

## BISMUTOTALITE FROM BRAZIL\*

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### ABSTRACT

Bismutotalite from Acari, Brazil, has been found in light brown, rounded stream pebbles. Cleavage {101}, {010}.  $G=8.84$  (meas.),  $8.98$  (cal.). Optically biaxial (+);  $n_X=2.388$ ,  $n_Y=2.403$ ,  $n_Z=2.428$  for Li light.  $2V=80^\circ$ ,  $r < v$ .  $X=a$ ,  $Y=b$ . Analysis gives:  $\text{Bi}_2\text{O}_3$  48.98,  $\text{Sb}_2\text{O}_3$  1.76,  $\text{Ta}_2\text{O}_5$  46.45,  $\text{Nb}_2\text{O}_5$  1.26,  $\text{Fe}_2\text{O}_3$  0.94,  $\text{SiO}_2$  0.16,  $\text{ZnO}$  0.38,  $\text{MnO}$  0.11, Ign. loss 0.62. Total 100.66. Formula:  $4[(\text{Bi,Sb})(\text{Ta,Nb})\text{O}_4]$ . The unit cell dimensions:  $a_0=4.97 \text{ \AA}$ ,  $b_0=11.80$ ,  $c_0=5.66$ ;  $a_0:b_0:c_0=0.4219:1:0.4801$ . Space group: *Pcmm* or *Pcn*.

### INTRODUCTION

Bismutotalite,  $\text{Bi}(\text{Ta,Nb})\text{O}_4$ , was described by Wayland and Spencer (1929) from Gamba Hill, southwest Uganda, Africa. Here it occurred in a pegmatite with black tourmaline and small amounts of cassiterite. To the present time this has remained its only locality.

In 1954 Mr. George W. Tower sent a mineral specimen to Harvard with a partial chemical analysis which identified it as bismutotalite. The specimen was a rounded stream pebble two inches in diameter, a fragment from a single crystal. It is a light brown color, and except for several small veins of iron oxide through it, is extremely homogeneous. Several additional rounded pebbles have recently been received but most of the data reported here were obtained on the single original specimen. This material came from Acari in northeastern Brazil in the Campina Grande area. Here it occurs as a placer mineral over a rather wide area, for rounded pebbles of it have been found in the beds of several streams many kilometers apart. Prospecting failed to yield the mineral in commercial quantity, although at one place 50 kilograms were found. It is believed by Mr. Gert Schroeder, in charge of the prospecting, that the bismutotalite "... was already a placer at the end of the first of the two erosion periods of the Brazilian shield as described by Johnson (1945). The second erosion destroyed this part of the old peneplane and dispersed the content to placers over a much larger area, where we find it to-day."†

### PHYSICAL PROPERTIES

The Brazilian bismutotalite bears little resemblance to the original material from Uganda, and familiarity with one would not aid greatly the determination by inspection of the other. A comparison of the physical properties of bismutotalite from the two localities is given in Table 1.

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† Private communication.

Bismutotantalite is orthorhombic. Wayland and Spencer (1929) described and figured large, well-formed crystals from Uganda having three directions of parting. No crystals of Brazilian bismutotantalite are available but the pebbles when broken show three well-developed cleavage directions. One perfect cleavage is at right angles to the other two. These lesser but distinct cleavages make an angle of  $82^{\circ}50'$  with each other as measured on the reflecting goniometer. This compares favorably with the angle of  $82^{\circ}42'$  between two "parting" directions as given by Wayland and Spencer. Orienting bismutotantalite to conform with Palache's (1940) orientation of stibiotantalite, this angle identifies the form as  $\{101\}$ . The perfect cleavage is, therefore,  $\{010\}$ .

Wayland and Spencer (1929) give three values for specific gravity of bismutotantalite as obtained on three separate specimens. Two of these

TABLE 1. PHYSICAL PROPERTIES OF BISMUTOTANTALITE

	Brazil	Uganda
Morphology	stream pebbles	large prismatic crystals
Color	light brown	black
Cleavage	$\{010\}$ , $\{101\}$	parting
Specific gravity	8.84	8.38
Hardness	5	5
Streak	yellow-brown	black
Luster	adamantine	sub-metallic

on analyzed material are: 8.06 and 8.44. They state that the higher value was obtained on "somewhat fresher looking material." The third determination, yielding a value of 8.15, was made by Max H. Hey at the British Museum. During the present study, determination of the specific gravity of the Uganda material using the Berman balance gave a value of 8.38. Specific gravity determinations were made on three stream pebbles of bismutotantalite from Brazil, yielding the values—8.72, 8.84, and 8.89. The value on the analyzed specimen was 8.84.

The Uganda bismutotantalite is black and quite opaque in thin section. It is partially metamict. X-ray powder photographs, taken before and after heating to  $800^{\circ}$  C. in both air and in vacuum, show that heating produces a marked increase in crystallinity. Fragments heated in air turned a light yellow with a waxy luster and became translucent. When heated in vacuum the mineral remained black and opaque. The Uganda bismutotantalite is slightly radioactive and an analysis by the U. S. Geological Survey gives 0.061 per cent  $U_3O_8$ .\* Although the amount is

\* Since the valence state was unknown, the uranium was reported by the analyst as 0.052 per cent U and here calculated as  $U_3O_8$ .

small, this uranium undoubtedly accounts for the metamict state. If the uranium is present as  $U^{+4}$ , it may also account for the opacity of the mineral since it is a powerful pigmenting agent. Moreover, the color change from black to yellow on heating is the type one would expect on a change from  $U^{+4}$  to  $U^{+6}$ .

A differential thermal analysis of the Uganda bismutotantalite showed that a marked exothermic reaction takes place at  $413^{\circ}$  C. A similar run on the Brazilian material showed no thermal reaction. This apparently is the temperature at which recrystallization and possibly oxidation takes place. When heated at  $350^{\circ}$  C. for thirty minutes, there was no change in color nor in the  $x$ -ray diffraction pattern. However, when heated at  $420^{\circ}$  C. for thirty minutes, the mineral turned yellow and showed the same increase in crystallinity as when heated to  $800^{\circ}$ . Kerr and Holland (1951) point out that a differential thermal analysis of david-

TABLE 2. OPTICAL PROPERTIES OF BISMUTOTANTALITE

Brazil		Uganda	
	$n_{Li}$		$n_{Li}$
X= <i>a</i>	2.388	X= <i>a</i>	2.395
Y= <i>b</i>	2.403	Y= <i>b</i>	2.408
Z= <i>c</i>	2.428	Z= <i>c</i>	2.426
Opt.(+)	2V=80°	Opt.(+)	2V=85°
	$r < v$		$r < v$
	G=8.84		G=8.51

ite gives an exothermic peak and indicate that this may be characteristic of metamict minerals.

When heated to  $800^{\circ}$  C., the specific gravity of the Uganda bismutotantalite increases from 8.37 to 8.51. This increase in specific gravity on heating is characteristic of many metamict minerals as pointed out by Pabst (1952).

Penfield and Ford (1906) describe strong pyroelectric effects in stibiotantalite with [010] the polar axis in the orientation of Palache (1940). Because of the close relationship between this mineral and bismutotantalite, the same effects might well be expected in bismutotantalite. However, no pyroelectric or piezoelectric effects were observed.

The optical properties of bismutotantalite are summarized in Table 2. The measurements were made in sulfur-selenium melts. Those for the Uganda material are for the mineral after it was heated in air. It is opaque before heating.

## CHEMICAL COMPOSITION

In Table 3 is given the chemical analysis of bismutotantalite from Brazil with the analysis from Wayland and Spencer (1929) of the "fresher looking material" from Uganda.

TABLE 3. CHEMICAL ANALYSES—BISMUTOTANTALITE

	Brazil		Uganda	
	1	1a	2	2a
Bi <sub>2</sub> O <sub>3</sub>	48.98	49.51	52.26	52.70
Sb <sub>2</sub> O <sub>3</sub>	1.76	1.78	0.04	.04
Ta <sub>2</sub> O <sub>5</sub>	46.45	46.95	40.12	40.46
Nb <sub>2</sub> O <sub>5</sub>	1.26	1.27	6.63	6.68
Fe <sub>2</sub> O <sub>3</sub>	0.94		0.11	
SiO <sub>2</sub>	0.16			
ZnO	0.38	0.38		
MnO	0.11	0.11	0.12	0.12
Ig. loss	0.62		0.33	
Total	100.66	100.00	99.61	100.00

1. Analysis by J. Ito, 1955.

1a. Analysis #1 recalculated to 100 per cent.

2. Analysis by W. O. R. Wynn in Wayland and Spencer (1929).

2a. Analysis #2 recalculated to 100 per cent.

It will be noted from the chemical analyses that the Uganda bismutotantalite is lower in tantalum and higher in niobium than the Brazilian material. One would, therefore, expect it to have the lower density as is borne out in the specific gravity determination. However, the specific gravity of both minerals falls considerably below the calculated values. From Uganda: measured 8.51 (after heating), calculated 8.73; from Brazil: measured 8.84, calculated 8.98.

## X-RAY STUDY

Rotation and Weissenberg photographs were taken of cleavage fragments of Brazilian bismutotantalite using copper radiation and nickel filter. Two orientations were used with the axes of rotation [010] and [100]. The dimensions of the unit cell determined from the Weissenberg photographs are given in Table 4. Inasmuch as bismutotantalite and stibiotantalite appear to be isostructural, the dimensions are given in the established orientation of stibiotantalite.

The unit cell dimensions of the Uganda bismutotantalite given in Table 4 were determined on the material before it was heated. After heating, the

cell dimensions are the same as for the Brazilian bismutotantalite. The unit cell volumes are: before heating, 338.3 Å<sup>3</sup>; after heating, 331.8. This is a decrease in cell volume of 2.1 per cent. The measured specific gravities show an increase (8.37–8.51) of 1.5 per cent.

TABLE 4. BISMUTOTANTALITE AND STIBIOTANTALITE UNIT CELL DIMENSIONS AND AXIAL RATIOS

	$a_0$	$b_0$	$c_0$	$a_0:b_0:c_0$
Bismutotantalite				
Brazil	4.97 Å	11.80	5.66	0.4219:1:0.4801
Uganda	5.00 Å	11.89	5.69	0.4205:1:0.4785
Stibiotantalite*				
Mesa Grande	4.92 Å	11.78	5.54	0.4173:1:0.4705

\* Cell dimensions from Dählström (1938).

From morphological crystal measurements Wayland and Spencer (1929) give the axial ratios of bismutotantalite from Uganda in the accepted orientation as:  $a:b:c=0.4266:1:0.4848$ .

Using the volume of the unit cell,  $V=331.8 \text{ Å}^3$ , and the measured specific gravity, 8.84, the molecular weight of the cell contents is calculated as  $M=1795$ . There are thus four formula units per cell and the structural formula is:  $4[(\text{Bi,Sb})(\text{Ta,Nb})\text{O}_4]$ .

TABLE 5. X-RAY POWDER SPACING DATA AND WITH POSSIBLE INDICES FOR BISMUTOTANTALITE

Copper radiation, nickel filter, in Angstrom units

$I$	$d(\text{meas.})$	$d(\text{cal.})$	$hkl$	$I$	$d(\text{meas.})$	$d(\text{cal.})$	$hkl$
1	4.575	4.579	110	2	1.861	1.865	202
1	3.723	3.732	101	2	1.774	1.779	222
3	3.555	3.558	111	3	1.735	1.739	113
10	3.148	3.143	121	1	1.681	1.687	123
6	2.945	2.945	040	2	1.604	1.590	301
2	2.819	2.828	002	1	1.574	1.571	242
2	2.743	2.747	012	2	1.537	1.525	330
2	2.700	2.705	131	2	1.473	1.475	080
2	2.543	2.548	022	1	1.415	1.414	004
1	2.481	2.485	200	1	1.370	1.373	024
$\frac{1}{2}$	2.308	2.289	220	1	1.350	1.343	332
1	2.080	2.083	132	1	1.308	1.323	124
1	1.987	1.968	231	3	1.270	1.274	044
2	1.897	1.887	142	2	1.234	1.247	400

The space group extinctions from the Weissenberg photographs are the same as those given by Dählström for stibiotantalite and lead to the space group *Pcmm*. This is on the assumption that the crystal class is rhombic dipyramidal as indicated by the absence of piezoelectricity. If, however, it is pyramidal, as its close similarity to stibiotantalite would indicate, the space group is *Pcn*.

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