ART. X.—*On Stibiotantalite;* by S. L. PENFIELD and W. E. FORD.

Historical.—Stibiotantalite was first described by G. A. Goyder* in 1892 and more minutely in 1893, as occurring in rounded water-worn fragments in the tin-bearing sands of Greenbushes, West Australia. No crystals were observed, but it was evident from the cleavage of the material and its action on polarized light that it possessed a crystalline structure, and it was assumed that it belonged to the orthorhombic system, though no convincing evidence was brought forth. An analysis, which is quoted later in this article, indicated that the mineral is essentially a combination of oxides of antimony and tantalum, with some niobium and a very little bismuth, but no formula was suggested. The physical properties were given as follows:—Hardness, 5 to 5·5. Specific gravity, 7·37. Luster, adamantine to resinous. Color, pale reddish-yellow to greenish-yellow. Fracture, subconchoidal to granular. Within the past few years a considerable quantity of this material has become available to collectors through the agency of several mineral dealers.

Crystals from Mesa Grande, San Diego County, California, a New Locality.

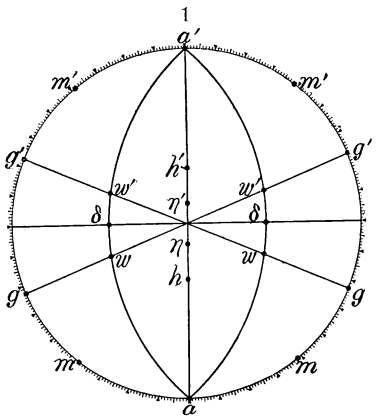
The material from Mesa Grande was brought to the attention of the present writers by Mr. Ernest Schernikow of New York. It was observed by him as occurring very sparingly with the wonderful tourmaline crystals found at the locality and described by Sterrett,† and great pains were taken to have every crystal and fragment carefully saved. In all, some twenty-five crystals have been found, representing several years savings from a vast amount of material, so it may be considered a rare mineral at the locality. Associated with it, besides the tourmaline already referred to, are large and wonderfully beautiful crystals of pink beryl of unusual habit, fine crystals of quartz, orthoclase and lepidolite, and, as a great rarity, cassiterite. The orthoclase is generally kaolinized to a considerable extent. Several crystals of stibiotantalite were observed grown on to, or over, pink tourmaline; one group has attached to it a little feldspar and lepidolite; the others are all detached crystals and some of them are doubly terminated. None of the detached crystals show fresh fractures, and they evidently were found loose in the deposit. Stibiotantalite appears to be

* Proceedings Chem. Soc., 1892, 9, p. 184. Journal Chem. Soc., 1893, lxiii, p. 1076.

† This Journal (4), xvii, p. 459, 1904.

of later origin than the tourmaline and lepidolite, though undoubtedly it was one of the primary minerals of the deposit.

The crystals are mostly of a rich dark-brown color, with resinous to adamantine luster. Fragments look exactly like the resinous variety of sphalerite, and a few pieces were found of light brown color, transparent, and so closely resembling the well known sphalerite from Picos de Europa, Spain, that by appearances the two can not be told apart.



Stibiotantalite crystallizes in the orthorhombic system and is hemimorphic. With few exceptions, the habit of the crystals gives no suggestion of hemimorphic development, which, according to the orientation adopted, is in the direction of the brachy- or *a*-axis. All the crystals that have been studied are polysynthetic twins, thus causing them to imitate the symmetry of the normal group. In habit they resemble columbite, and, as will be shown, the two minerals are related both in chemical composition and axial ratio. In order to bring out the crystallographic relationship, however, it has been necessary to assign rather complex symbols to some of the forms of stibiotantalite, but it is believed that it is better to do so than to give simpler symbols to the forms and refer them to other axes. The axial ratio of the two minerals are as follows:

Stibiotantalite	$a : b : c = 0{\cdot}7995 : 1 : 0{\cdot}8448$
Columbite	$a : b : c = 0{\cdot}8285 : 1 : 0{\cdot}8897$

The forms observed on stibiotantalite are shown in stereographic projection in figure 1, but, owing to polysynthetic twinning, it is impossible to state as regards some of them whether they occur both in front and behind, or intersect only one end of the brachy-axis, as demanded by hemimorphism. The symbols are as follows:

a (100)	η (209)
a' ($\bar{1}$00)	η' ($\bar{2}$09)
m (110) or ($\bar{1}$10)?	h (203), probably also h' ($\bar{2}$03)
q (130)	δ (043)
q' ($\bar{1}$30)	w (4·12·9) probably also w' ($\bar{4}$·12·9)

The only crystals observed which exhibit a marked hemimorphic development are represented in figures 2, 3 and 4. They are orientated according to pyroelectric deportment, the a faces to the front all developing negative electricity on cooling, as tested by the carmine-sulphur-lycopodium mixture suggested by Bürker.* The crystal shown by figure 2 has at the top two ridges and a valley, but no reëntrant angle at the sides: The two ridges on cooling develop positive, and the valley negative electricity. This crystal is a polysynthetic twin, and may be taken as a type for illustrating the structure of other crystals. The vertical axis is the twinning axis, and the macropinacoid a the composition face. If it is assumed as in figure 5 that a hemimorphic crystal has the prism g (130) and the dome η (209) intersecting the front end of the a-axis only, a lamella in twin position, figure 6 (as indicated by the letters underlined), would give a ridge and a valley at the top, corresponding to figure 2, but also reëntrant angles at the sides, which do not occur on the crystal shown in figure 2. It seems therefore necessary to assume that, in addition to g to the front, there is a corresponding g' ($\bar{1}30$) behind and, as will be shown, also, an η' ($\bar{2}09$) behind, figure 7: These forms appear in twin position as shown in figure 8, and an interspersed twin lamella, as in figure 9, may then show at the sides the prism g' corresponding in direction with g. The prism lettered g, figure 2, is therefore to be regarded as a composite face, composed partly of g and partly of g'. At the top of such a crystal there may be, as in figures 2 and 9, a ridge and a valley, provided that in the twin lamella there occurs in connection with g' not η' sloping to the front but η sloping behind. As a matter of fact, only a few of the crystals

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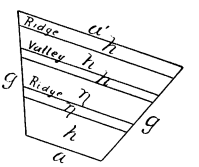

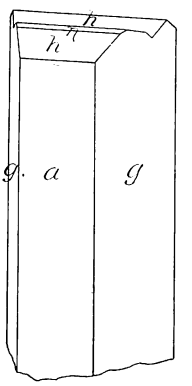

*Annalen der Physik, 1900, I, p. 474. *Note.* Bürker states that with this mixture carmine goes to positively electrified surfaces and sulphur plus lycopodium to negative, which seems contrary to reason, for sulphur should become strongly negatively electrified by agitation and go to a positively electrified surface, the same as with the method of dusting with red oxide of lead and sulphur. As a matter of fact, sulphur does go to the positively electrified pole, but each grain, as may be seen with the microscope, is loaded with a fine dust of carmine and gives a red effect. The lycopodium, on the other hand, goes to the positive pole, and is very free from any admixture of either carmine or sulphur, hence it gives with the sulphur-carmine mixture a strong and sharp contrast of color.

show reentrant angles at the top, and the faces of later figures lettered η or η' must in reality be regarded as composite, made up partly of η and partly of η'.

Figures 3 and 4 both show hemimorphic character by the development of η' behind, but this face is in reality composite, composed in part of η in twin position. Figure 3 shows prominent reentrant angles at the sides, compare figure 6: none of the other crystals show these so prominently,

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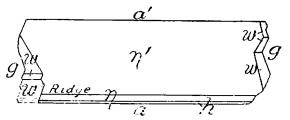

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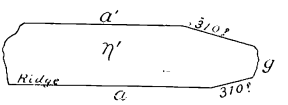

and as a rule reentrant angles are so small as to give the effect of fine striations parallel to the vertical axis, or a rounding of the obtuse edge between g and g', as if resulting from oscillatory combination, figure 4. The crystal represented by figure 4 is the only one showing any prominent development of a replacement of the edges between a and g; the form, however, is so striated and distorted by the development of vicinal faces that no satisfactory measurements could be obtained; it approximates to (301) respectively ($\bar{3}$01), but the symbols are

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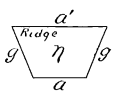

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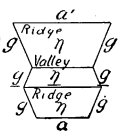

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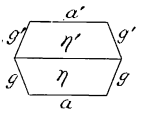

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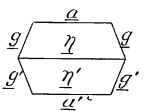

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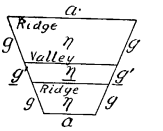

questionable. The pyramid w is developed to so slight an extent and the crystals are so complicated by polysynthetic twinning that it is impossible to state whether it occurs only in front or only behind; hence it is assumed that both forms, w (4.12.9) and w' ($\bar{4}$.12.9), are present. With the exception of the three crystals just described, the general habit is like that of the normal group of the orthorhombic system, as illustrated by figures 10 to 13, in which the forms are represented with ideal symmetry, whereas they all show vertical striations on the pinacoid and prism faces, and some rounding of the edges between g and g'. One crystal only, figure 12, is shorter in

the vertical than the horizontal direction. The largest crystal of the types illustrated is shown in about natural size in figure 13, which measured in the direction of the a, b and c axes, respectively, $6\times25\times30^{mm}$, while the remaining ones average

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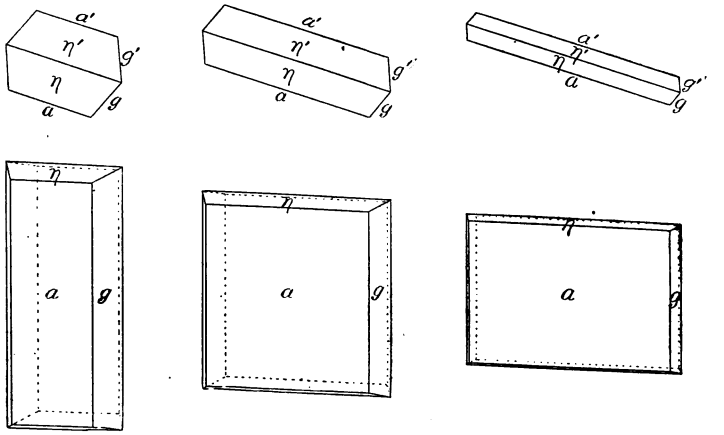

about one-fourth this size. Figure 14 shows in detail one of the corners of the crystal idealized in figure 13; it is rather unusual in showing the η and η', and w and w' faces with

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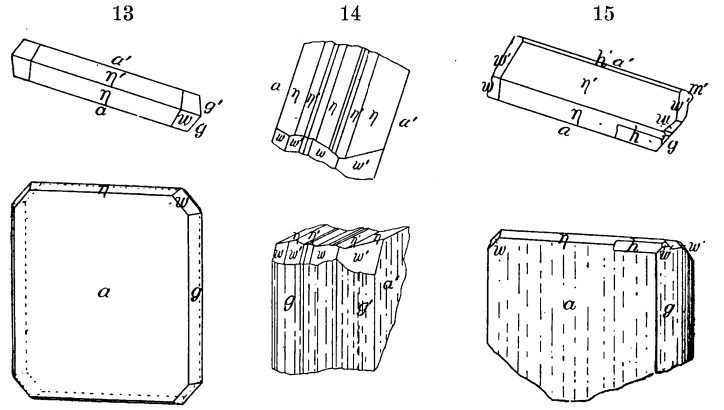

numerous reentrant and salient angles, while the g and g' faces are finely striated and round into one-another. At the opposite end of the crystal the η and w faces appear without reentrant angles.

The general resemblance to columbite is shown by the prominent development on both species of the macropinacoid a, parallel to which stibiotantalite has a highly perfect and columbite a distinct cleavage, while both minerals have an indistinct cleavage parallel to the brachypinacoid b (010). The prism g is always present on stibiotantalite, while on columbite it is seldom wanting and often prominent. The macrodome h occurs on both minerals but is not common, while the prominent development of rather flat macrodomes, η (209) on stibiotantalite, and k (103) and l (106), respectively (206) and (2.0.12), on columbite is a feature common to both species. The pyramid w (4.12.9), although not occurring on columbite, is in the same vertical zone as two of its prominent pyramids, s (263) and u (133), respectively, (4.12.6) and (4.12.12). If the crystals of stibiotantalite were black and of metallic luster they certainly might be mistaken for columbite, because of similarity in appearance, habit, occurrence and association. Columbite, it should be stated, is not hemimorphic and does not exhibit pyroelectricity.

Crystals of stibiotantalite show certain peculiarities as regards the development of the forms and the character of the surfaces, as follows:—

The macropinacoids a and a', which are generally the most prominent of all the forms, have a bright luster and are usually striated vertically, the striæ being rather fine and seldom giving rise to much rounding or irregularity of the surface: on a few crystals they appear almost free from striations. Both (100) and ($\bar{1}$00) occur without any apparent difference, except when tested for pyroelectricity, and then it generally appears that the same surface develops two kinds of electricity owing to twinning and interpenetration.

The prisms g (130) and g' ($\bar{1}$30) are present on all of the crystals and are always striated vertically, due to polysynthetic twinning and in part perhaps to oscillatory combination, both causes giving rise to a rounding of the edge between g and g', or as is frequently the case, to a considerable distortion when one prism face predominates over the other, figure 14. In almost all of the crystals, however, portions of the prismatic faces are quite free from striations, so that good measurements may be had. Any modification of the edge between a and g was rarely observed. On two crystals distinct replacements, indicating the presence of a prism corresponding to m (110) or m' ($\bar{1}$10) were noted, but the faces were too poorly developed to give good measurements; compare figure 15.

The macrodomes η (209) and η' ($\bar{2}$09) are prominent on all of the crystals as shown by the figures. A single face is generally composed of both η and n' as explained on page 58.

The domes are generally free from striations and dull in comparison with the other faces, appearing as if corroded, but on a few of the crystals they are bright and somewhat striated, not sufficiently so, however, to interfere with measurements. The domes h (203) and perhaps h' ($\bar{2}03$) occur on only a few of the crystals, two of which are shown as nearly as possible in true proportions in figures 2 and 15. On both crystals the surfaces were so dull, seemingly etched, that on the goniometer they gave no reflections of the signal, but by placing bits of microscopic cover glass against the faces satisfactory measurements were obtained which leave no doubt as to the correctness of the symbol. Owing to the interposition of a twin lamella, the dome h, in front, shown in figure 15, extends only about one-third way across the crystal.

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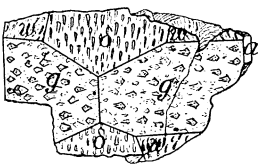

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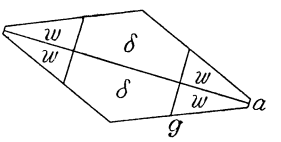
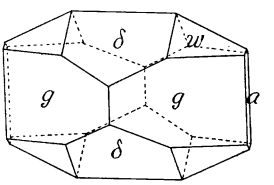


The pyramid w (4.12.9) appears on only a few of the crystals, is never very prominent and its development is so complicated by polysynthetic twinning, that it is difficult to state whether it occurs in front (4.12.9), or behind ($\bar{4}$.12.9), or in both positions. The pyramid faces are often striated parallel to the edge $4.12.9 \wedge \bar{4}.12.9$, as if in oscillatory combination, and frequently distinct reentrant angles occur, figures 3, 14, and 15, which indicate rather that the striations result, in part at least, from polysynthetic twinning. The pyramid faces generally have bright surfaces which yield good reflections even when the accompanying dome faces are dull.



A basal plane c and brachypinacoid b have not been observed, but occasionally owing to oscillatory combinations of $g \wedge g'$, or as a result of polysynthetic twinning, a striated surface results, approximating in position to b.

The surfaces as a whole are not the best for reflecting light, and striations gave rise to further difficulties, but it is believed that the measurements and axial ratios derived therefrom must be very nearly correct.

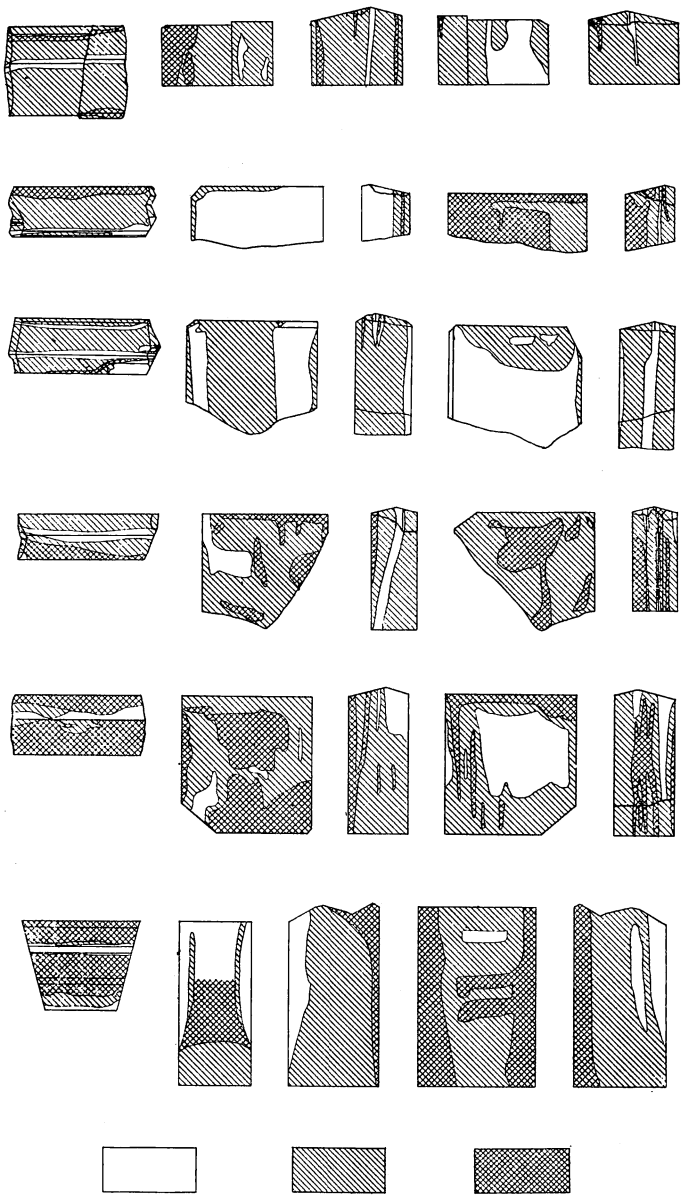
The crystal shown in figure 16, considerable portions of which are missing, is unique. It measures about 5^{cm} in length, 4 in height and 3 in thickness, respectively in the directions of the a, c and b axes, and weighs 150 grams (over 5 ounces), or

six times as much as the next largest crystal, which is of the type shown by figure 13. It was found at a considerably later period than the other crystals, and at a different part of the deposit. It was picked up in two pieces, and the fracture surfaces do not appear fresh, as if recently broken in taking the crystal from the matrix. Originally it must have been quite symmetrical in development and in shape about as shown in figure 17, which, as is also the case with figure 16, is drawn with the a faces to the right and left, instead of front and back, in order to show the form to best advantage. It was attached at the lower left-hand corner to pink tourmaline, bits of which are still adhering to it. The upper and lower edges, and a considerable portion of the lower, right-hand corner have been broken away. The a, a' faces to the right and left are fresh-looking cleavage surfaces; and whether the pinacoids a and a' were originally present, as shown in figure 17, or whether adjacent g faces came together at the acute edges, cannot be told.

The habit of this crystal is entirely different from that of the others, and the peculiarities of its surface are also different. The brachydome δ (043) has been observed only on this crystal. The prism g is not striated vertically. The surfaces are all etched, so that only measurements with a contact goniometer may be had, but these all agree with those obtained from other crystals. The best-formed etchings on the prism g are rather deep depressions, shaped about as shown in figure 16, though the majority are much more rounded: in places they join one-another, giving rise to furrows running irregularly over the surface. The etchings on the brachydome δ are long depressions, some of them quite deep, while those on the pyramid w are also long, but somewhat comma-shaped, the tails pointing away from the edge $w \wedge \delta$. The crystal is light yellowish-brown in color, more transparent than any of the others, and has a specific gravity of 6·69.

The crystal is a polysynthetic twin, though the outward form gives no evidence of it. The two large fragments which make up the specimen do not of themselves exhibit pyroelectricity, probably because of numerous cracks running through the material, but a small homogeneous fragment, when tested, exhibited alternating bands of positively and negatively excited material, remarkably uniform and not over 2^{mm} in width.

Throughout a portion of its interior the crystal is curiously cavernous, although the exterior is firm and consists of remarkably pure, transparent material. The cavity looks as though it had been eaten out by some solvent, and is lined with some secondary material which without endangering the specimen could not be gotten out in sufficient quantity for a satisfactory



a, negatively electrified areas ; *b*, neutral areas ; *c*, positively electrified areas.

Plate showing the distribution of negatively electrified, neutral and positively electrified areas of crystals when cooled.

test. Resting on this secondary material are a few very minute pyramids of cassiterite.

Pyroelectricity.—The pyroelectric phenomenon which is exhibited by all of the crystals is a matter of interest. It reveals a complex polysynthetic twinning structure, as the result of which the crystals with few exceptions appear as if they possessed normal orthorhombic symmetry. Each crystal has its own peculiar polysynthetic development, and it seems sufficient to select a few examples as types, in which the distribution of the electrically excited surfaces is indicated diagrammatically, as in the accompanying plate, page 63. The crystals are represented, as it were, unfolded; there is given first a top view, then in turn views of the front, right-hand side, back and left-hand side. Lower ends have not been represented because, with few exceptions, they are fracture surfaces. As stated on page 63, the crystals were tested for pyroelectricity with a mixture of carmine, sulphur and lycopodium, with which negatively and positively electrified surfaces are coated respectively, white by lycopodium, and red by sulphur coated with carmine. In the diagrams the negative surfaces are indicated by white (lycopodium), the positive by cross lines (red, sulphur and carmine), while the neutral, brown surface of the crystals is simply lined. The diagrams illustrate how irregularly the lamellae are intergrown and, to a certain extent, how complex the twinning really is, but they do not do the subject full justice, for often the lamellae are very thin and red and white alternate in bands, too narrow to be represented by line drawings.

Two pebbles of the stibiotantalite from Greenbushes, Australia, belonging to the Brush Collection, were tested for pyroelectricity, but in their entirety gave no effect; when broken up, however, small homogeneous pieces gave the reaction distinctly, and it may be assumed that failure to get a response from the larger pebbles is because of the numerous cracks which permeate the material.

Crystal Measurements.—The measured and calculated angles are as follows:—

			Measured.	Calculated.
$g \wedge g'$, 130	$\wedge \bar{1}30$	=	45° 16′*	
$g \wedge w$, 130	$\wedge$ 4.12.9	=	39 20*	
$m \wedge m'''$, 110	$\wedge 1\bar{1}0$	=	approximately	77° 18′
$w \wedge w'$ 4.12.9	$\wedge \bar{4}.12.9$	=	34 43	34 38
$w \wedge w'''$, 4.12.9	$\wedge 4.\bar{1}\bar{2}.9$	=		91 6
$\eta \wedge \eta$, 209	$\wedge \bar{2}09$	=	26 30	26 26
$a \wedge h$, 100	$\wedge 203$	=	54 30	54 50
$\delta \wedge \delta'$, 043	$\wedge 0\bar{4}3$	=	approximately	96 48

From the measurements marked by an asterisk the axial ratio given on page 62 was calculated.

Orthorhombic symmetry was shown by the measurements of $g \wedge w$ in four upper octants of one crystal, which, though varying from 39° 15′ to 39° 25′, are as nearly alike as the character of the reflections warrant. The crystal on which these measurements were made is the one shown in figure 15, where the distribution of the w faces is like that of the normal group of the orthorhombic system, owing perhaps to polysynthetic twinning.

Optical Properties.—Thin sections cut parallel to the three pinacoids, when examined in polarized light, all showed extinction parallel to directions corresponding to the crystallographic axes. Some of the sections were not uniformly colored throughout, some portions being darker than others, but whether this phenomenon is due to any essential variation in chemical composition or not has not been determined. It is believed that if the difference in color indicates any variation in chemical composition, it is probably slight.

The indices of refraction vary somewhat for crystals of different specific gravity. Determinations have been made on two crystals; one having a specific gravity of 6·818, and the other of 6·299. In both cases the indices of refraction were determined from two prisms; one with a face parallel to the base and its edge parallel to the a-axis, which gave with 90° incidence the values for rays vibrating parallel to the a and b axes, respectively, β and a; the other prism with its edge parallel to the c-axis gave the value γ. The optical orientation is therefore $a=\mathfrak{b}$, $b=\mathfrak{a}$ and $c=\mathfrak{c}$. With basal sections, also, 2H acute was measured in potassium mercuric iodide solution, $n_y=1{\cdot}7156$. The values for the two crystals are as follows:—

Specific gravity 6·818, corresponding to about 39 per cent Ta_2O_5 and 17·5 per cent Nb_2O_5.

	a	β	γ	$2V$, Calculated		$\gamma-a$
For Li....	2·3470	2·3750	2·4275	∴ 73°	40′	·0805
" Na	2·3742	2·4039	2·4568	∴ 75	5	·0826
" Tl.....	2·4014	2·4342	2·4876	∴ 77	38	·0862

" Na .... $2Ha = 119° 10' \therefore 2V = 75° 58'$

Specific gravity 6·299, corresponding to about 22·5 per cent Ta_2O_5 and 30 per cent Nb_2O_5.

	a	β	γ	$2V$, Calculated		$\gamma-a$
For Li....	2·3686	2·3876	2·4280	∴ 70°	0′	·0594
" Na....	2·3977	2·4190	2·4588	∴ 73	25	·0611
" Tl	2·4261	2·4508	2·4903	∴ 77	50	·0642

" Na $2Ha = 113° 11' \therefore 2V = 72\ 37'$

As may be seen from the above, the mineral is characterized by an unusually high index of refraction, the values γ for yellow, 2·4568 and 2·4588, being somewhat higher than that of diamond, 2·418, and considerably above that of sphalerite, 2·369, yet so near the latter that, both minerals being of the same color and possessing good cleavage, it is evident that fragments of the two must look exactly alike. An unusually strong dispersion, $\rho < \upsilon$, is a marked feature of the mineral, and also a high birefringence, $\gamma - \alpha$ for yellow being for the crystal of higher specific gravity ·0826, and for the other ·0611. The character of the birefringence is positive. The plane of the optical axes is the macropinacoid (100), and the vertical axis c is the acute bisectrix.

The divergence of the optical axes, $2V$, is so great that $2E$ can not be observed; in fact, the mean index of refraction of the mineral is so far above that of our highest refractive liquids that it was with the greatest difficulty that $2H$ could be observed: This was due in part to the fact that the sections, prepared from the same crystals from which the prisms were cut, contained some dark inclusions which interfered with the transmission of light. $2H$ therefore was measured only for sodium light, the illumination from lithium and thallium flames being too weak to yield distinct interference figures. It seems rather anomalous to have $2H$ acute as high as 119° and 113°, but this is due to the very high index of refraction of the mineral. In both crystals the agreement between the values of $2V$, as calculated from the three indices of refraction and from $2Ha$, are as satisfactory as could be expected, considering the difficulties encountered in preparing the prisms and sections, and making the measurements. As shown by the tabulated results, the substitution of Nb_2O_5 for Ta_2O_5 causes a slight increase in the values of the indices of refraction, a decrease in birefringence $(\gamma - \alpha)$ and, except in the case of thallium, a decrease in $2V$. The dispersion is much more marked in the crystal of lower specific gravity, the differences of $2V$ for green and red being in the one about 4° and in the other about 7°.

Chemical Composition.—For chemical analysis two crystals were employed, one having a specific gravity of 6·72, and the other 5·98. The method of analysis was as follows: The mineral was dissolved, without heating, in hydrofluoric acid in a platinum dish, and the antimony and bismuth precipitated by hydrogen sulphide. The precipitate was collected on a filter and then digested with a solution of sodium sulphide in order to separate antimony from bismuth. The undissolved bismuth sulphide was collected, dissolved in warm nitric acid and, after removal of the latter, reprecipitated by hydrogen sulphide. The precipitate was then collected on asbestos,

ignited in a current of carbon dioxide and weighed as Bi_2S_3. The antimony separated from the bismuth was reprecipitated as sulphide, collected on asbestos, and, after heating in carbon dioxide, weighed as Sb_2S_3. Preliminary experiments with known amounts of bismuth and antimony proved that the methods as given above yielded correct results. The filtrate from the original sulphide precipitate, containing the niobium and tantalum, was evaporated to dryness and the residue decomposed by fusion with acid potassium sulphate. The fusion was then digested with water and the insoluble niobium and tantalum oxides were filtered, ignited and weighed. Qualitative tests indicated that there were not determinable quantities of other substances present. The results of the analysis of the original stibiotantalite from Australia by Goyder, together with those of two varieties of the mineral from Mesa Grande, are as follows :—

	Australia.	Mesa Grande.			Mesa Grande.		
Specific gravity	7·37		6·72		5·98		
		I	II	Average	I	II	Average
$(Ta,Nb)_2O_5$	58·69	55·22	55·44	55·33	50·57	50·03	50·30
Sb_2O_3	40·23	44·31	44·21	44·26	49·07	49·49	49·28
Bi_2O_3	·82	·31	·34	·33	·53	·54	·53
				99·92			100·11
NiO	·08						
H_2O	·08						
	99·90						

The results of the analyses indicate that with decrease in specific gravity there is an increase in antimony oxide, and a proportional decrease in the combined acid oxides, due to the isomorphous replacement of heavier Ta_2O_5 by lighter Nb_2O_5. As there is no satisfactory method for separating tantalum from niobium, the attempt has been made to determine the proportions of the two oxides by taking the specific gravity of the mixed oxides as obtained from the analyses, and comparing the results with those of pure Ta_2O_5 and Nb_2O_5, which are quite widely separated. This method has been tested sufficiently to indicate that it gives fairly satisfactory results, and from the values given below and a consideration of the ratios, which in both analyses are almost exactly 1 : 1, it may be seen that the percentage of the Ta_2O_5 and Nb_2O_5 must be reasonably exact:—

Sp. gr. = 6·72.		Ratio.			Sp. gr. = 5·98.		Ratio.	
Ta_2O_5	36·35	·0815	·1523	1·00	11·16	·0250	·1710	1·00
Nb_2O_5	18·98	·0708			39·14	·1460		
Sb_2O_3	44·26	·1536	·1543	1·01	49·28	·1711	·1722	1·01
Bi_2O_3	·33	·0007			·53	·0011		
	99·92				100·11			

Goyder, in his analysis of the original stibiotantalite from Australia, made no separation of the tantalum and niobium oxides, but assuming that the ratio of $(Ta,Nb)_2O_5 : (Sb,Bi)_2O_3 = 1 : 1$, the proportions of Ta_2O_5 and Nb_2O_5 were determined indirectly. Thus, considering the first of our analyses, where the per cent of $(Ta,Nb)_2O_5$ is 55·33; the per cent of Ta_2O_5 may be taken as x, when that of Nb_2O_5 will be $55{\cdot}33-x$: now having the molecular weights, $Ta_2O_5 = 446$, $Nb_2O_5 = 268$, $Sb_2O_3 = 288{\cdot}4$ and $Bi_2O_3 = 465$, the following equation results:

$$\frac{x}{446} + \frac{55{\cdot}33-x}{268} = \frac{44{\cdot}26}{288{\cdot}4} + \frac{0{\cdot}33}{465}, \text{ from which } x = 35{\cdot}15.$$

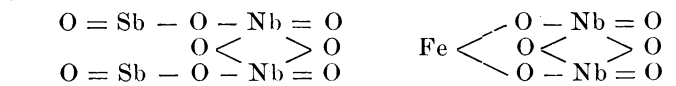
Treating all three analyses in like manner, the results, together with the theoretical composition of the end products, are as follows:

	Theory for $(SbO)_2Ta_2O_6$				Theory for $(SbO)_2Nb_2O_6$
Sp. gr.	7·90	7·37	6·72	5·98	5·73
Ta_2O_5	60·73	51·13 (52·16)*	35·15	10·60	0·00
Nb_2O_5	0·00	7·56 (6·53)	20·18	39·70	48·17
Sb_2O_3	39·27	40·23	44·26	49·28	51·83
Bi_2O_3	----	0·82	·33	·53	----
NiO	----	0·08	----	----	----
H_2O	----	0·08	----	----	----
	100·00	99·90	99·92	100·11	100·00

The results of the indirect determination of Ta_2O_5 and Nb_2O_5 in the last two analyses show a very satisfactory agreement with the values derived from the specific gravities of the oxides, and it may be pointed out that a slight variation in the per cent of Sb_2O_3 causes about four times as great a variation in the percentages of Ta_2O_5 and Nb_2O_5, while, also, variations up to 4 per cent in Ta_2O_5 or Nb_2O_5 have little effect upon the ratio owing to the large molecular weights of the acid oxides.

The ratios in the two new analyses, being almost exactly 1 : 1, indicate that in chemical composition stibiotantalite is an isomorphous mixture of $Sb_2O_3.Ta_2O_5$ and $Sb_2O_3.Nb_2O_5$, with a little bismuth replacing the antimony. It is a curious and interesting fact that, in materials from such widely separated localities, the amounts of bismuth should be so nearly alike.

The chemical relation between stibiotantalite and columbite may perhaps be represented best by developed formulas, as follows:



* The percentages given in parentheses result from the molecular weights made use of in this article. The figures given by Goyder vary somewhat because he used slightly different molecular weights.

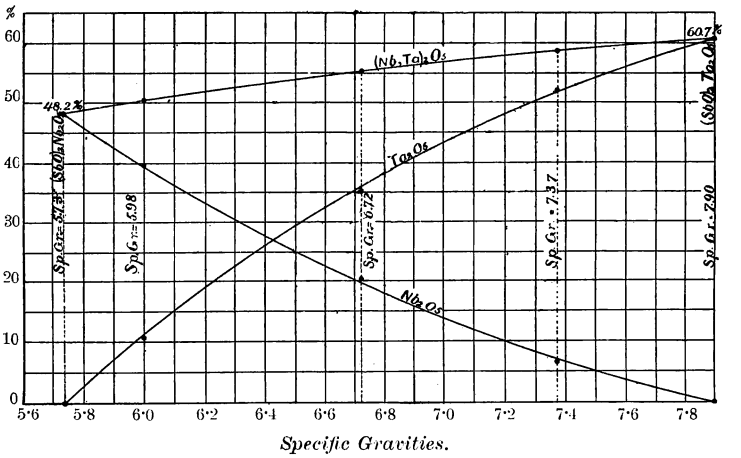
What it is desired especially to bring out by the formulas is that in stibiotantalite two univalent *antimonyl* radicals (O=Sb) play the same rôle as a bivalent atom of Fe in columbite, hence, chemically, the mineral is regarded as a basic antimony tantalate, respectively, niobate. Following ordinary methods, the formulas would be written $(SbO)_2(Ta,Nb)_2O_6$ and $Fe(Ta,Nb)_2O_6$. It may be that the similarities in habit, cleavage and axial ratios between stibiotantalite and columbite, as pointed out earlier in this paper, are mere matters of accident, but, taken in connection with the chemical formulas, this does not seem at all probable. It is assumed that the antimony-oxide radical, known in chemistry as *antimonyl*, plays the part of a metal in stibiotantalite, replacing the hydrogen atoms of tantalic, respectively, niobic acid. This tendency may be noted in a number of compounds of the antimony-bismuth group, where we have basic salts containing the *antimonyl* (SbO) and *bismuthyl* (BiO) radicals. If the crystallographic relationship to columbite is disregarded, the formula of stibiotantalite may be simplified to $(SbO)(Ta,Nb)O_3$, or, looked at in another way, to $Sb(Ta,Nb)O_4$, the latter an antimony salt of normal tantalic, respectively, niobic acid. Against the latter assumption, however, it may be argued that normal salts of tantalic and niobic acid are almost unknown, and the tendency to form a basic salt containing the antimonyl radical would probably be greater than to form an antimony salt of the normal acids. Among minerals which are normal salts of tantalic and niobic acids, there are only two closely related species, fergusonite and sipylite, $(Y,Er,Ce)(Ta,Nb)O_4$ and $Er(Ta,Nb)O_4$, but these may as well be written as basic salts, for example, $(ErO)_2(Ta,Nb)_2O_6$, conforming to the columbite type of formula.

That the antimony in stibiotantalite is trivalent and not pentavalent is known by the summation of the analyses and also by the results of the following experiment:—Some powdered mineral was dissolved in hydrofluoric acid, and the precipitate thrown down by hydrogen sulphide was collected, dried and tested by heating in a closed tube. Had the antimony been pentavalent, the precipitate would have been either Sb_2S_5 or a mixture of Sb_2S_3 and sulphur, and have yielded an abundant sublimate of sulphur when tested in a closed tube; it gave, however, only a trace of sulphur, the same as stibnite, Sb_2S_3, when similarly heated.

By means of the data given in connection with the three analyses which have been made, it is possible to represent the relations between the specific gravity and chemical composition of stibiotantalite graphically, as shown in figure 18, where the specific gravities are taken as abscissas and per cents as

ordinates. Referring to page 73, the percentages of the total acid oxides, $(Nb,Ta)_2O_5$, of the three analyses have been plotted on the vertical lines corresponding to the specific gravities. The three points thus found do not fall quite on a straight line, hence a circular arc is drawn through them and continued. As given on page 74, the theoretical percentages of Nb_2O_5 and Ta_2O_5 in $(SbO)_2Nb_2O_6$ and $(SbO)_2Ta_2O_6$ are, respectively, 48·2 and 60·7; hence where the $(Nb,Ta)_2O_5$ curve intersects, horizontal lines corresponding to the above figures must determine approximately the specific gravities of the two unknown end products, namely 5·73 and 7·90. Next, the percentages of Nb_2O_5 and Ta_2O_5, as given on page 74, were plotted, and, as shown by the figure, these fall very near two circular arcs, one

18



Specific Gravities.

passing from 0 per cent to 48·2 per cent Nb_2O_5, the other from 0 per cent to 60·7 per cent Ta_2O_5. The greatest variation of the determinations of Nb_2O_5 and Ta_2O_5 from these curves is not over one per cent, which is well within the errors of analysis. If instead of using the values for Nb_2O_5 and Ta_2O_5 given on page 74, which were obtained indirectly from the percentages of Sb_2O_3 and Bi_2O_3 and were selected because the three analyses received like treatment, the values as given for our two analyses on page 73 are plotted on figure 18, the points fall almost exactly on the Nb_2O_5 and Ta_2O_5 curves. Certainly, considering the difficulties of the analyses, the close conformity of the determinations to the two curves is a most satisfactory confirmation of the reliability of the results obtained. It was by means of the diagram that the approximate composition of the two crystals studied optically, as

given on page 71, was determined. The majority of the crystals examined range in specific gravity from 6·6 to 6·7.

Pyrognostics.—Stibiotantalite, when heated intensely at the tip of the blue flame, is fusible at about 4 and imparts a pale bluish-green color to the flame due to volatilization of antimony. After driving off a part of the antimony there is left an infusible mass of niobium and tantalum oxides generally darkened by antimony. If the flame from the mineral is directed against a piece of charcoal a considerable coating of oxide of antimony collects on the coal.* When fused with 3 or 4 times its volume of sodium carbonate on charcoal, a coating of antimony oxides and small globules of metallic antimony are obtained. The powdered mineral is not appreciably attacked by ordinary acids, not even by boiling, concentrated sulphuric, but is readily soluble in hydrofluoric acid. Unchanged when heated in closed and open tubes and gives no characteristic reactions with the fluxes.

Summary.—Stibiotantalite is a mineral first found in rounded, water-worn pebbles in Australia and recently in well-crystallized specimens in California, In chemical composition it is an isomorphous mixture of $(SbO)_2Nb_2O_6$ and $(SbO)_2Ta_2O_6$, exhibiting a wide range in specific gravity, from 5·98 to 7·37, depending upon the proportions of Nb_2O_5 and Ta_2O_5 present. The crystals belong to the hemimorphic group of the orthorhombic system, although, owing to twinning, they imitate the symmetry of the normal group. In axial ratio, development and occurrence of several forms, the mineral is related to columbite. Stibiotantalite is characterized by an unusually high index of refraction, above diamond, a high birefringence and a wonderful luster.

In closing, the writers take special pleasure in expressing their thanks to Mr. Ernest Schernikow, of New York, who has most generously placed at their disposal for study all of the crystals which the locality, so far as known, has afforded. He may well be proud that his eagerness to promote the science of mineralogy has enabled him to bring to light a mineral of such unusual beauty and scientific interest.

Mineralogical Laboratory of the
Sheffield Scientific School of Yale University,
New Haven, Conn., February, 1906.

*Tried in the same way as when testing for zinc; Brush-Penfield Determinative Mineralogy and Blowpipe Analysis, p. 131.