

## HYDROTUNGSTITE, A NEW MINERAL FROM ORURO, BOLIVIA

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### ABSTRACT

A survey of the literature on hydrous tungstic oxide reveals that only one form, tungstite ( $\text{H}_2\text{WO}_4$ ) has been established as a naturally-occurring mineral. A second hydrous oxide has been encountered in a study of material from Calacalani, Department of Oruro, Bolivia. It has the composition  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  and has been named *hydrotungstite* to show its relationship to tungstite. It occurs in minute green tabular crystals as an alteration product of ferberite. The physical and optical properties of hydrotungstite are described and chemical and x-ray data are given. Artificial  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  has been prepared which corresponds to the natural mineral in structural and optical constants. Dehydration data indicate that the second molecule of water is held in a different manner from the first. It is believed, as a result, that the formula of tungstite may be best expressed as  $\text{H}_2\text{WO}_4$  and that of hydrotungstite as  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ .

### PREVIOUS WORK

The first mention of the occurrence of tungstic ocher in nature was made by Silliman (1822). He recorded the discovery of a "massive yellow oxid of tungsten" at Lane's Mine, near Huntington, Connecticut. This material was assumed to have the composition  $\text{WO}_3$  and was so described in the literature for a number of years. Following Silliman's discovery, the mineral was noted by others in various tungsten deposits. By 1858, such names as wolframochre (Hausmann—1847), scheelsaure (Naumann—1852) and wolframine (Greg and Lettsom—1858) had been applied to what was apparently the same material. Dana (1868) first employed the name "tungstite" for anhydrous  $\text{WO}_3$  and suggested that this name be used to replace the other less desirable terms. Up to this time, no record had been made of a water determination on the mineral.

Carnot (1874) described specimens of tungsten ocher from Meymac, France, and applied the name "meymacite" to the mineral. Carnot's samples were mixtures of limonite, scheelite and hydrous tungsten oxide. The analyses of meymacite varied in water content from 6.85% to 12.93%, and Carnot concluded that the material was a mixture of tungstite (anhydrous  $\text{WO}_3$ ) and a hydrous tungstic oxide. He noted the impure character of the samples, as well as the wide variation in water content and after subtracting for the impurities, suggested that the formula of "meymacite" was probably " $2\text{WO}_3 \cdot 5\text{HO}$  or  $\text{WO}_3 \cdot 2\text{HO}$ ."

After Carnot's description of "meymacite," the name was employed for some time for any water-bearing oxide of tungsten. Hoffman (1896), for example, described "meymacite" from Beauce County, Quebec, which contained 7.2%  $\text{H}_2\text{O}$ .

Lovisato (1907) reported chemical analyses of hydrous tungstic oxide from Sardinia, and considered the material a mixture of tungstite and "meymacite." He appears to have recognized that the supposedly anhydrous tungstite of Silliman was hydrous but failed to ascertain the ratio of  $\text{WO}_3$  to  $\text{H}_2\text{O}$  in either tungstite or "meymacite" because of the impure nature of his samples.

Walker (1908) indicated the probable identity of Carnot's "meymacite" and Silliman's earlier tungstite. He obtained a relatively pure hydrous tungstic oxide from Salmo, British Columbia, which carried 7.20%  $\text{H}_2\text{O}$ . This water content corresponds to a theoretical ratio  $\text{WO}_3:\text{H}_2\text{O}$  of 1:1. Walker believed that the Salmo material corresponded to the mineral listed by Dana as tungstite and suggested that this name be applied to the monohydrate, and that Carnot's name "meymacite" should be abandoned. Walker's conclusions appear to have been generally accepted. Hess (1917), for example, says "Tungstite (hydrous tungsten oxide,  $\text{WO}_3 \cdot \text{H}_2\text{O}$ ), or tungsten ocher, was originally described as free from water, and was later named meymacite by Carnot, a French chemist, who thought he had discovered a new mineral because it contained water, but Walker has shown that water is a normal constituent of tungstite." Later optical determinations by Larsen (1921) were made on type material from Salmo.

Ahlfeld (1932) reviewed the tungsten deposits of Bolivia and in the course of his discussion of the Oruro district, mentioned the occurrence of two forms of tungstite which differed in their water content. Impure samples prevented the establishment of the chemical composition of each.

While some of this earlier work may have suggested that two water-bearing tungstic oxides occur in nature, the only one which has been satisfactorily separated, analyzed and described is the monohydrate, tungstite, established by Walker.

Three other hydrous tungsten minerals have been described and should be mentioned here. Schaller (1911) described ferritungstite from Germania, Washington. On the basis of his chemical analyses he assigned the formula  $\text{WO}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  to this mineral. Scrivenor and Shenton (1927) described thorotungstite from the Federated Malay States and considered it to be related to tungstite, but to contain appreciable quantities of  $\text{ThO}_2$ ,  $\text{ZrO}_2$  and the rare earths. Schaller (1932), in studying cuprotungstite from Cave Creek, Arizona, found this mineral to be hydrous and assigned to it the formula  $\text{WO}_3 \cdot 2\text{CuO} \cdot \text{H}_2\text{O}$ . X-ray and optical studies of these three minerals show that they differ from the two simple hydrous tungstic oxides.

## ACKNOWLEDGMENTS

About twenty-four years ago, through the efforts of the late Professor A. J. Moses, a suite of tungsten specimens from Calacalani, Department of Oruro, Bolivia, was added to the Columbia University collection. Notes and memoranda in the departmental files indicate that Professor Moses had examined the material with care and had recognized the presence of two hydrous tungstic oxides. Unfortunately the study had not been completed at the time of his death. Recently other specimens from Calacalani have been secured, new determinations made and more positive data accumulated. While it has not been possible to include all of Professor Moses' observations we wish to acknowledge the assistance of data which, even after a long lapse of time, have been most helpful.

The writers also wish to take this opportunity to thank Dr. H. E. Merwin of the Geophysical Laboratory who kindly supplied high index melts with low melting points which were used in the determination of the indices of tungstite; and Dr. Roland B. Snow of the U. S. Steel Corporation, Research Laboratories, for his helpful suggestions on the preparation and use of the sulfur-phosphorus-methylene iodide liquids employed in determining the indices of hydrotungstite. We also wish to acknowledge the assistance of the Penrose Fund of the Geological Society of America for funds used to obtain chemical analyses. Dr. A. L. Parsons of the University of Toronto and the Royal Ontario Museum has kindly assisted by providing tungstite from Salmo, B. C., representing the late Professor T. L. Walker's original material. Dr. E. A. Lucas, Vice-President of the Molybdenum Corporation of America, has generously cooperated by furnishing artificial  $H_2WO_4$  together with an analysis.

## TUNGSTITE

The occurrence of tungstite at Calacalani, Bolivia, has been referred to by Hess (1921) and Ahlfeld (1932). According to the latter the chief ore mineral is ferberite which occurs with pyrite and stibnite in a quartz-siderite gangue replacing schist. The tungstite is found in the oxidized zone of the deposit where it has formed as an alteration product along cleavages and fractures of the ferberite.

*Physical Properties*

Tungstite occurs as rounded aggregates which are light yellow, greenish-yellow or dark orange-yellow in color. These aggregates vary from one to three mm. in diameter and consist of radiating crystals which range in length from 5 to 75 microns and in width from 3 to 20 microns.

Earthy incrustations on ferberite and quartz are also common. Occasional isolated crystals may be seen, but these are too small for goniometric measurement.

The material is characterized by a resinous luster when fresh but becomes earthy upon further alteration. The hardness is between 1 and 2. The specific gravity was not determined with sufficient accuracy to justify recording, but is apparently somewhat greater than the value for hydrotungstite. The specific gravity given by Walker (1908) as corrected by subtracting the effect of impurities in the Salmo material is 5.517. Before the blowpipe the mineral gives the usual blue color of tungsten in the salt of phosphorus bead. Fused with sodium carbonate and dissolved in HCl the solution assumes a deep blue color upon the addition of zinc. Heated alone in forceps or on charcoal, tungstite slowly bleaches, then darkens and finally volatilizes without leaving a sublimate. In the closed tube it gives off abundant water. The mineral is virtually insoluble in acids but dissolves readily in warm  $\text{NH}_4\text{OH}$ .

#### *Optical Properties*

Under the microscope the small crystals appear to be simple orthorhombic prisms with angles of 82 and 98 degrees. They are terminated by the basal pinacoid {001}. Cleavage parallel to this direction is perfect and results in thin plates of rhombic outline.

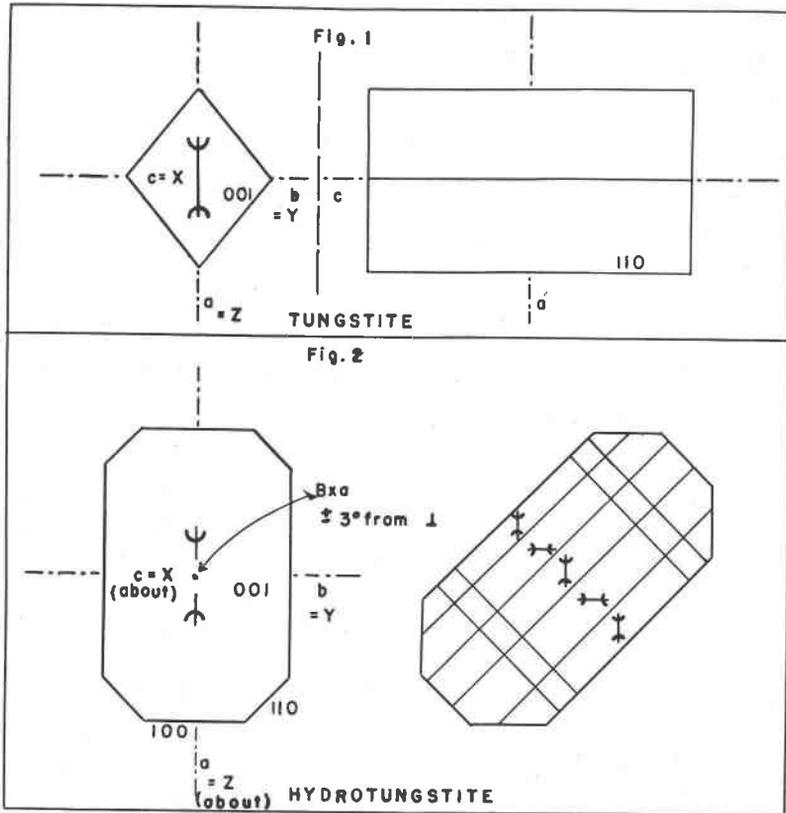
The indices of refraction as determined with sulfur-phosphorus-methylene iodide liquids are:  $\alpha=1.82$ , and  $\gamma=2.04$ , both  $\pm 0.02$ . These are somewhat lower than corresponding values listed by Larsen (1921) who gives  $\alpha=2.09$ ,  $\beta=2.24$  and  $\gamma=2.26$  for the Salmo tungstite. In this connection it should be noted that the indices of refraction of this material change as the water is driven off. Since tungstite begins to lose water at  $120^\circ$ , attempts to determine the indices with melts which become liquid only above this temperature may give erratic results.

The birefringence,  $n_\gamma - n_\alpha = .22$ , but this is difficult to check in fragment mounts due to the high body color of the mineral. A strong change in relief observed as the stage is rotated above a single nicol is confirmatory.

The absorption in the longitudinal sections is marked, changing from colorless along X to deep yellow along Y or Z. In the rhombic section the mineral is not noticeably pleochroic, but with a dichroscope a difference in color may be observed with the Z-direction darker than the Y-direction. Thus the absorption may be expressed  $Z > Y > X$ . This differs from that given by Larsen (1921) who records the absorption of the Salmo tungstite as  $X > Y > Z$ .

The extinction is parallel to the length in longitudinal sections and parallel to the diagonals in rhombic sections.

The trace of the optic plane on cleavage fragments is parallel to the long diagonal of the rhombic outline. The angle  $2V$  as measured on the universal stage is  $27^\circ$  and the acute bisectrix is X, thus the mineral is optically negative. The crystals are elongated parallel to X. Figure 1 shows the orientation of the crystals.



FIGS. 1 and 2. Orientation diagrams for tungstite and hydrotungstite.

### Chemical Data

Chemical analyses of the Calacalani tungstite, artificial  $H_2WO_4$  and the Salmo material are given in Table 1. The analyses of the natural minerals are expressed in terms of the mineral constituents in Table 2. Separate chemical analysis has shown that the ferberite from Calacalani

carries only one-half of one percent MnO and since the samples of the hydrous oxides which were submitted for analysis from this locality contained only small amounts of ferberite, the manganese content is disregarded in the calculations. In Table 3 the tungstite content of each analysis has been recast to 100% and is compared with the theoretical composition of pure  $\text{H}_2\text{WO}_4$ .

#### HYDROTUNGSTITE

##### *Physical Properties*

A second alteration product of ferberite from Calacalani is a green mineral to which the name hydrotungstite is assigned.

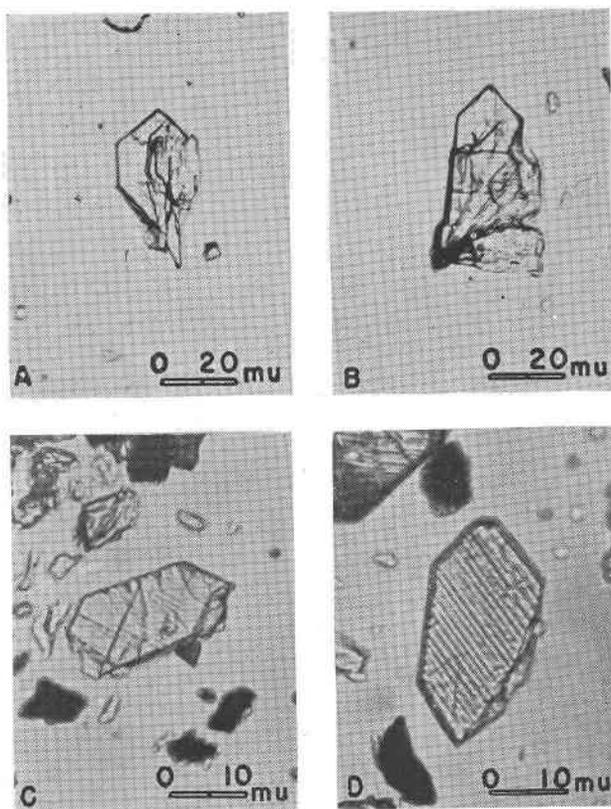


FIG. 3. Photomicrographs of hydrotungstite. Note twinning lamellae visible even under ordinary light. This is due to the great difference in relief of lamellae of opposite orientation. (A and B =  $\times 500$ ; C and D =  $\times 1000$ . Reproduced without reduction of the photomicrographs.)

It occurs as platy crystals which vary in maximum dimension from 5 to 75 microns. These crystals are usually intergrown and twinned and even under high magnification, simple crystals are rarely seen (Fig. 3). No crystals suitable for goniometric measurement were found.

The color when freshly broken is dark green but may become yellowish upon continued exposure to the air. The luster is vitreous, becoming dull upon exposure. Hydrotungstite has a hardness of about 2.

TABLE 1. CHEMICAL ANALYSES

	Tungstite			Hydrotungstite	
	(1)	(2)	(3)	(4)	(5)
WO <sub>3</sub>	91.30	86.20	91.03	80.31	85.49
H <sub>2</sub> O	7.46	7.72	8.75	12.52	14.39
SiO <sub>2</sub>	.96		.04	6.65	
Fe <sub>2</sub> O <sub>3</sub>	.18	4.14	.05	.08	
FeO	n.d.	1.21		n.d.	
CaO	—	.54		—	
MoO <sub>3</sub>	n.d.		.07	n.d.	
NH <sub>3</sub>	n.d.			n.d.	.01
Chlorides	n.d.		.02	n.d.	
Total	99.90	99.81	99.96	99.56	99.89

- (1) Tungstite, Calacalani, Bolivia. F. A. Gonyer, analyst.
- (2) Tungstite, Salmo, B. C. T. L. Walker (1908)
- (3) Artificial H<sub>2</sub>WO<sub>4</sub>. Sample and analysis kindly furnished by the Molybdenum Corp. of America.
- (4) Hydrotungstite, Calacalani, Bolivia. F. A. Gonyer, analyst.
- (5) Artificial H<sub>2</sub>WO<sub>4</sub> · H<sub>2</sub>O. A. M. Morely (1930).

The specific gravity as determined on a sample weighing about one-half gram utilizing the pycnometer is 4.60. The sample represented the residue from treatment with a high intensity magnet to remove ferberite and a bromoform separation to remove lighter gangue.

The blowpipe reactions are similar to those of tungstite. The added water is noticeable in the closed tube when compared directly with that of tungstite, but probably would not be distinguishable without direct comparison. In the forceps or on charcoal, the mineral decrepitates slightly, turns yellow, darkens and finally volatilizes. As with tungstite, the mineral is insoluble in ordinary acids but is readily dissolved by NH<sub>4</sub>OH.

TABLE 2. ANALYSES IN TERMS OF THE MINERAL CONSTITUENTS.

	(1) Tungstite Calacalani, Bolivia	(2) Tungstite* Salmo, B.C.	(4) Hydrotungstite Calacalani, Bolivia
Tungstite	98.26	87.11	—
Hydrotungstite	—	—	92.61
Ferberite	.68	5.09	.30
Quartz	.96	—	6.65
Scheelite	—	2.78	—
Limonite	—	4.83	—
	99.90	99.81	99.56

\* Recast with excess H<sub>2</sub>O in tungstite for comparison with other analyses.

### Optical Properties

Under the microscope, hydrotungstite is seen to occur as tiny green plate-like crystals which show polysynthetic twinning. The most prominent form is the basal pinacoid and fragment mounts are made up almost entirely of tiny crystals resting on a pinacoidal face. These basal plates are bounded by prisms {110} and the two pinacoids, {100} and {010}. In some of the mounts examined on the universal stage, low-angle domes were also seen but no measurements were possible.

The intersection of the vertical pinacoid faces makes an angle of 90 degrees. The optic plane was found to be parallel to the {010} plane. Figure 2 illustrates the orientation of hydrotungstite as determined from microscopic examination. Polysynthetic twinning is prominent parallel to the prism faces and forms a fine grid-like structure in many cases. In such instances the orientation of adjacent twin lamellae is reversed (Fig. 2).

The indices of refraction of hydrotungstite as determined according to the method of West (1936) with sulfur-phosphorus-methylene iodide liquids (Na-light) are:  $\alpha = 1.70$ ,  $\beta = 1.95$  and  $\gamma = 2.04$ , all  $\pm 0.02$ . The birefringence as calculated from the refractive indices is 0.34.

Imperfect cleavage parallel to {010} may be seen in some crystals. The extinction as measured against the basal plane on crystals tilted to have the plane appear as a line corresponding to the edge {001}  $\wedge$  {010} is three degrees. On this basis it seems likely that hydrotungstite is monoclinic.

Fragments mounted in balsam yield an absorption corresponding to that of tungstite; namely  $Z > Y > X$ , with  $Z = \text{dark green}$ ,  $Y = \text{yellow-}$

green (not markedly different from Z unless observed through a dichroscope), and X= colorless. Few fragments were noted which showed the X-direction since the platy character of the crystals caused this direction to lie perpendicular to the stage of the microscope.

TABLE 3. COMPOSITIONS OF TUNGSTITE AND HYDROTUNGSTITE.\*

<i>Tungstite</i>				
	Theoretical	Calacalani, Bolivia Analysis (1)	Salmo, B. C. † Analysis (2)	Artificial $H_2WO_4$ Analysis (3)
$WO_3$	92.80	92.41	91.93	91.23
$H_2O$	7.20	7.59	8.07	8.77
Ratio	1:1	1:1.059	1:1.134	1:1.239
$WO_3:H_2O$				
<i>Hydrotungstite</i>				
	Theoretical	Calacalani, Bolivia Analysis (4)	Artificial $H_2WO_4 \cdot H_2O$ Analysis (5)	
$WO_3$	86.57	86.48	85.59	
$H_2O$	13.43	13.52	14.41	
Ratio				
$WO_3:H_2O$	1:2	1:2.015	1:2.170	

\* All analyses recast to 100%.

† Recast with excess  $H_2O$  in tungstite for comparison with other analyses.

### *Chemical Data*

Analyses of hydrotungstite from Calacalani and artificial  $H_2WO_4 \cdot H_2O$  are shown in Table 1. The natural mineral is recomputed in terms of its mineral constituents in Table 2 and both analyses are recast to 100% in Table 3. The analyses agree quite well with the theoretical ratio  $WO_3:H_2O$  of 1:2.

### *Artificial $H_2WO_4 \cdot H_2O$*

Morely (1930) made a chemical and x-ray study of the various artificial tungstic acids. In the course of his work he produced artificial  $H_2WO_4 \cdot H_2O$ . Using Morely's method, the writers prepared a small quantity of the material for comparison with the natural mineral. Ten grams of ammonium tungstate  $(NH_4)_6W_7O_{24} \cdot 6H_2O$ , were dissolved in 225 cc. of distilled water. This solution was poured slowly into 250 cc. of

1.126 *N* HCl. The mixture was held at 20°C. and stirred constantly during this operation. A yellowish-white precipitate formed which was allowed to settle. This was carefully washed with distilled water. Decantation was continued for about 24 hours when the liquid suddenly assumed a silky sheen with a darker yellow color. The precipitate was then filtered and dried at 35°C.

Microscopic examination of the precipitate indicated that it was the same as that produced by Morely. Figure 4 illustrates the type of crystals produced. The crystals agree in their optical properties with those described under the natural mineral. Twinning was prominent but simple crystals were more common than in the natural material. An *x*-ray diffraction pattern of the artificial product is shown as Fig. 5F and corresponds to that of the Calacalani hydrotungstite.

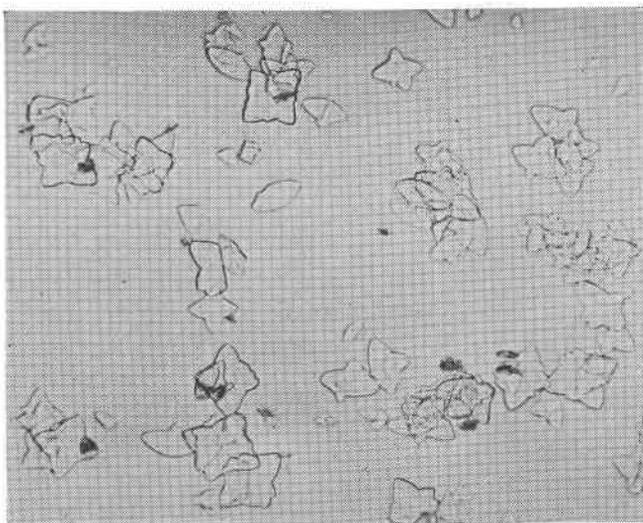


FIG. 4. Artificial  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ . ( $\times 1000$ ) Note cruciform twins. (Reproduced without reduction of photomicrograph.)

Buchholz (1940) also studied artificial  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  which he produced by adding HCl to a solution of silver tungstate. His description and illustrations indicate that he was dealing with the same compound.

#### X-RAY STUDIES

Samples of both tungstite and hydrotungstite have been selected with care for *x*-ray diffraction studies. Both have been checked for purity with the microscope and it is believed that the lines on the patterns secured may be attributed entirely to these minerals.

Although a few preliminary patterns were taken with molybdenum radiation, the data recorded are based entirely upon K-series reflections from an iron target. Crystals as yet found have been too small to yield results with any of the recognized single crystal methods. Powder cameras have been used entirely, both the Debye-Scherrer and the Phragmen-Bohlin types being employed. Samples have been kept in motion throughout exposure to avoid preferred orientation.

The technique of  $x$ -ray powder studies with the Phragmen-Bohlin camera has become well recognized in recent years as one of the more precise methods. The three camera system as employed covers the range of a single Debye-Scherrer photograph, allowing a determination of the interplanar spacings with greater certainty.

Comparative photographs of tungstite and hydrotungstite for the three different Phragmen-Bohlin cameras are shown in Fig. 6. Since the pictures compared in each case were taken in the same camera the dimensions of the exposed areas of the films for two cameras of corresponding position are substantially the same. With this in mind the pronounced difference between the patterns of tungstite and hydrotungstite in the inner, middle and outer cameras is convincing evidence of the difference in crystallization of the two minerals.

Computations of approximate  $\sin^2 \theta$  values and corresponding interplanar spacings in Angstrom Units are shown in Table 4. Although in the patterns upon which the table is based alpha-1, alpha-2 and beta lines of the K-series of iron are represented, only the alpha-1 lines of the more intense reflections have been recorded. The intensities of the lines have been compared approximately and those with an intensity less than one on the arbitrary scale chosen have been omitted from final computation.

The Debye-Scherrer photographs have been used for more general comparison. Here again the patterns of tungstite and hydrotungstite yield numerous lines, the two differing widely in distribution. In addition to the comparison of tungstite and hydrotungstite the Debye-Scherrer patterns have been used for the comparison of tungstite from different sources. In this connection four tungstite patterns secured from different sources are shown in *A*, *B*, *C*, and *D* of Fig. 5. Here the pattern of tungstite from Calacalani, Bolivia, may be seen to agree with tungstite from Salmo, B. C., and also artificial  $H_2WO_4$ . At the same time a sample of hydrotungstite from Calacalani from which one molecule of water has been removed by heating may be observed to yield the tungstite pattern.

The last two patterns of Fig. 5 (*E* and *F*) represent hydrotungstite. One is hydrotungstite from Calacalani, Bolivia. The other is artificial  $H_2WO_4 \cdot H_2O$ .

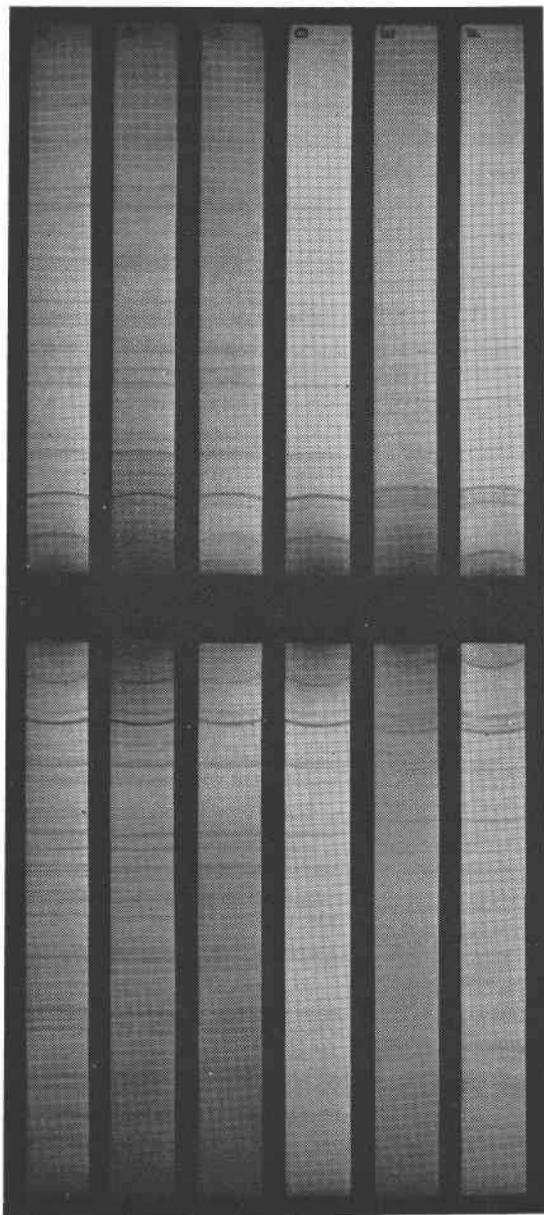


FIG. 5. X-ray diffraction patterns of tungstite and hydrotungstite.

A. Tungstite, Calacalani, Bolivia

B. Tungstite, Salmó, B.C.

C. Artificial  $H_2WO_4$

D. Hydrotungstite, Calacalani, Bolivia, converted to tungstite by heating.

E. Hydrotungstite, Calacalani, Bolivia

F. Artificial  $H_2WO_4 \cdot H_2O$ .

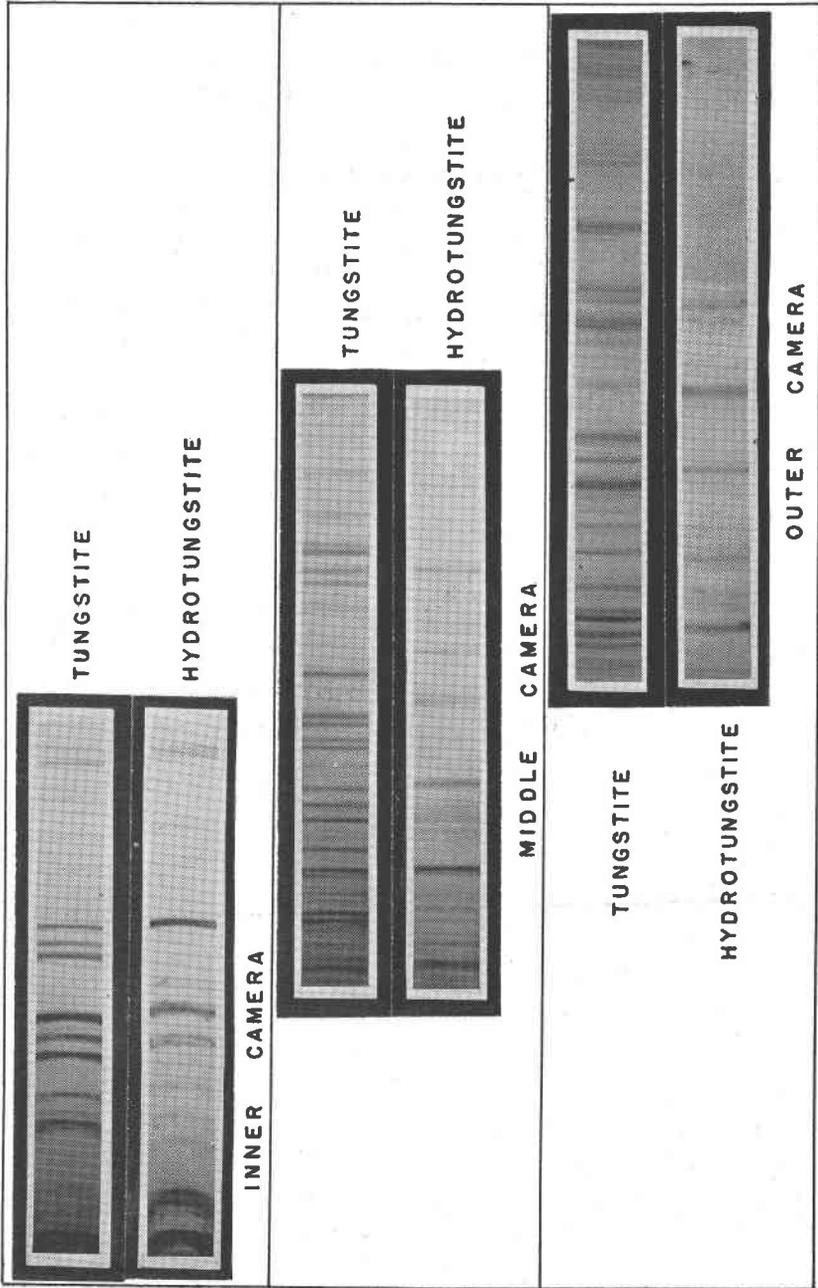


FIG. 6. Phragmen-Bohlin camera photographs of tungstite and hydrotungstite.

TABLE 4  
X-RAY DIFFRACTION DATA FOR THE MORE INTENSE LINES OF  
BOHLIN-PRAGMEN CAMERA PHOTOGRAPHS

Tungstite					Hydrotungstite				
Camera	Arc in mm.	Est. Intensity	Sin <sup>2</sup> $\theta$	$d$ in AU.	Camera	Arc in mm.	Est. Intensity	Sin <sup>2</sup> $\theta$	$d$ in AU.
Inner	2.8	10	.076796	3.49	Inner	3.6	10	.077814	3.46
	10.6	2	.089116	3.24		8.6	5	.085828	3.30
	20.9	3	.106962	2.95		10.45	5	.088886	3.24
	21.6	6	.108227	2.94					
	26.65	4	.117590	2.82					
	33.2	9	.130181	2.68					
	36.2	6	.136063	2.62					
	39.5	9	.142737	2.56		41.2	4	.146031	2.53
	49.55	4	.163953	2.39		42.2	1	.148093	2.51
	51.6	2	.168294	2.35					
	54.45	3	.174705	2.31		55.45	8	.177056	2.30
	69.3	1	.208617	2.12					
	75.7	1	.223983	2.04*					
	81.5	2	.236046	1.99*		84.0	2	.244008	1.96*
	83.8	1	.243981	1.96*					
	Middle	0.75	2	.220993		2.06*	Middle	4.35	5
3.10		5	.240009	1.97*					
4.30		3	.245150	1.95*					
6.95		2	.256721	1.907					
9.35		2	.267318	1.868					
10.90		6	.274246	1.845					
12.22		5	.280182	1.825					
15.27		2	.294045	1.782					
18.20		3	.307427	1.742					
19.30		6	.312656	1.728	20.0	6		.315726	1.719
22.7		4	.328452	1.686					
27.6		6	.350967	1.631					
30.1		5	.363978	1.601					
32.72		3	.376696	1.574	34.25	3		.383822	1.559
39.5		4	.409968	1.509					
40.8		3	.416410	1.497					
43.3	3	.428815	1.475	48.20	1	.452770	1.436		
51.6	3	.470301	1.409	56.40	1	.493823	1.375		
Outer	2.10	2	.522303	1.337	Outer	8.45	3	.559832	1.291
	3.30	1	.529385	1.328					
	5.75	4	.543980	1.310					
	7.40	5	.553744	1.298					
	10.20	6	.570153	1.2794					
	11.35	3	.576903	1.2778					
	15.35	2	.600434	1.2467					
	21.35	3	.635099	1.2122		20.10	1	.627657	1.2194
	25.70	2	.659811	1.1893					
	30.55	1	.686857	1.1656					
	31.90	6	.694278	1.1594					
	36.70	2	.719882	1.1386		34.85	1	.709880	1.1465
	40.10	2	.738212	1.1244					
	59.10	4	.830648	1.0600		47.90	3	.777356	1.0957
	61.15	1	.839692	1.0542					
	64.80	2	.855301	1.0446		62.30	1	.844050	1.0515
	74.80	3	.894519	1.0214					
	86.00	2	.931820	1.0007					
	97.25	1	.961583	0.9852					
101.30	2	.962272	0.9810						

\* Lines duplicated in adjacent portions of different cameras.

## RELATION OF TUNGSTITE AND HYDROTUNGSTITE

It might be well at this point to indicate the reasons for considering the structure of tungstite and hydrotungstite to be best expressed by the formulae  $\text{H}_2\text{WO}_4$  and  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ , respectively.

In his attempts to distinguish the two alteration products in the Calacalani material, Professor Moses made a study of their temperatures of dehydration. He determined the loss in weight for each mineral at intervals of  $10^\circ$  from  $50^\circ$  to  $250^\circ\text{C}$ . with a final determination at  $310^\circ$ , above which point volatilization occurred. These observations have been plotted in the form of two sets of curves which are reproduced as Figs. 7 and 8. Figure 7 shows the curves for loss of water from  $50^\circ\text{C}$ . The total water expelled from the tungstite is slightly above that required by the formula. This was probably adsorbed water and accounts for the small amount of water lost by that mineral below  $120^\circ$ . If the curve for hydrotungstite is examined it will be seen that almost exactly one-half of the water (one molecule) lost is driven off below  $120^\circ$  while above that temperature the curve resembles that of tungstite.

To further check this point, the loss of water of the two minerals above  $120^\circ$  was recalculated to 100% and is shown in Fig. 8. Although the two curves do not coincide, their similarity suggests that the water lost above that temperature is held in the same manner in both minerals. While further study of the dehydration behavior of the two minerals might show this relation more clearly, the data given by Professor Moses are sufficient for purposes of comparison.

This would indicate that the two molecules of water of hydrotungstite are held in different ways. One is loosely held and is driven off at a temperature below  $100^\circ$  while the other is held in the same manner as the single molecule of water in tungstite and is not expelled until the temperature is raised above  $120^\circ$ . On the basis of this evidence the writers would consider the structures as best expressed by  $\text{H}_2\text{WO}_4$  and  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ .

Further support of this conclusion is furnished by Morely (1930) who carried on similar experiments with the artificial material. He gives no data on the method or temperatures employed in his study but he states: "The evidence therefore clearly points to the formula  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$  for tungstic acid A." (p. 1998); on the basis of his chemical studies described earlier in his paper he concludes: "The results show that two definite compounds exist of composition  $\text{H}_2\text{WO}_4$  and  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ , other tungstic acids being mixtures containing several constituents" (p. 1988).

To further check the validity of this conclusion, a sample of hydrotungstite was held at  $100^\circ\text{C}$ . for nine days. At the end of this period an

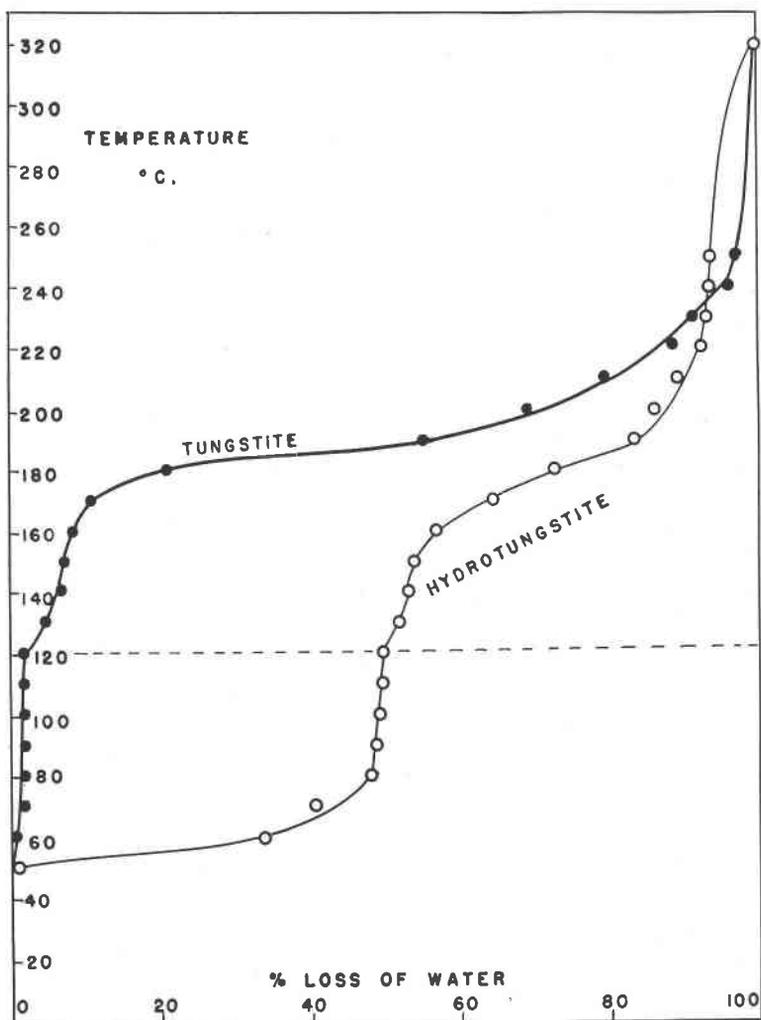


Fig. 7. Curves showing loss of water by tungstite and hydrotungstite in per cent from 50°C.

$\alpha$ -ray pattern was run as shown in Fig. 5D. Careful comparison shows this pattern to agree with patterns of tungstite. Thus the pattern of the heated material indicates that after the loss of the loosely-held molecule of water, the structure has changed from that of hydrotungstite to that of tungstite.

It is likely that the hydrotungstite of the Calacaluni deposit has formed as the initial alteration product of the ferberite. The tungstite

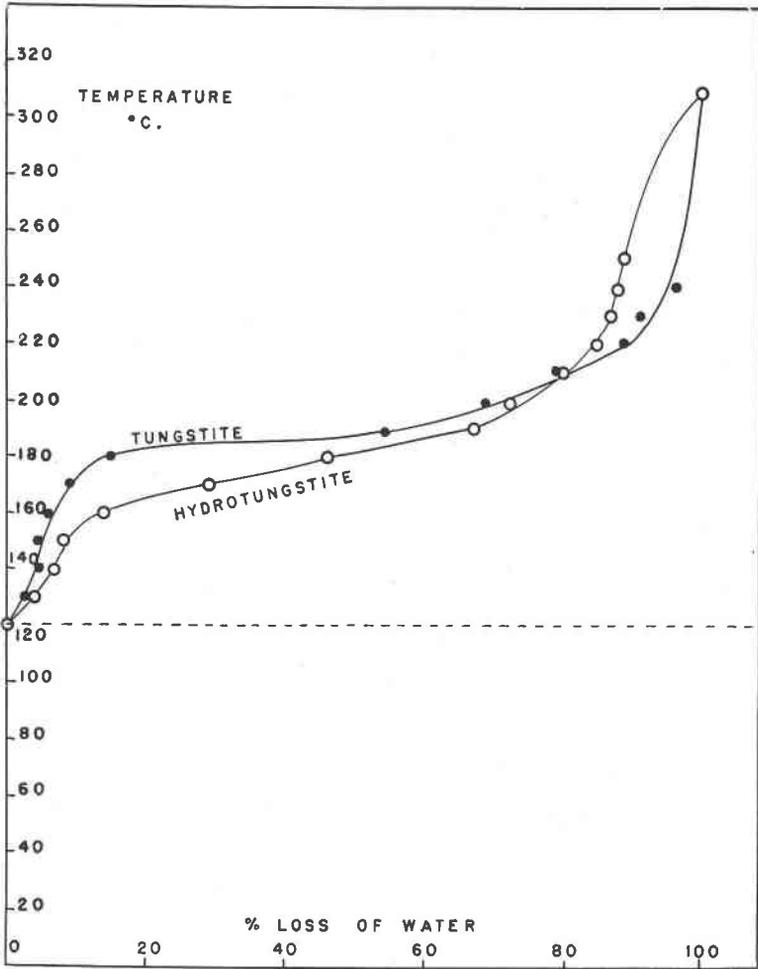


Fig. 8. Curves showing loss of water by tungstite and hydrotungstite in per cent from 120°C.

appears to be later and in many cases seems to have formed from the hydrotungstite. This has been observed on some of the specimens stored in a warm dry room for several years. These have an earthy surface coating of pulverent greenish-yellow tungstite while on breaking the specimen to expose a fresh surface, lustrous green hydrotungstite is found. Whenever tungstite and hydrotungstite are found together in these specimens, the tungstite invariably forms a coating on the hydrotungstite. It may also be observed that the ferberite of those specimens which contain hydrotungstite alone is less altered. Nearly all clusters of hydrotungstite

contain cores of unaltered ferberite, while larger masses of tungstite are often found to be completely free from ferberite.

From the above evidence it is concluded that hydrotungstite is an intermediate mineral of a more hydrous form which may represent a stage in the formation of tungstite. Because of the chemical relationship of the two minerals it seems appropriate to apply the name hydrotungstite to this new mineral.

## SUMMARY

Since the major problem involved in this study has been the distinction between the two oxides, it is felt that a tabulated comparison of the

TABLE 5. COMPARISON OF PROPERTIES OF TUNGSTITE AND HYDROTUNGSTITE

Property	Tungstite	Hydrotungstite
1. Composition	$H_2WO_4$	$H_2WO_4 \cdot H_2O$
2. Form	Fine rounded aggregates of acicular crystals; earthy masses.	Minute reticulated intergrowths of platy crystals.
3. Color	Yellow; greenish-yellow, yellowish-orange.	Dark green to yellowish-green.
4. Luster	Resinous to earthy.	Vitreous to dull.
5. Sp. gravity	5.517	4.60
6. Hardness	1-2	2
7. Closed tube	Yields water and bleaches.	Yields abundant water, turns yellow, then bleaches.
8. On charcoal	Darkens and volatilizes, no sublimate.	Decrepitates, turns yellow, darkens and volatilizes, no sublimate.
9. Salt of Phosphorus bead.	Blue color due to tungsten.	Blue color due to tungsten.
10. Solubility	Insoluble in acids, soluble in $NH_4OH$ .	Insoluble in acids, soluble in $NH_4OH$ .
11. System	Orthorhombic	Monoclinic (?)
12. Cleavage	Perfect {001}	Imperfect {010}
13. Extinction	Parallel to edge in longitudinal sections and to diagonal in cross sections.	$3^\circ$ measured on {010}.
14. Indices	$\alpha = 1.82, \gamma = 2.04$	$\alpha = 1.70, \beta = 1.95, \gamma = 2.04$
15. Birefringence	Strong = 0.22	Extreme = 0.34
16. Absorption	$Z > Y > X$ $Z =$ dark yellow, $Y =$ light yellow, $X =$ colorless.	$Z > Y > X$ $Z =$ dark green, $Y =$ yellow green, $X =$ colorless.
17. Orientation	Optic plane parallel to the long diagonal in cross section. $Bx_a = X$ (negative). Crystals length slow.	Optic plane $\parallel$ to {010}. $Bx_a$ about $3^\circ$ from the $\perp$ to {001}. $Bx_a = X$ (negative). Crystals length slow or fast.
18. 2V	Ca $27^\circ$	Ca $52^\circ$
19. Dispersion	$r < v$	$r < v$

properties of each would be convenient. Such a comparison is given in Table 5.

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