

## MANGANOMOSSITE RESTUDIED

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## ABSTRACT

Manganomossite from Yinnietharra, Western Australia, is metamict columbite with  $\text{UO}_2=0.96$  per cent. The untreated mineral with density = 6.17 and R.I. = 2.27, gives weak, diffuse powder and single crystal patterns with relatively few lines or spots, but after being heated in vacuo at  $800^\circ\text{C}$ . or at  $1,200^\circ\text{C}$ . for periods of  $\frac{1}{4}$  hour, the density of the mineral showed an increase to 6.32 in each case, and powders prepared therefrom yielded identical but strong patterns with numerous lines, although some diffuseness remains in the high  $2\theta$  region. This  $x$ -ray pattern may be indexed for an orthorhombic unit cell with the following dimensions:  $a_0=5.09\text{ \AA}$ ,  $b_0=14.31\text{ \AA}$ ,  $c_0=5.725\text{ \AA}$ , but it is not possible to index the films on the basis of tetragonal symmetry. Autoradiographs show that zonal distribution of radioactivity may or may not be present, but the mineral appears to be free from radioactive centers or inclusions.

A complete analysis of the mineral after elimination of water leads to the formula:  $(\text{Mn, Fe, U, Th})_{3.97}(\text{Nb, Ta, Ti})_{7.99}\text{O}_{24}$ .

## INTRODUCTION

In his annual report, Bowley (1923, p. 120) states that a mineral found by a Mr. R. C. Black at Yinnietharra, Western Australia, exhibits physical and chemical properties that suggest that it is either orthorhombic "manganocolumbite," or more probably "the corresponding tetragonal species which has not yet received a name." However, the name "manganomossite" was indeed suggested in this report but with some hesitation. At a slightly later date, it was reported by Spencer (1925, p. 460) under the title of manganomossite in his "Tenth List of New Mineral Names." From that time until publication of the first volume of the seventh edition of Dana's System of Mineralogy the original nomenclature was retained and accepted, but Palache, Berman, and Frondel (1946, p. 776) and later Hutchinson (1955, p. 445) clearly draw attention to the doubtful status of the mineral in question. Finally in "Minerals of Western Australia" (Simpson, 1952, p. 184), the mineral is listed once more as manganomossite, but with the comment that it is more probably the tetragonal rather than the orthorhombic species.

During a recent study of tapiolite, the problem arose as to the extent to which tantalum may be replaced by niobium in this mineral group and the mineral described by Bowley appeared worthy of further study. Through the courtesy of Mr. J. C. Hood, Director of the Western Australia Government Chemical Laboratories, a type specimen of manganomossite from Yinnietharra was secured. Upon completion of the work recorded here with the material just mentioned, a second specimen labelled "manganomossite, W. Australia" was found in an old collection. Whether this latter material is from Yinnietharra is quite uncertain, but

it should be noted that the density and x-ray diffraction patterns are identical with those determined for the precisely located specimen. In only one respect, however, may some distinction be made, and this concerns the different autoradiographs obtained from the two specimens.

#### PHYSICAL PROPERTIES

When crushed, manganomossite breaks into fragments bounded by strikingly brilliant conchoidal fracture surfaces; this is characteristic of many minerals that have been transformed into the metamict state, such as polycrase-euxenite, eschynite-priorite and many others. On the other hand, the general appearance of the fragments of manganomossite is rather distinct from that found for undoubted tapiolite-mossite from several localities, e.g. mossite from Råde, Norway, and tapiolite from Tazenakht, Morocco. In oblique illumination, the black or dark brown fragments exhibit an adamantine luster with occasional deep red internal reflections, and the very thin edges of conchoidally fractured particles are translucent and deep brown in color. In thin section or in particles less than 0.02 mm. in thickness, the Yinnietharra mineral, which appears to be quite homogeneous, is translucent with a clear brown color reminiscent of that observed for picotite. Most particles are isotropic but a range of birefringence is apparent in others, and although no exact measurements have been made, a value of 0.015 is certainly not exceeded, and it is usually very much less than this. The refractive index, determined by mounting finely crushed material in sulphur-selenium melts, is 2.27.

The density of carefully hand-picked fragments was determined with a microbalance, and for untreated pure material, a value of  $6.17 \text{ gm/cm}^3 \pm 0.01$  at  $21^\circ \text{ C.}$  was obtained. The same fragments were then sealed in vacuo in silica capillaries and heated in turn to  $800^\circ \text{ C.}$  and  $1,200^\circ \text{ C.}$  for  $\frac{3}{4}$  hour, and following these two heat-treatments, the density of the particles was found to be  $6.32 \text{ gm/cm}^3 \pm 0.02$  at  $20^\circ \text{ C.}$  in each case. These data are to be compared to the figure of 6.21 reported by Bowley (1923), presumably for untreated material. Now all of these values seem to be too low for a member of the tapiolite-mossite series, but are comparable to those expected for a member of the orthorhombic columbite-tantalite group of minerals. Heating at  $1,200^\circ \text{ C.}$  for periods of time ranging up to 14 hours did not produce any significant change in density from that found for the shorter period of time. This situation is in contrast to the circumstances reported by Arnott (1950, pp. 397-8) for euxenite.

Autoradiographs were prepared with polished sections of the two specimens of manganomossite. The Yinnietharra material exhibits a weak but perfectly uniform distribution of radioactivity, and there are

no indications of inclusions or highly radioactive centers. On the other hand, the radiograph (Fig. 1) yielded by material from an unspecified Western Australia locality clearly shows regular distribution of radioactive matter. A distinct range of uranium and thorium content is evident in the different zones, but there is no progressive increase or decrease in radioactivity from center to periphery. A somewhat similar circumstance has been reported by Heinrich and Giardini (1956, p. 1705) for columbite from an unspecified locality in Canada.

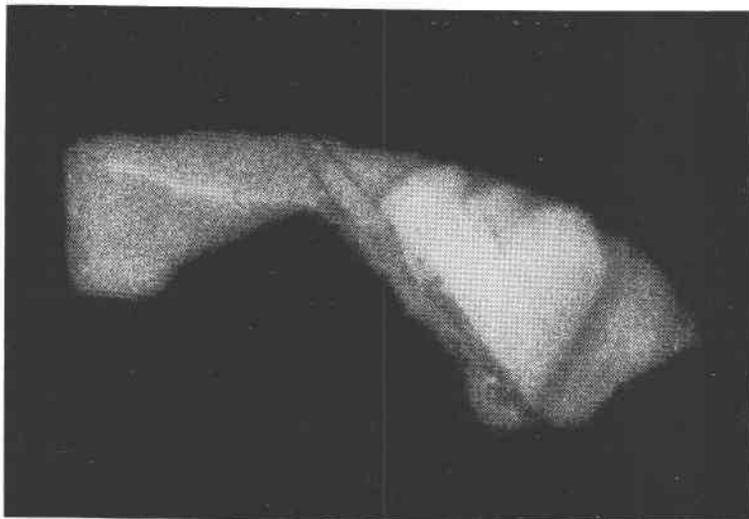


FIG. 1. Autoradiograph of manganomossite (= columbite), from an unspecified locality in Western Australia. Exposure time: 192 hours. Magnification:  $\times 5.5$ .

#### X-RAY DATA

The powder pattern yielded by untreated manganomossite exhibits relatively few lines, and those that are found at angles greater than about  $65^\circ 2\theta$  are so faint and diffuse that accurate measurement is out of the question. This pattern suggests that the mineral is in a metamict condition, and a single fragment, instead of a powder, was employed as diffraction material to check this suggestion. In the film thus obtained, reflections at low  $2\theta$  angles are distinct but not precise spots; at angles greater than  $65^\circ 2\theta$ , the reflections are so streaked out that imperfect lines or arcs result.

When the mineral is heated in vacuo at  $800^\circ\text{C}$ . or at  $1,200^\circ\text{C}$ . for  $\frac{3}{4}$  hour, single fragments of the material so prepared are now found to yield similar but much more precise reflections than before, although streak-

ing out of spots into arcs is still quite evident above  $90^\circ 2\theta$ . In the powder pattern, the lines are much more precisely defined than in films yielded by unheated manganomossite, except at high  $2\theta$  angles, where bands up to 2.0 mm. in width are found. Heat-treatment of this mineral at lower temperatures and for a wide range of periods of time failed to produce material that yielded films with greater sharpness in the back-reflection region.

X-ray diffraction powder patterns for unheated and heated manganomossite are given in Table 1 together with a powder pattern of tantalite from Quixeramobim, Ceará, Brazil. It will be noted that the lines yielded by the unheated material correspond in a general way only with the stronger lines found in the pattern for heat-treated manganomossite. It is evident, however, that the former has slightly larger cell dimensions than the heat-treated mineral; this is in conformity with the data obtained by density determinations. The similarity of the  $d$ -spacings for manganomossite and tantalite is clear, although a number of fainter lines yielded by the former are not matched in the tantalite pattern.

The powder pattern of the recrystallized mineral may be indexed on the basis of orthorhombic, but not tetragonal, symmetry, and it has been possible to determine the approximate unit cell dimensions. Calculated and measured  $d$ -spacings conform reasonably well up to about  $62^\circ 2\theta$ , but beyond that point, diffuseness of lines has rendered measurements less precise than is desirable, thus preventing refinement of dimensions. Furthermore, without the benefit of single crystal photographs, the large number of choices renders indexing of the larger  $2\theta$  values less meaningful. It will be noted that it has not been possible to index four lines, *viz.* 4.62, 3.30, 3.10, and 1.801, and since freedom from impurities seems assured by the care taken to prepare the samples studied, one is led to the belief that heat-treatment may have produced a minute quantity of a second, but as yet unidentified, phase. The unit cell dimensions determined from the powder patterns are as follows:  $a_0 = 5.09 \text{ \AA}$ ,  $b_0 = 14.31 \text{ \AA}$ ,  $c_0 = 5.725 \text{ \AA}$ ; thus  $a_0:b_0:c_0 = 0.355:1:0.393$ , or  $a:b:c = 0.393:1:0.355$  if the orientation of Schrauf (Palache, Berman, and Frondel, 1946, p. 780) is adopted. These values are comparable to those recorded previously for members of the columbite<sup>2</sup>-tantalite series (Sturdivant, 1930, p. 89), and therefore, there seems little doubt that manganomossite of Yinnie-tharra, Western Australia is a member of this group of minerals.

#### CHEMICAL COMPOSITION

A sample of nearly five grams was prepared for chemical analysis by electromagnetic fractionation of material that had been crushed and graded to give a particle-size range of 44–62 microns. The material sub-

TABLE 1. X-RAY DIFFRACTION DATA FOR TANTALITE AND COLUMBITE  
(=MANGANOMOSSITE)Radiation:  $\text{CuK}\alpha=1.5418 \text{ \AA}$   
Camera diameter: 114.59 mm.

A $d \text{ \AA}$	B		C			
	$d$ meas.	I	$d$ meas.	$d$ calc.	I	$hkl$
7.11	—		7.07	7.15	2	020
—	—		5.30	5.31	1	011
—	—		4.62	—	<1	—
—	—		—	{3.67}		{111
3.66	3.66	3	3.66	{3.66}	6	{031
3.57	—		3.57	3.58	1	040
—	3.325	<1	3.30	—	2	—
—	—		3.10	—	<1	—
2.97	2.98	5	2.97	2.97	10	131
2.86	—		2.852	2.863	3	002
2.54	2.585	1	2.54	2.544	2	200
2.49	2.505	1	2.49	2.494	4	102
—	—		—	{2.397}		{220
2.38	2.38	<1	2.388	{2.386}	3	{060
—	—		—	2.244	<1	230
—	2.221	<1	2.238	{2.211}		{221
—	—		—			
2.21	—		2.208	{2.2095}	2	{132
—	—		—			
2.09	2.109	<1	2.081	2.091	3	231
2.04	—		2.045	2.046	1	142
1.907	—		1.900	1.901	3	202
1.833	1.824	<1	1.835	1.833	4	062
1.799	—		1.801	—	<1	—
—	—		—	{1.772}		{033
1.774	1.773	<1	1.7715	{1.767}	5	{232
—	—		—	{1.7405}		{260
1.740	1.751	1	1.7405	{1.734}	3	{123
—	—		—			
1.724	1.721	2	1.725	1.725	6	162
—	—		1.6745	1.673	<1	133
—	—		1.6125	—	<1 B	—
—	—		1.578	—	<1	—

A: Tantalite; Quixeramobim, Ceará, Brazil (Tavora, 1955, table 1, p. 18). Nine  $d$ -spacings listed by Tavora are omitted from Table I.

B: Manganomossite, Yinnietharra, Western Australia. Specimen is unheated.

C: As for B, but specimen has been heated in vacuo for  $\frac{3}{4}$  hour at  $1,200^\circ \text{C}$ .

(Continued on the next page)

TABLE 1—(Continued)

A <i>d</i> Å	B		C			
	<i>d</i> meas.	I	<i>d</i> meas.	<i>d</i> calc.	I	<i>hkl</i>
1.541	1.551	1	1.5395	—	5	
1.488	—		1.4855	—	2	
—	—		1.471	—	4	
1.461	1.461	2 B	1.4545	—	5	
—	—		1.431	—	<1	
—	—		1.398	—	<1	
1.379	1.384	<1	1.380	—	3	
—	—		1.350	—	<1 B	
1.312	1.338	<1	1.314	—	2	
—	—		1.285	—	<1	
1.275	—		1.272	—	1	
1.247 B	—		1.245	—	2	
1.222 B	—		1.224	—	3	
1.193 B	—		1.195	—	5	
—	—		1.163	—	1	
1.137	—		1.139	—	2	
1.123	—		1.1235	—	1	
—	—		1.1165	—	1	
1.102	—		1.103	—	4	
1.089	—		1.091	—	1 B	
1.076 B	—		1.080	—	2 B	
—	—		1.059	—	<1 B	
—	—		1.0445	—	1 B	
1.035 B	—		1.0335	—	4 B	
1.022 B	—		1.022	—	2 B	
—	—		1.0125	—	1 B	
0.995 B	—		0.995	—	4 B	
0.982 B	—		0.980	—	3 B	
—	—		0.958	—	2 B	
0.932 B	—		0.932	—	3 B	
0.923 B	—		0.925	—	3 B	
—	—		0.916	—	3 B	
0.901 B	—		0.904*	—	1 B	

\* About sixteen more lines are present in the film but they are too broad and diffuse to justify any attempt at measurement.

sequently analyzed was rejected at 0.29 amps. and attracted at 0.31 amps. when the Frantz separator was set with a longitudinal slope of 15° and a tilt of 10°.

The analysis of manganomossite carried out by the author is reported here (Table 2) with some reservations owing to the difficulties that were encountered in the work. The methods employed involved, in the main,

pyrosulphate fusion of the finely powdered mineral, and after separation of iron etc., fractionation of niobium and tantalum by the tannin procedure (Schoeller, 1937). Although iron is reported as  $\text{Fe}^{2+}$ , this element was determined as total iron in the ferric state, and titanium has been determined colorimetrically in a separate portion. Water given off above  $105^\circ \text{C}$ . was determined by the standard Penfield method.

The new analysis shows slight differences from that made at an earlier

TABLE 2. ANALYSES OF MANGANOMOSSITE, YINNIETHARRA,  
WESTERN AUSTRALIA

	A	B	C	D	Total No. of Metal Atoms
MnO	12.02	9.42	9.66	2.18	3.97
FeO	4.64	7.61	7.77	1.74	
UO <sub>2</sub>	—	0.96	0.96	.05	
ThO <sub>2</sub>	—	0.059	0.06	—	
Nb <sub>2</sub> O <sub>5</sub>	34.64	40.69	41.53	5.03	7.99
Ta <sub>2</sub> O <sub>5</sub>	44.53	38.86	39.66	2.89	
TiO <sub>2</sub>	3.92	0.40	0.41	.07	
H <sub>2</sub> O+	0.26	2.16			
H <sub>2</sub> O—	—	0.31			
	100.1	100.47	100.00		

Formula:  $(\text{Mn, Fe, U, Th})_{3.97}(\text{Nb, Ta, Ti})_{7.99}\text{O}_{24}$

A: Manganomossite, Yinnietharra, Western Australia. Anal. D. G. Murray (Bowley, 1923, p. 120). The analyst found  $\text{SnO}_2$  to be absent.

B: Manganomossite, Yinnietharra, Western Australia. Anal. C. Osborne Hutton. U and Th were determined by Mr. Harry Levine, and that analyst's figure for U has been recalculated by the author as  $\text{UO}_2$ .

C: Analysis B, after elimination of water, has been recalculated to give a summation of 100, Mr. Levine's figures for U and Th excepted.

D: Metal atoms, calculated from analysis C, on the basis of 24 atoms of oxygen to the unit cell.

date by Murray (Bowley, 1923), notably in the higher ratios of Nb:Ta and Fe:Mn in the former. Through the courtesy of Dr. Esper S. Larsen 3rd, very careful determinations of both uranium and thorium were made by Mr. Harry Levine on a split of the magnetically fractionated material that was used for the full chemical analysis. Mr. Levine reported the following results:  $\text{ThO}_2 = 0.059$  per cent,  $\pm 0.001$ , and  $\text{U} = 0.86$  per cent,  $\pm 0.02$ ; these figures are averages of four and eight determinations respectively.

The analysis in Table 2, column C, has been recalculated on the basis

of 24 oxygens to give the numbers of metal ions in the unit cell (column D), and owing to similar ionic sizes,  $U^{4+}$  and  $Th^{4+}$  have been grouped with  $Mn^{2+}$  and  $Fe^{2+}$ , whereas  $Ti^{4+}$  has been placed with  $Ta^{5+}$  and  $Nb^{5+}$ . When this is done, the ratio of A:B ions does not depart significantly from the ratio of 4:8 required by the formula for members of the columbite-tantalite series. The presence of a small amount of titanium and uranium in the mineral described here might lead one to suspect the presence of inclusions of samarskite, or other multiple oxides of Nb, Ta, and Ti, similar to the circumstances described by Karunakaran and Neelakantan (1948) or Grigoriev (1945) for columbite-samarskite intergrowths from Nellore, India, and the Ilmen Mountains, Russia, respectively. However, the *x*-ray diffraction data, autoradiographs, and optical study would seem to discredit this idea, and, therefore, it is believed that titanium, uranium, and thorium are all present as ions in the structure of the Western Australia columbite. In this connection, it should be noted that the mineral described by Ellsworth (1926, pp. 332-334) as toddite contains a high percentage of uranium ( $U = 9.65$  per cent) and a minor amount of titanium ( $TiO_2 = 0.85$  per cent). Hey (1955, p. 225) and Palache, Berman and Frondel (1946, p. 786) suggest that this mineral is a mixture of columbite and perhaps, euxenite, but it is the present writer's view that the low titanium content relative to uranium suggests that some mineral other than euxenite may be a more probable contaminant; samarskite would seem to be a much more likely possibility.

From the relationship,  $density = 5.20 + (0.03 \times \% Ta_2O_5)$  established for the columbite-tantalite series, the mineral analyzed by the present writer should have a density of about 6.38, compared to the values 6.39 calculated from unit cell dimensions and composition, and 6.32 determined experimentally for the heat-treated material. Furthermore, according to the diagram of Hermann and Gastellier (1946, p. 81) a member of the columbite-tantalite series with 38.83 per cent  $Ta_2O_5$  would be expected to have a density of 6.18-6.31, whereas the data of Mathieu (*vide* Herman and Gastellier, 1946, p. 81) suggest a figure of 6.24. The density for manganomossite recorded by Bowley is 6.21, presumably for unheated material, and since Murray's analysis lists an insignificant amount of water, it is assumed that heat-treatment would not alter this figure to any marked degree. Accordingly, a member of the columbite-tantalite series with this density would be expected to have approximately 33.66 per cent  $Ta_2O_5$  compared to the figure of 44.54 per cent reported by Bowley. Alternatively, if we assume that the percentage of  $Ta_2O_5$  in Murray's analysis is correct, or nearly so, the corresponding density would be close to 6.53. These anomalies cannot be clearly re-

solved, but the data set out here suggest that the mineral analyzed by Murray may have contained a great deal more water than the amount reported by him, that is, of course, assuming that his figures for tantalum and niobium are correct or approximately so.

#### NOMENCLATURE

Physical and chemical data presented here would clearly seem to indicate that manganomossite from Yinnietharra, Western Australia is a member of the columbite-tantalite series, and that it does not belong to the tetragonal tapiolite-mossite group of minerals. Furthermore, the mineral is metamict. In an earlier note on this mineral, and on the basis of a preliminary determination of niobium by fluorescence analysis, the writer (Hutton, 1957) defined this mineral as tantalite. This is incorrect, since the chemical analysis reported here shows that niobium is in excess of tantalum (molecular ratio), and since the ratio Fe:Mn=1.74:2.18, neither of these elements is sufficiently dominant to require specific mention in the mineral name. Accordingly, the mineral previously called manganomossite should be removed from that category, and referred to, instead, as metamict columbite.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- ARNOTT, R. J. (1950), X-ray diffraction data on some radioactive oxide minerals: *Am. Mineral.*, **35**, 386-400.
- BOWLEY, H. (1923), *Ann. Rep. Dept. Mines, W. Australia (for 1922), Div. 7, Sec. 2, Mineralogy. Mineral Technology, and Geochemistry*, 117-120.
- ELLSWORTH, H. V. (1926), Toddite—A new uranium mineral from Sudbury District, Ontario: *Am. Mineral.*, **11**, 332-334.
- GRIGORIEV, D. P. (1945), Regular intergrowth of samarskite and columbite from the Ilmen Mts., *Mem. Soc. Russe Min.*, **74**, 57-60.
- HEINRICH, E. WM. AND GIARDINI, A. A. (1956), Radioactive columbite-tantalite: *Geol. Soc. Amer. Bull.*, **67**, 1704-1705.
- HERMAN, P., AND GASTELLIER, S. (1946), Détermination rapide de teneurs en Ta<sub>2</sub>O<sub>5</sub> et Nb<sub>2</sub>O<sub>5</sub>. Des columbités: *Bull. du Service Géologique Congo Belge et Ruanda-Urundi*, no. **2**, pt. 1, 73-83.

- HEY, M. H. (1955), An index of mineral species and varieties arranged chemically: British Museum, London.
- HUTCHINSON, R. W. (1955), Preliminary report on investigations of minerals of columbium and tantalum and of certain associated minerals: *Am. Mineral.*, **40**, 432-452.
- HUTTON, C. OSBORNE (1957), Metamict tantalite from Western Australia: *Nature*, **180**, 248.
- KARUNAKARAN, C., AND NEELAKANTAM, K. (1948), Samarskite from Nellore District. Part 1. Uranium and earth acid contents: *Proc. Indian Acad. Sci., Sect. A*, **25**, 404-407.
- PALACHE, C., BERMAN, H., AND FRONDEL, C. (1946), Dana's System of Mineralogy, 7th ed., Vol. I, John Wiley and Sons, Inc., New York.
- SCHOELLER, W. R. (1937), The Analytical Chemistry of Tantalum and Niobium, Chapman and Hall, Ltd., London.
- SIMPSON, E. S. (1952), *Minerals of Western Australia*, vol. 3, Govt. Printer, Perth, W. Australia.
- SPENCER, L. J. (1925), Tenth list of new minerals names; with an index of authors: *Mineral. Mag.*, **20**, 44-477.
- STURDIVANT, J. R. (1930), The crystal structure of columbite: *Zeits. Krist.*, **75**, 88-108.
- TAVORA, E. (1955), X-ray diffraction powder data for some minerals from Brazilian localities: *Anais da Acad. Brazil. de Ciências*, **27**, 7-27.

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