	1.609
25	12	1.554	7	1.541	60	1.560
26	—	—	—	—	50	1.540
27	1	1.521	1	1.513	20	1.504
28	1	1.490	1	1.481	30	1.480
29	—	—	—	—	100	1.468
30	29	1.459	18	1.454	10	1.442
31	1	1.380	5	1.374	60	1.387

[1] Matias' intensity data were given on a scale of 10. His intensity values have been multiplied by a factor of 10 to bring them to a comparable scale of 100.

DISORDERED COLUMBITE-TANTALITE, OR PSEUDO-IXIOLITE

During the course of the investigation, specimens from a number of different localities were found to produce *x*-ray powder diffraction pat-

TABLE 11. HEATING EXPERIMENTS ON IXIOLITE M-6591

Temp. ° C.	Time hrs	Cooling Rate	Intensity of Extra Reflections
700	2	rapid	nil
700	2	slow	weak
700	18	rapid	weak
800	2½	rapid	moderate
800	18	rapid	moderate
800	2½	slow	strong
800	18	slow	strong
950	17	rapid	moderate
950	17	rapid	moderate

terns that were very similar to ixiolite. After heating these samples under the same conditions as those used for ixiolite, low-angle lines appeared in the diffraction patterns, but these extra lines, which occur at 7.1 and 5.3 Å, are not characteristic of heated ixiolite but of columbite-tantalite.

If it is assumed that the absence of the low-angle diffraction peaks is due to cation disorder and that their presence is due to cation order, then it is apparent that, on heating, the cations in the two types of mineral must become ordered in different ways. This is probably related to compositional differences and, since one of the criteria in Nordenskiöld's original definition of ixiolite was its composition, then the ixiolite-like minerals that convert to columbite-tantalite on heating cannot be considered as true ixiolites. For want of a better name, it is suggested that they be referred to as disordered columbite-tantalite, or as "pseudo-ixiolite."

One of these pseudo-ixiolites, labelled "Manganotantalite, Greenbushes, Australia" was obtained from the Geological Survey of Canada. It was analyzed chemically and the results are shown in Table 12.

This analysis differs from that of ixiolite chiefly by virtue of its high

TABLE 12. CHEMICAL ANALYSIS OF PSEUDO-IXIOLITE (MANGANOTANTALITE) FROM GREENBUSHES, AUSTRALIA

Ta_2O_5	68.93%
Nb_2O_5	15.42
MnO	13.82
FeO	1.05
SnO_2	0.48
	99.70%

MnO:FeO ratio and its low tin content. It is unlikely that the high manganese content alone is responsible for the different response to heating, since Nielsen (1956) reported crystals of $FeTa_2O_6$ being converted from a disordered form to normal tantalite. The determining factor is therefore probably the tin content. This conclusion derives support from the fact that the low angle lines of heated ixiolite correspond to lines in the olovotantalite pattern, both minerals containing substantial amounts of tin (ixiolite—12.27% SnO_2; olovotantalite—9.06% SnO_2).

Several other samples produced the same *x*-ray powder patterns before and after heating as the Greenbushes specimen, and can consequently also be regarded as pseudo-ixiolites. One of them is a sample of "tantalite" (B.M. 35301) from the Ilmen Mountains in the Urals, obtained from the British Museum. The *x*-ray powder data for this mineral were included in an early edition of the A.S.T.M. card index (card no. 2-0691), but the card has been deleted and does not appear in more recent editions. Another sample is from the Varuträsk pegmatite in Sweden, obtained from Professor Quensel. This specimen (no. 7039) is noted in a paper by Åmark (1941). Still other specimens of pseudo-ixiolite were found in samples from a pegmatite in Steele Township, Ontario.

There are several literature references to minerals with powder diffraction patterns similar to that of ixiolite. Schröcke (1961) reported powder data for a synthetic $FeNb_2O_6$, which correspond to the ixiolite powder data. Hutton (1959) presented data for what he termed a partially metamict columbite (manganomossite) from Yinnietharra, W. Australia, that produced a generally weak diffraction pattern with no low-angle diffractions. After heating, the mineral was reported to produce the normal columbite-tantalite pattern.

There is probably a gradation from a completely ordered end-member (columbite-tantalite) to a fully disordered one (pseudo-ixiolite), the degree of ordering being indicated by the intensities of the 7.1 and 5.3 Å diffractions. The powder pattern of pseudo-ixiolite from Greenbushes, Australia, for example, did not contain these lines, although single-crystal films had some very weak spots indicating the larger unit cell (columbite-tantalite); consequently, it is not completely disordered. Berman's data (1955) for columbite from Mitchell County, N. C. indicate a powder pattern with a weak 7.1 Å line that was enhanced by heating; this sample presumably has an intermediate degree of ordering.

At present there is insufficient data to correlate degree of ordering with composition. C. O. Hutton (1959) attributed disordering in his mineral from Yinnietharra, W. Australia to the presence of radioactive elements. Donnay and Donnay (1961) found that members with a high Mn:Fe ratio have a characteristic morphology that they attribute to a disordered

structure. On the other hand, the data presented by Nielsen (1956) and Schröcke (1961) indicate evidence for disorder among some iron-rich members. The possibility that the degree of oxidation may be a factor probably warrants consideration.

It is evident from the number of apparently contradictory facts that much remains to be discovered about the columbite-tantalite group and related minerals. It is hoped that phase equilibrium work now being done by A. C. Turnock at the Mines Branch will help to clarify the picture.

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