

PRELIMINARY REPORT ON INVESTIGATIONS OF MINERALS OF COLUMBIUM AND TANTALUM AND OF CERTAIN ASSOCIATED MINERALS

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ABSTRACT

This paper is a progress report of an investigation of columbium and tantalum minerals. The rotation properties of the columbite-tantalite series have been investigated in detail and the results and their application to identification are discussed. The optical properties of some other columbium-tantalum minerals including ytrotantalite, bismutotantalite, stibiotantalite, tapiolite and ilmenorutile are also discussed so far as they have been determined. The relationship between the orthorhombic columbite-tantalite series and the tetragonal mosite-tapiolite series is critically examined. All specimens of ilmenorutile so far studied were found to be intergrowths of two minerals, columbite and rutile. Related features of this intergrowth are discussed. Some optical properties of minerals commonly associated with columbium-tantalum minerals have also been determined and have been of value in the investigation. Data for these minerals are presented.

INTRODUCTION

An investigation of the opaque minerals of columbium and tantalum was begun in 1952 in the Laboratory of Economic Geology at the University of Wisconsin. This report summarizes the results of the first year's investigations, and although research is not yet complete, certain interesting features have been found that warrant publication of a progress report.

The identification of columbium and tantalum minerals is a problem of many years' standing. The minerals can be distinguished by a combination of x-ray and chemical techniques, but these methods are time-consuming and are not readily applicable to the identification of small grains, or of mixtures of columbium-tantalum minerals with other opaque minerals. The present investigation was designed especially to obtain information regarding the optical properties of the columbium-tantalum minerals in the hope that these would facilitate identification. Particular attention was paid to their rotation properties, which were unknown yet seemed to offer promise of being useful in identification. It was hoped that if the rotation properties (5)¹ of members of the isomorphous columbite-tantalite series were functions of the Cb-Ta content, it would be possible to determine the $\text{Cb}_2\text{O}_5:\text{Ta}_2\text{O}_5$ ratio of a given sample by optical methods.

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¹ Numbers in parentheses refer to the bibliography at the end of the paper.

Of the minerals studied, tapiolite and ilmenorutile proved to be particularly interesting, and they are discussed in some detail in this report. Study of tapiolite led to an examination of the relationships between the tetragonal mossite-tapiolite series and the orthorhombic columbite-tantalite series, and certain tentative conclusions are presented. Ilmenorutile in our specimens proved to be an intergrowth of columbite and rutile. This intergrowth is described and its origin is discussed.

During the investigation it became apparent that optical information was needed for certain minerals that are commonly associated with the columbium-tantalum minerals. Studies of these minerals were made and the results are also presented in this report.

Suitable samples of the various columbium-tantalum minerals were difficult to obtain, and this factor was one of the major problems of the investigation. All available samples required checking by means of x -ray diffraction techniques, and in some cases chemical determinations had to be procured.

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The investigation was carried out in the Laboratory of Economic Geol-

ogy at the University of Wisconsin under the supervision of Dr. E. N. Cameron. Dr. Cameron has furnished much of the material studied, has helped the writer during the investigation, and has given helpful advice and criticism in the preparation of this report. Sincere thanks are also due to Mr. S. W. Bailey, of the University of Wisconsin Geology Department, for his assistance with the x -ray determinations which were essential to the study.

COLUMBITE-TANTALITE AND RELATED MINERALS

Methods and Scope of the Investigation

Twenty-nine specimens of columbite-tantalite were obtained for study of the optical properties of the orthorhombic series $(\text{Fe}, \text{Mn})\text{-Cb}_2\text{O}_6\text{-}(\text{Fe}, \text{Mn})\text{Ta}_2\text{O}_6$. For each crystal or specimen permitting it, three oriented (critical) sections were cut, mounted in bakelite, and polished. Optical studies of all these surfaces were completed in the manner outlined by Cameron *et al.* (5, 6). The rotation properties of these specimens as determined are summarized in Table 1. In order to relate the optical properties to chemical composition, chemical analyses of some of the specimens were obtained.

The chemical determinations were done by x -ray fluorescence analysis and the results, expressed in terms of oxides of the elements, are shown in Table 2. The lower sensitivity ranges of this analytical method for the elements shown in the analyses are as follows,

	<i>Per Cent</i>
Cb.....	0.05 to 0.1
Ta.....	0.1 to 0.2
Fe.....	0.01 to 0.05
Mn.....	0.01 to 0.1
Sn.....	0.2
Zr.....	0.02 to 0.05
Y.....	0.03 to 0.05
W.....	2.0
Ti.....	5.0

The notation *n.d.* on Table 2 indicates that titanium was present in amounts less than the sensitivity for this element.

The accuracies of the quantitative results shown in Table 2 can be expressed in per cent of the amounts of the elements present (% P.E.). For the elements that are present in amounts near the sensitivity limits shown above, accuracies of $\pm 10\%$ P.E. may be expected. For the elements present in higher concentrations (Cb, Ta, Fe and Mn), the determinations should be accurate to $\pm 1\%$ P.E.

The compositional range covered by the specimens studied is shown

TABLE 1. ROTATION PROPERTIES OF COLUMBIITE-TANTALITE

Univ. Wis. Ref. No.	Mineral Designation and Locality	S.G.	DR_r	A_r			DA_r	Amount of Dispersion
				Red	White	Blue		
50-50- 1	Columbite, E. E. Smith Mine, Alexandria, New Hampshire	5.789	ess. nil	1.5	1.3	.9	$r > v$, distinct	.6
50-10- 1	Tantalite,* Etta Mine, Keystone, South Dakota	7.041	ess. nil	1.5	1.4	1.1	$r > v$, weak	.4
50-12- 3	Columbite-tantalite,* Rough and Ready Mine, Tinton, South Dakota	6.392	ess. nil	1.5	1.4	1.1	$r > v$, weak	.4
50-10-11	Columbite-tantalite, Peerless Mine, Keystone, South Dakota	5.979	ess. nil	1.5	1.3	.9	$r > v$, distinct	.6
51-27- 1	Columbite,* Van der Made Claim, Erongo Schlucht, S. W. Africa	5.607	ess. nil	1.5	1.5	1.3	ess. nil	.2
51-27- 8	Columbite,* Van der Made Main Pegmatite, Erongo Schlucht, S. W. Africa	5.660	ess. nil	1.6	1.5	1.3	$r > v$, very weak	.3
51-32- 1	Columbite, Krom River Beryl Deposits, Urnais Farm, Warmbad District, S. W. Africa	5.503	ess. nil	1.5	1.3	1.0	$r > v$, weak	.5
51-30- 3	Columbite, Spencer #11 Claim, Farm Duawib East, S. W. Africa	5.732	ess. nil	1.5	1.4	1.0	$r > v$, weak	.5
50-51- 1	Columbite,* DeStafany Ta-Bc Mine, Great Slave Lake, N.W.T., Canada	5.808	ess. nil	1.5	1.3	.8	$r > v$, strong	.7
50-52- 1	Columbite,* Quartz Creek Pegmatite District, Gunnison County, Colorado	5.691	ess. nil	1.6	1.4	.9	$r > v$, strong	.7
53-85- 2	Columbite, Neira Pegmatite, Alto Ligonha, Portuguese East Africa	—	ess. nil	1.3	1.2	.9	$r > v$, weak	.4
53-85- 4	Columbite, Marige Pegmatite, Alto Ligonha, Portuguese East Africa	—	ess. nil	1.3	1.2	.8	$r > v$, weak	.5
53-85- 1	Columbite, Muiane Pegmatite, Alto Ligonha, Portuguese East Africa	—	ess. nil	1.4	1.3	.9	$r > v$, distinct	.5
53-85- 3	Columbite, Nahora Pegmatite, Alto Ligonha, Portuguese East Africa	—	ess. nil	1.3	1.2	.8	$r > v$, weak	.4
53-80- 1	Columbite, Mirruccu Area, Alto Ligonha, Portuguese East Africa	—	ess. nil	1.4	1.3	.9	$r > v$, strong	.6

TABLE 1—(continued)

Univ. Wis. Ref. No.	Mineral Designation and Locality	S. G.	DR_r	d_r		DA_r	Amount of Dispersion
				Red	Blue		
53-13- 1	Columbite,	—	ess. nil	1.3	1.2	$r > v$, weak	.4
49-11-13	Umcis Farm, S. W. Africa Tantalite,* Old Mike Pegmatite, Custer County, South Dakota	—	ess. nil	1.3	1.2	$r > v$, weak	.4
53- 8- 1	Ytrotantalite,*	5.85	none, sample is isotropic, metamict with internal reflections				
53-10- 1	Renders Claim, Bikita, Rhodesia Ytrotantalite,	—	none, sample is isotropic, metamict with internal reflections				
53-11- 1	Johnson Claim, Bikita, Rhodesia Columbite,	—	ess. nil	1.0	.9	$r > v$, weak	.3
53-83- 1	Warmbad District, S. W. Africa Columbite, Lot 26136,	—	ess. nil	1.4	1.3	$r > v$, weak	.3
53-83- 3	Union Carbide Columbite, Lot 6424,	—	ess. nil	1.5	1.3	$r > v$, strong	.6
53-83- 2	Union Carbide Columbite, Lot 6262,	—	ess. nil	1.3	1.2	$r > v$, weak	.4
53-83- 4	Union Carbide Columbite, Lot 6425,	—	ess. nil	1.5	1.4	$r > v$, strong	.6
53-84- 3	Union Carbide Manganotantalite, Wodgina, West Australia	—	ess. nil	1.1	1.0	ess. nil	.2
53-84- 4	Manganotantalite, Pilbara, West Australia	—	ess. nil	.7	.6	ess. nil	?
53-84- 1	Bismutotantalite, Uganda	—	ess. nil	?	small	$r > v$, distinct	?
53-84- 2	Stibiotantalite, Mesa Verde, California	—	ess. nil	1.3	1.2	$r > v$, distinct	.4
H.L.-16	Columbite, Hidden Lake, N. W. T., Canada	—	ess. nil	1.5	1.4	$r > v$, strong	.6

* Indicates specimen has been analyzed and is listed in Table 2.

TABLE 2. ANALYSES OF SPECIMENS

Univ. Wis. Ref. No.	Mineral	Locality	S.G.	Per Cent Composition by Elemental Oxides											
				Cb ₂ O ₅	Ta ₂ O ₅	Cb:Ta ratio	FeO	MnO	Fe:Mn ratio	SnO ₂	WO ₃	ZrO ₂	Y ₂ O ₃	Rare Earths	TiO ₂
50-52-1	Columbite	Quartz Creek Pegmatite District, Gunnison County, Colorado	5.691	73	10	7.30:1	9.5	6	1.58:1	—	<2	—	—	—	n.d.
51-27-8	Columbite	Van der Made Main Pegmatite, Erongo Schuchert, Southwest Africa	5.660	70	10	7.00:1	7.5	9	1:1.20	—	<2	—	—	—	n.d.
50-51-1	Columbite	DeStafany Ta-Be Mine, Great Slave Lake, N.W.T., Canada	5.808	59	23	2.56:1	11	4	2.75:1	—	<2	tr.	—	—	n.d.
51-27-1	Columbite	Van der Made Claim, Erongo Schlucht, Southwest Africa	5.607	56	26	2.15:1	—	16	zero	—	<2	—	—	—	n.d.
50-12-3	Columbite-tantalite	Rough and Ready Mine, Tinton, South Dakota	6.392	37	45	1:1.22	6	7	1:1.11	—	<2	—	—	—	n.d.
50-10-1	Tantalite	Etta Mine, Keystone, South Dakota	7.041	18	63	1:3.50	5	8	1:1.60	3.0	<2	—	—	—	n.d.
49-11-13	Tantalite	Old Mike Pegmatite, Custer County, South Dakota	—	15	65	1:4.33	8.5	3.5	2.43:1	3.5	<2	tr.	—	—	n.d.
50-53-1	Tapolite	Peg Tantalum Mine, Ross Lake, N.W.T., Canada	7.550	9	73	1:8.11	14	.7	20.0:1	—	<2	—	—	—	n.d.
53- 8-1	Yttrio-tantalite	Renders Claim, Bikita, Rhodesia	5.85	1	56	1:56	5	1	5:1	2	<2	tr.	12	5-10	<6

 * In addition to listed oxides this specimen contains U₃O₈.

by the analyses. Samples approaching the theoretical end-members were most difficult to obtain. Columbite from Gunnison County, Colorado (Table 2) has a $\text{Cb}_2\text{O}_5:\text{Ta}_2\text{O}_5$ ratio of 7.3:1. Tantalite from the Old Mike pegmatite, Custer County, South Dakota has a $\text{Cb}_2\text{O}_5:\text{Ta}_2\text{O}_5$ ratio of 1:4.33. These two specimens are the nearest approaches to the end-members of the series in the material studied. The compositions of several intermediate members of the series are also listed in Table 2. It was impossible to obtain chemical determinations for all the specimens, but the samples submitted for analyses were carefully selected on the basis of specific gravities and variations in optical properties, in order to cover as wide a compositional range as possible.

A few samples of some rare varieties of tantalite, including manganese-, yttrium-, rare-earth-, antimony-, and bismuth-rich types were also obtained. Their identification was first checked, wherever possible, by x-ray diffraction powder photographs. Their optical properties were then investigated using oriented polished surfaces.

Difficulty in procuring specimens of these varieties of columbite-tantalite was again a problem. Only one of these samples, yttriotantalite from Bikita, Rhodesia, has been analyzed. Its composition is indicated in Table 2. Because of these difficulties, data obtained for the rare varieties of columbite-tantalite are too incomplete to justify any final conclusions, but the results of the limited studies are discussed briefly.

Rotation Properties

(a) Apparent Angle of Rotation in White Light

Tables 1 and 2 clearly indicate that in white light there is essentially no variation in the apparent angle of rotation in the isomorphous series columbite-tantalite, because none of the specimens studied shows significant differences in the apparent angle of rotation between Cb- and Ta-rich varieties. The angle of rotation in white light for columbite from Gunnison County, Colorado, is 1.4 degrees while the rotation angle for tantalite from the Old Mike pegmatite is 1.2 degrees. All other specimens studied also have angles of rotation that lie in the range from 1.2 to 1.5 degrees for white light in air. This variation is within the limits of experimental error (5, p. 746).

(b) Dispersion

Significant variations in strength, or amount, of dispersion of the apparent angle of rotation were found and are recorded in Table 1. Qualitatively the variation in strength of dispersion is shown by varying intensity of color fringes in the polarization figures of different columbite-tantalites. It was quantitatively determined by measuring the apparent

angles of rotation for monochromatic red and monochromatic blue light. The difference between the two values obtained is the amount of dispersion. The amount of dispersion varies from .2 to .7 degree. This is a significant and measurable difference. Thus far, oil immersion methods have been attempted only on a limited scale, but immersion in oil of R.I. 1.515 increases the range of the variation to .3 to 1.1 degrees.

This variation is apparently not due to varying $\text{Cb}_2\text{O}_5:\text{Ta}_2\text{O}_5$ ratios, for samples of columbite-tantalite with widely varying ratios have similar dispersions. Table 2 shows that the specimen (51-27-8) from the Van der Made main pegmatite, Southwest Africa has a $\text{Cb}_2\text{O}_5:\text{Ta}_2\text{O}_5$ ratio of 7:1, while tantalite from the Etta Mine at Keystone, South Dakota, has a ratio of 1:3.5. Table 1 shows that both specimens have very similar dispersions. The analyses indicate that the amount of dispersion is related to the FeO content, or more specifically to the FeO:MnO ratio. When the ratio of FeO to MnO is high (greater than unity), the amount of dispersion tends to be high (.5 to .7 degree), and the color fringes in the polarization figure at the 45-degree position are strong. Columbite from Gunnison County, Colorado, and from Great Slave Lake in Canada are examples. Table 2 shows that both these specimens have high FeO:MnO ratios, and Table 1 shows that they have strong dispersions. One apparent exception is tantalite from the Old Mike pegmatite which has a high FeO:MnO ratio of 2.43:1 as shown in Table 2, but has only an intermediate dispersion. This discrepancy is explained, however, by the high content of tin which presumably substitutes for manganese in the sample. If the tin content is computed with manganese, the ratio (of FeO:MnO+SnO₂) becomes 1.2:1, and this figure is in agreement with the intermediate dispersion.

When the ratio of FeO:MnO is low (less than unity), dispersion is correspondingly weak (.2 to .4 degree) and color fringes in the polarization figure are weak or absent. Specimen 51-27-1 from the Van der Made Claim, Southwest Africa, is an excellent example. Table 2 shows that it contains essentially no iron whatever but is rich in manganese, and Table 1 records that it has essentially no dispersion. Samples in which the FeO:MnO ratio is near unity have intermediate dispersions (.4 or .5 degree). The analyzed specimen from Tinton, South Dakota, has an FeO:MnO ratio near unity, and an intermediate dispersion of .4 degree is shown for the sample in Table 1.

An independent test of this relationship was carried out on additional samples for which approximate analyses were available. It was possible to select, on the basis of strength of dispersion alone, which of these samples were FeO-rich and which were high in MnO.

Additional samples of both iron and manganese varieties are being

obtained and will be studied to substantiate this relationship further. It seems probable that with additional data (especially using oil immersion) an empirical scale can be set up that will make it possible to determine the FeO:MnO ratio of a given sample from its amount of dispersion.

Conclusions

(a) The apparent angle of rotation does not vary significantly with composition in the columbite-tantalite series.

(b) The amount of dispersion in the columbite-tantalite series appears to vary with the FeO:MnO ratio. Additional samples, analyses and measurements are required to substantiate the relationship.

(c) Comparison of chemical analyses and specific gravities clearly shows that specific gravity alone can be used only in a general way to place a given sample in the columbite-tantalite series, because both FeO:MnO and $\text{Cb}_2\text{O}_5:\text{Ta}_2\text{O}_5$ ratios affect the specific gravity.

Yttrotantalite

Two specimens of yttrotantalite were obtained and studied. Optically both are noticeably different from normal tantalite. They are isotropic or very weakly anisotropic, and neither sample shows the degree of anisotropism common to normal tantalite. Internal reflections are much stronger than those usually encountered in tantalite and they interfere drastically with the determination of rotation properties.

It was suspected that both crystals were partially, or wholly, metamict in nature and perhaps radioactive. Tests with a simple Geiger counter showed that both samples are strongly radioactive. X-ray diffraction powder patterns of both specimens, in general, match that of yttrotantalite. In both cases, however, there are broad diffuse bands instead of sharp lines. This suggests a partial breakdown of the crystal structure.

An analysis of one of the samples was subsequently obtained and is given in Table 2. It reveals appreciable amounts of yttrium, rare-earths and uranium, thus accounting for the radioactivity and metamict properties. In polished surface the specimen is notably impure and contains tiny inclusions of other unidentified minerals. Whether these mineral impurities contain the radioactive elements disclosed by the analysis is not known.

No general conclusions are justified on the basis of the two specimens studied, but it appears that the yttrotantalite is partially metamict as indicated by Dana (9, p. 763). This could result normally from the presence of the rare-earth elements and uranium that are present in the sample. The metamict condition would explain the isotropism of the specimens in reflected light.

Bismutotantalite and Stibiotantalite

A single sample of each of these minerals was obtained and studied. Microscopic examination showed that both are impure and contain varying amounts of an unidentified mineral that appears to replace them along cracks and fissures. Stibiotantalite is semi-transparent and is softer than normal tantalite with stronger internal reflections, lower anisotropism and stronger dispersion. Bismutotantalite also is softer and has lower anisotropism and stronger internal reflections than tantalite. Thus stibiotantalite and bismutotantalite are similar to each other in optical properties in reflected light, and Dana (8, p. 697) states that for bismutotantalite, "angles show similarity to those of stibiotantalite." Since the antimony variety is semi-transparent, oriented thin sections must be prepared for the determination of its optical properties in transmitted light.

X-ray diffraction powder photographs of both samples were taken. The specimen of stibiotantalite gives a pattern that matches the *A.S.T.M.* index card for that mineral. No card is available for bismutotantalite, but its pattern resembles the pattern of stibiotantalite more closely than it does the pattern of normal tantalite. The similarity in *x*-ray patterns is also reported by Dana (9, p. 770). For the two specimens studied, the resemblance between *x*-ray powder patterns was especially close with regard to the positions of the strong lines. Weaker lines in the bismutotantalite pattern were closer in position to the corresponding lines of normal tantalite. The crystal structure of stibiotantalite is known (10; 20, p. 227), and is different from that of normal tantalite (2; 22). In bismutotantalite, as in stibiotantalite, a trivalent cation takes the place of the bivalent iron and manganese cations found in normal tantalite. In view of this fact and of the observations given above, it seems likely that bismutotantalite is very similar in crystal structure to stibiotantalite. It is evident, however, that additional studies of the varieties containing the trivalent cations are needed.

Manganotantalite

Two samples designated as manganotantalite from West Australia were secured and investigated. Their optical and rotation properties, as well as their *x*-ray diffraction powder photographs are similar to those of the ordinary columbite-tantalites studied. It is interesting to note that in these two samples dispersion of the apparent angle of rotation is weak as shown in Table 1. Although no analyses of these samples are available, the weak dispersion is in accordance with a high manganese content (or low FeO:MnO ratio), and therefore supports the designation of these specimens as manganotantalites.

MOSSITE-TAPIOLITE

Methods and Scope of the Investigation

It was desired to investigate the optical properties of the mossite-tapiolite series in a manner similar to that outlined for the columbite-tantalite series. Unfortunately very few specimens of the tetragonal series were available. Only three proven samples were obtained, but one other, from the Old Mike pegmatite, has optical properties that warrant its assignment to this group. The rotation properties of these specimens were determined and are summarized in Table 3.

TABLE 3. ROTATION PROPERTIES OF SOME TAPIOLITES

Univ. Wis. Ref. No.	Mineral	Locality	S.G.	DR_r	A_r			DA_r	Amount Dispers.
					Red	White	Blue		
B.B. 4	Tapiolite	Best Bet Pegmatite, Drever Lake, N.W.T., Canada	—	ess. nil.	2.9	2.7	1.6	$r > v$, strong	1.3
Peg. M-3	Tapiolite	Peg Tantalum Mines, Ross Lake, N.W.T., Canada	—	ess. nil.	2.0	1.8	.9	$r > v$, strong	1.1
49-11-13	Tapiolite	Old Mike Pegmatite,* Custer County, South Dakota	—	ess. nil.	1.8	1.5	?	$r > v$, strong	n.d.
50-53-1	Tapiolite	Peg Tantalum Mines,† Ross Lake, N.W.T., Canada	7.550	ess. nil.	1.9	1.7	.8	$r > v$, strong	1.1

* This tapiolite occurs as inclusions in tantalite.

† Indicates specimen has been analyzed and is listed in Table 2.

One of the samples was analyzed, and its composition as shown in Table 2 indicates that it is a tapiolite. Another of the samples studied consists of inclusions in the specimen of tantalite from the Old Mike pegmatite. Inasmuch as the host tantalite has a low $Cb_2O_5:Ta_2O_5$ ratio (Table 2) it seems likely that the inclusions (if they could be analyzed) would also prove to be tantalum-rich. The composition of the other two specimens is not known. Thus it is evident that the writer is in no position to discuss the relation between optical properties and composition in the mossite-tapiolite series, but the results of the limited studies are briefly presented.

The search for specimens of the mossite-tapiolite series, together with x-ray work on available samples and a study of the literature, led, however, to a critical examination of the relationship between the tetragonal

mossite-tapiolite series and the orthorhombic columbite-tantalite series. Certain aspects of this subject are of interest and are discussed below.

Rotation Properties

(a) Distinction of Mossite-Tapiolite from Columbite-Tantalite

Polarization figures and rotation properties offer a simple, quick and effective technique for distinguishing between tapiolite and columbite-tantalite in polished surfaces. Previously the similarity of the two minerals has made their distinction a matter of extreme difficulty. The physical and chemical properties of the two minerals are almost identical, and *x*-ray work on small impure grains in polished surfaces is difficult. The two minerals can be rapidly distinguished, however, by their rotation properties and relative reflectivities (Table 4).

(b) Angle of Rotation and Dispersion

Significant and measurable differences in the apparent angle of rotation in air were found for the various specimens of tapiolite. The values of the angle recorded in Table 3 range from 1.7 to 2.9 degrees. Variations in the strength of dispersion similar to those described for columbite-tantalite have also been encountered. Tapiolite from Ross Lake, Northwest Territories, and from the Old Mike pegmatite have strong blue and pink color fringes in their polarization figures at the 45-degree position. Tapiolite from Drever Lake in the Northwest Territories has blue and yellow color fringes.

Although it is impossible at present to relate the variations in rotation angles and dispersion to changing composition in the mossite-tapiolite series, it is interesting to note that those tapiolites that occur in iron-rich tantalite have high dispersion. Strength of dispersion may be related to the FeO:MnO ratio. Investigations using *x*-ray diffraction precession photographs of tapiolite from Ross Lake, Northwest Territories, have shown that this material (specimen 50-53-1, Tables 2 and 3) is disordered and has a rutile structure. Goldschmidt reported (13, p. 17; 14) that tapiolite is ordered, with tri-rutile structure and a superlattice. Thus it seems that there are two distinct forms of the tetragonal mineral tapiolite, and the observed variation in optical properties may be related to the degree of ordering.

Relationship between the Orthorhombic Columbite-Tantalite Series and the Tetragonal Mossite-Tapiolite Series

In the Ta-rich tantalites examined from the Old Mike pegmatite and from the Etta Mine, inclusions of tetragonal mossite-tapiolite were found; but inclusions belonging to the tetragonal series were never dis-

TABLE 4. ROTATION PROPERTIES OF MINERALS

Mineral	Cryst. System	Dispersion of Reflection Rotation	Apparent Angle of Rotation			Dispersion of Apparent Angle of Rotation	Reflectivity relative and listed in descending order
			Red	White	Blue		
Hematite	hex.	$r > v$, weak	2.4			$v > r$, distinct	highest
Rutile	tet.	$r > v$, weak to distinct	3.2	2.9	2.4	$r > v$, weak or masked	creamy-white
Ilmenite	hex.	$v > r$, distinct	2.2	2.9	3.1	$v > r$, distinct	
Tapiolite	tet.	ess. nil	2.9	2.8	1.7	$r > v$, strong	nearly equal to ilmenite
Columbite-tantalite	orth.	ess. nil.	1.5	1.4	1.0	$r > v$, weak to strong	orange-cream
Euxenite	iso.	ess. nil	none			none	
Cassiterite	tet.	ess. nil	1.9			$r > v$, weak often masked	grayish-cream
Ferberite	mono.	ess. nil	2.6	2.3	1.6	$r > v$, distinct	
Monazite	mono.	all dispersions and rotation properties masked by internal reflections					gray
Zircon	tet.	all dispersions and rotation properties masked by internal reflections					

covered in any of the numerous Cb-rich columbites. Columbium is a much more abundant element than tantalum (19, pp. 604-605) and this is reflected in the fact that columbite is much more abundant than tantalite. By the same standard mossite should be much commoner than tapiolite. This is not the case. Dana (9, p. 775) lists only two occurrences of mossite. The first of these was described by Brögger (3) and is the original material from Moss, near Obstfold, Norway, from which the mineral takes its name. The analysis of this specimen given in Dana's table (9, p. 776) shows only combined columbium-tantalum content. A

OFTEN ASSOCIATED WITH Cb-Ta MINERALS

Internal Reflections	Separation of Isogyres in % of Field Diameter	Description of Figure upon Rotation of Analyzer, Mineral in Crossed Position	Description of Figure in 45-degree Position, Polarizer and Analyzer Crossed
rare, weak & reddish if present	35%	black isogyres, weak violet fringes on concave side, deep green on convex side, center of field yellow	black isogyres, violet fringes on concave side, blue-green fringe on convex side, center of field yellow
numerous, strong & reddish	40%	gray to reddish isogyres, narrow pink fringe on concave sides, narrow blue fringe on convex sides	black to reddish isogyres (if internal reflections present), concave sides pale blue, convex sides pink (or masked)
very rare	30%	black isogyres, weak blue fringe on concave side, pink fringe on convex	black isogyres, distinct pink fringe on concave sides, green-blue fringe on convex
none	35%	black isogyres, no distinct color fringes	black or dark green-blue isogyres, blue green fringe on concave side, yellow convex
rare, weak & reddish	20%	black isogyres, fringes indistinct	black isogyres, concave side pale blue, convex sides pink, fringes weak to strong
none or very rare	none	black isogyres, no color fringes	black cross, no separation of isogyres
numerous & varied white, gray, brown, red	30%	black isogyres, essentially no color fringes (or pink concave, blue convex and very weak)	black isogyres, fringes very weak often masked by internal reflections—appear blue concave, pink convex but this weak and possibly due to internal reflections
rare	30%	black isogyres, no color fringes	black isogyres, fringes distinct—concave side blue, convex orangey-pink
numerous & strong, always present, white, brown, red, patchy	cannot tell	figure unobtainable, internal reflections flood field	figure unobtainable, internal reflections flood field
strong & always present, reddish	cannot tell	figure unobtainable, internal reflections flood field	figure unobtainable, internal reflections flood field

later analysis of this material in 1906 (23) revealed a Ta_2O_5 content of 52% and a Cb_2O_5 content of 31%. This material is therefore tantalum-rich and should properly be called tapiolite. Schaller believed (21, p. 16) that the mineral name mossite proposed by Brögger for this specimen should be dropped because the sample is a columbic tapiolite. The second sample listed by Dana is a "mangano-mossite" from West Australia and it is described (9, p. 776) as doubtful, and possibly a columbite.

All these features lead one to question the existence of mossite and of a complete tetragonal mossite-tapiolite series. The suggestion is ad-

vanced here that there may be no complete tetragonal series of composition $(\text{Fe}, \text{Mn})\text{Cb}_2\text{O}_6$ - $(\text{Fe}, \text{Mn})\text{Ta}_2\text{O}_6$ but only an orthorhombic series. In the high tantalum ranges, the orthorhombic form may revert to tetragonal symmetry in the mineral tapiolite. This would explain the anomalous features described above including the absence of mossite inclusions in columbite and the over-all rarity of mossite despite the relative abundance of columbium.

Dana stated (9, p. 776) that it has not been established that the natural tetragonal series extends to a high columbium member. Brandt (2, p. 6) reported that if a mineral analysis gives more than 25 atom per cent of columbium, a columbite phase must exist. She further stated that if larger amounts of tantalum are found in an iron-manganese mineral either orthorhombic or tetragonal compounds can be formed. Apparently synthesis of the high tantalum members can yield either tetragonal tapiolite or orthorhombic tantalite, but at the high columbium end only an orthorhombic member has been obtained. This lends support to our hypothesis which is also in accordance with the geologic occurrence of columbite, tantalite and tapiolite. Columbite forms early in pegmatites while tantalite and tapiolite are later (7, pp. 69 and 99). This may be explained by the greater relative abundance of columbium, which, in the course of differentiation, causes the early crystallization of columbium-rich compounds. Tantalum becomes enriched to the point of crystallization at a later time and results in the formation of tantalite or (because of the enrichment in tantalum relative to columbium) tapiolite.

Polymorphism

The cause of polymorphism in the proposed columbite-tantalite-tapiolite series is not now understood. Order-disorder cannot be the solution as it would mean that tapiolite (the higher symmetry and supposedly disordered form) would be early while tantalite (the low symmetry and ordered form) would be late. This is the reverse of the geologic occurrence of these minerals in pegmatites. It is also known that a superlattice is present in some tapiolite (24, p. 17; 13, p. 17) and this indicates that it is, in fact, an ordered structure and finally rules out order-disorder as a cause of polymorphism.

If the radius ratio of the quinquevalent columbium and tantalum ions to the oxygen ion fell on the borderline between two different co-ordination ranges, the small size difference of the columbium and tantalum ions might cause a change of symmetry in the Ta-rich range. In actual fact, however, the radius ratio (of quinquevalent columbium and tantalum ions to the oxygen ion) lie centrally in the octahedral co-ordination range.

It may be significant that tapiolite has a tri-rutile or rutile structure based on the mineral rutile while columbite-tantalite is based on the brookite structure (2, p. 4; 13; 17) The cause of polymorphism in tapiolite-tantalite may be similar, or comparable, to the cause in the case of rutile-brookite but this has not been determined. Heating and cooling experiments to determine whether orthorhombic tantalite can be converted to tetragonal tapiolite at high temperatures, and vice versa, would be of interest in studying the polymorphic relationships. Additional syntheses of the columbite-tantalite-tapiolite minerals would also be of value.

Summary and Conclusions

(a) Tapiolite can be distinguished quickly and readily from the columbite-tantalites in polished surfaces by the use of polarization figures and rotation properties.

(b) The apparent angle of rotation varies significantly in the different specimens of tapiolite studied. This variation may be related to compositional differences or to the degree of ordering.

(c) Strength of dispersion also varies in the different tapiolites studied. This variation may be related to varying FeO:MnO ratios in the specimens investigated.

(d) The existence of the mineral mossite, and of a complete tetragonal mossite-tapiolite series is questioned. It is proposed that only a single series of composition $(\text{Fe}, \text{Mn})\text{Cb}_2\text{O}_6$ - $(\text{Fe}, \text{Mn})\text{Ta}_2\text{O}_6$ occurs in nature and includes the minerals columbite, tantalite and tapiolite. This proposal is an hypothesis only, and should be critically examined in the light of further information.

(e) The cause of polymorphism in tantalite-tapiolite is not understood. Additional work, including heating and cooling and synthesis experiments, is needed to determine the cause of the dimorphic relationship.

(f) A second distinct form of tapiolite was encountered in this study. Goldschmidt previously described (13, p. 17) an ordered form with tri-rutile structure and a superlattice. The analyzed specimen from Ross Lake, however, is a disordered form with rutile structure. The relationship between degree of ordering and optical properties needs further investigation.

ILMENORUTILE

General Statement

The name ilmenorutile was originally proposed by Koksharov (16, pp. 352-355) for what he called "a new variety of rutile." Later analyses apparently showed that this material contained appreciable columbium and minor tantalum. Dana (9, p. 558) described ilmenorutile as colum-

bian rutile, and this is the accepted definition at the present time.

A number of specimens believed to be ilmenorutile were obtained and studied. The first two samples received were crystals from M'ba, French Cameroons and from the Tonkolili District, Sierra Leone. Oriented polished surfaces of these crystals were prepared. Subsequently twenty additional sand samples from pits alongside streams, also from Sierra Leone, were obtained. These were believed to contain ilmenorutile and polished surfaces of them were prepared. The results of the studies of these materials to date are presented below.

Observations and Discussion

The crystals from M'ba, French Cameroons and from the Tonkolili District of Sierra Leone proved to be complex, intricate intergrowths of columbite and rutile. Identification of the constituent minerals was first accomplished using rotation properties and polarization figures on polished surfaces. The identification was later substantiated by means of x -ray diffraction powder photographs. The x -ray patterns obtained showed strong rutile lines and weak columbite lines. There was no apparent shift in position of the rutile lines (from the pattern of "normal" rutile) of the kind often resulting from substitutional solid solution.

Examination of a number of the concentrates in polished surfaces revealed that the non-magnetic portion of each sample¹ also contained some mineral grains that are intergrowths of columbite and rutile. These intergrowths, therefore, account for at least part of the columbium content of these specimens. In addition to the intergrowths, each non-magnetic fraction contains numerous grains of homogeneous rutile.

From one of the non-magnetic samples of concentrates, several grains were selected, and individual x -ray diffraction powder photographs of these grains were taken. These photographs showed that there was no visible shift of the rutile lines between a grain of pure rutile and a grain containing the intergrowth of columbite and rutile. In both cases the rutile lines agreed with the *A.S.T.M.* index card for normal rutile and with the pattern of a different check sample of our own rutile. This is, at best, a rough experiment but it indicates that little columbium is contained in solid solution in either the homogeneous rutile grain, or in the grain of rutile that has the columbite intergrowth. If columbium is present in the rutile, it is in insufficient amounts to cause a shift in position of the lines of the rutile powder pattern.

Data at hand, therefore, suggest that ilmenorutile as a distinct min-

¹ Each of the concentrate specimens had been divided into magnetic and non-magnetic fractions.

eral is not present in the material studied, but only intergrowths of columbite with ordinary rutile. This fact raises some doubt about the existence of ilmenorutile as an independent mineral, and led the writer to an examination of the literature in this regard.

Prior (18, pp. 88-89) concluded that strüverite was an independent mineral and was related to ilmenorutile. He considered strüverite from Italy to be a solid solution of the tapiolite molecule with the rutile molecule. He also believed that ilmenorutiles from Norway and Russia were solid solutions of the mossite molecule with rutile. His conclusions and formulae, however, were based on chemical analyses and thus do not take into account the possibility of mineral intergrowths.

Schaller (21, p. 38) stated that ilmenorutile was a distinct mineral subspecies of rutile in which Fe, Cb and Ta were present in isomorphous mixtures. This conclusion also was based on chemical analyses, and likewise does not allow for the presence of fine mineral intergrowths.

A more recent article in a bulletin of the *Imperial Institute of London* (15) described ilmenorutile from the Tonkolili District of Sierra Leone as a distinct columbium-bearing variety of rutile. The optical properties of the specimen in transmitted light are discussed, but the sample was not apparently examined in reflected light or by x-ray diffraction methods. All our specimens from this area contain the intergrowth of columbite and rutile.

X-ray information concerning the mineral ilmenorutile is scarce. Wyckoff (24, p. 17) indicated that columbium is present in ilmenorutile in solid solution and is disordered. Ando and Nitta published the results (1) of some x-ray studies of Japanese ilmenorutile but their article was not available to the writer. Hence the results of their investigation are not considered here.

The nature of the intergrowth in the samples studied is of interest. In the two crystalline specimens of ilmenorutile the following features were observed.

(1). Rutile is invariably the more abundant component of the intergrowth and constitutes the host mineral. For this reason the intergrowth may be described as columbite in rutile.

(2). Grains and blebs of columbite are of irregular shape and have various orientations, but are rather evenly distributed throughout the host crystals of rutile.

In the samples of concentrates, the following features have been noted.

(1). Rutile is invariably the more abundant component of the intergrowth and constitutes the host mineral.

(2). The orientation of intergrown columbite grains varies in a single grain of rutile, so far as can be determined.

(3). The size of the intergrown columbite grains varies in a single grain of the host from tiny to large (relative to the size of the host grain).

(4). The shape of intergrown columbite grains is extremely irregular.

(5). The distribution of columbite intergrowths varies within a single rutile grain. Portions of one rutile grain may contain more columbite than other portions.

(6). Columbite intergrowths generally occur in the more cracked and pitted grains of rutile. Perfect unpitted and unfractured grains of rutile tend to be homogeneous and lack columbite intergrowths. This is a generalization and exceptions were encountered. Whether the imperfections are earlier or later than the intergrowth is not known.

The origin of the intergrowth is yet another problem. No information is available to the writer concerning the geologic occurrence of the ilmenorutile studied from M'ba, French Cameroons. The specimens from the Tonkolili District of Sierra Leone are reported to occur in alluvial stream gravels (15). The following information concerning the possible derivation of the ilmenorutile has been summarized from additional references (4; 11; 12).

The streams in which the alluvium is found drain an area of crystalline rocks, including various granites and a belt of schists and migmatites. Ilmenorutile is thought to occur in sugary quartz veins, in different kinds of medium- and coarse-grained granite, near migmatitic fringes of the schist belt. It may also occur in pegmatites. Unfortunately this information is not of direct aid in understanding the origin of the intergrowth.

The laboratory findings are, likewise, inconclusive. The irregular physical characteristics of the intergrowth are unlike those of many other intergrowths of unmixed origin. If unmixing is the answer, then we would expect to find some content of columbium still in solid solution in rutile from grains showing the intergrowth. Present *x*-ray experiments do not indicate that this is the case, but more detailed *x*-ray studies are essential. Thus the observations to date do not seem to support an unmixing origin but it may be argued that they do not exclude it entirely.

Other possible explanations would be that the intergrowth is of replacement origin, or that it is the result of simultaneous (eutectic) crystallization. Observation (1) above would satisfy either of these possibilities. Replacement of rutile by minor amounts of columbite could result in this feature, but so could eutectic crystallization. The fact that some grains of rutile contain the intergrowth, whereas others are homogeneous could also be due either to replacement or to eutectic crystallization where rutile was the initial pure phase to crystallize. Observation (6) above would support a replacement origin only if we could be certain that it is a causative feature.

Conclusions

(a) In the specimens studied, ilmenorutile is not an independent mineral but is an intergrowth of two distinct mineral phases, namely columbite and rutile.

(b) The origin of the observed intergrowth is not known. Unmixing seems unlikely to be the answer but is not excluded. Either replacement or eutectic crystallization could also account for the observed features.

(c) Further work is needed to determine whether ilmenorutile occurs as an independent mineral in nature, and to determine the origin of the intergrowth.

OPTICAL PROPERTIES OF MINERALS ASSOCIATED WITH COLUMBIUM-TANTALUM MINERALS

General discussion

During the course of the optical investigations of columbium-tantalum minerals it became apparent that the distinction of these minerals from certain of their common associates was a problem. It was decided to investigate the optic properties of these minerals, and especially their rotation properties, in the hope that the problem could be simplified. The minerals investigated, in addition to columbite, tantalite and tapiolite were hematite, ilmenite, rutile, cassiterite, euxenite, monazite, zircon and ferberite.

Some of the optical properties of these minerals, including their apparent angles of rotation in air, dispersions and relative reflectivities have been determined and are summarized in Table 4. Since most of these minerals are known to vary in composition, the data given apply only to the specific material studied. Additional data for other compositional members may later be found to modify or extend the range of properties given. Nevertheless, it was found that the properties so far measured and recorded are extremely valuable in the distinction and identification of the various oxides. They permit simple and rapid identification in polished surfaces, and are of special value where work with mixtures of the minerals is involved.

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