On Stokesite, a new mineral containing tin, from Cornwall.

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WHILE engaged last summer in arranging the Carne collection of minerals acquired for the Cambridge Mineralogical Museum in the early part of 1899, my attention was attracted by a single, colourless, transparent crystal, about 10 mm. long, implanted in a shallow cavity on a specimen of crystallised axinite from the St. Just district of Cornwall. In general appearance the crystal resembled somewhat closely one of selenite of the ordinary habit, and indeed was entered as gypsum in the catalogue of the Carne collection. The unusual nature of the occurrence led me to make as complete a crystallographic and chemical examination as the limited amount of material at my disposal would allow. The results obtained have established the existence of a new mineral species for which, in a preliminary communication,[1] the name Stokesite was proposed, in honour of Sir George Gabriel Stokes, Bart., Lucasian Professor of Mathematics in the University of Cambridge. I am now able to lay before the Society a detailed account of the measurements and experiments which have been made.

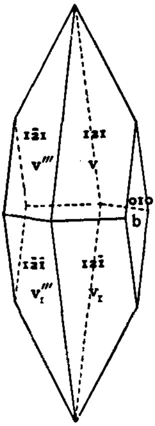

Fig. 1.

1. *Crystallographic characters.*

System: Prismatic (bipyramidal or holohedral class):—

$$a : b : c = \cdot 3463 : 1 : \cdot 8033.$$

Forms present: $b(010)$, $v(121)$, both largely developed; $c(001)$, $s(565)$ and $t(122)$, all three very small. Faces of the form $m(110)$ can be produced by cleavage.

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[1] *Phil. Mag.* 1899, Series V, XLVIII, 480.

TABLE OF ANGLES.

Angle.	Calculated.	Observed Mean.	Limits.	Edges.
$121 : \bar{1}21$ vv'	101°38′	101°38′	100°11′—101°59′	4
$121 : \bar{1}\bar{2}1$ vv''	—	141 0*	140 36—141 2	4
$121 : 1\bar{2}1$ vv'''	64 54	64 52	64 37— 65 9	4
$121 : 12\bar{1}$ $vv_{,}$	39 0	38 57	38 32— 39 24	4
010 : 121 *bv*	—	57 33*	56 40— 58 1	8
010 : 110 *bm*	70 54	70 32	70 50— 70 14	2
010 : 565 *bs*	69 7	68 55	68 52— 68 58	2
110 : 121 *mv*	24 48	24 49	——	1
$110 : 1\bar{2}1$ mv'''	56 10	56 45	——	1
121 : 122 *vt*	15 48	16 17	——	1

The axial ratios have been calculated from the mean values obtained for the two angles vv'' and *bv*. The habit of the crystal is shown in the figure. It was regularly developed and nearly complete, being attached to the wall of the small depression in which it was found by a crystal of axinite, which penetrated it. The basal pinakoid *c* was developed as a small rough face at one end of the crystal only; the plane *t* was also observed but once, and lay between *c* and one of the faces of the form *v*. The form *s* was represented by two very narrow planes lying on the edge vv'''. These faces were not sufficiently bright to enable their angular positions to be determined with much accuracy. Fair reflections were obtained from the eight faces of the bipyramid *v*, and from the two faces of the brachy-pinakoid *b*. Some of these planes were, however, rather rounded, and the elements given above cannot be regarded as more than moderate approximations to the truth, and will doubtless require modification when further material is available for examination.[1] The crystal has been so placed as to enable the cleavage faces *m* to be taken as belonging to the prism 110. The bipyramid *v* may then receive the indices 121.

2. *Physical Characters.*

Cleavage: *m* perfect; *b* less so. Fracture conchoidal. Brittle. Hardness about 6. Specific gravity, 3·185 at 22·9°C (determined by suspending a small fragment in methylene iodide diluted with benzol). Lustre vitreous, pearly on *b*. Transparent, colourless; streak white.

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[1] Some of the numerical values here stated differ slightly from those given in the *Philosophical Magazine*. The numbers now adopted are the final results of a careful re-calculation.

Special Optical Characters.

The plane of the optic axes is parallel to $b\,\{010\}$; the acute bisectrix is perpendicular to $c\,\{001\}$.

As the amount of material available did not allow of the preparation of any sections, the angle between the optic axes was measured when the crystal was immersed in a liquid whose index of refraction was approximately equal to the mean principal index of the crystal. For this purpose quinoline, $\mu=1{\cdot}616$ at 22°C. (sodium light), was found suitable, the border between a crystal fragment and the liquid being examined under the microscope.

For sodium light $2V=69\frac{1}{2}^\circ$ approximately; for thallium light the value is about $20'$ greater, hence $\rho < v$ and $2E=134^\circ$.

The crystal is optically positive, and the principal index, γ, of a ray vibrating parallel to the acute bisectrix, can be determined by using as prisms, pairs of faces of the form $v\,\{121\}$ such as 121 and $\bar{1}\bar{2}1$. Measurements were made for two pairs of faces, and the angle of minimum deviation D was found to have a mean value of $26^\circ 25'$. The prism-angle $A=39^\circ$. We have therefore—

$$\gamma=\frac{\sin\frac{1}{2}\,(39^\circ+26^\circ 25')}{\sin 19^\circ 30'}=1{\cdot}619 \text{ (sodium light).}$$

These prisms give also a second refracted image, due to the wave-velocity p, which is connected with the two principal wave-velocities a and b by the equation $p^2=a^2\sin^2\theta+b^2\cos^2\theta$, where θ is the angle between the normal to the plane bisecting the refracting angle of the prism and the minor axis of the ellipse ab.

Since γ and $2V$ are known, we can now calculate the two principal indices α and β from the equations—

$$\text{(i)}\quad p^2 = a^2\sin^2\theta+b^2\cos^2\theta$$

$$\text{(ii)}\quad \tan V=\sqrt{\frac{a^2-b^2}{b^2-c^2}}$$

$$\text{(iii)}\quad c^2=\frac{1}{\gamma^2}.$$

In (i) we have $\theta=34^\circ 42'$, $\sin^2\theta={\cdot}3241$ and $\cos^2\theta={\cdot}6759$. The deviation of the extraordinary ray D' was found to be $26^\circ 5'$, and the prism angle $A=39^\circ$.

Hence from the formula $\mu=\dfrac{\sin\frac{1}{2}\,(A+D')}{\sin\frac{1}{2}A}$ we get $\dfrac{1}{p}=1{\cdot}6114$ and $p^2={\cdot}3851$.

If now in (ii) we substitute for c^2 its numerical value ·3815, we have—

$$\text{(i)} \quad \cdot 3851 = \cdot 3241\, a^2 + \cdot 6759\, b^2$$

$$\text{(ii)} \quad \cdot 4813\, (b^2 - \cdot 3815) = a^2 - b^2$$

$$\text{Hence } \alpha = 1 \div a = 1\cdot 609$$

$$\beta = 1 \div b = 1\cdot 6125$$

$$\text{and } \gamma = 1 \div c = 1\cdot 619$$

3. *Chemical Composition.*

As the crystallographic and optical characters failed to lead to the identification of the mineral, it was resolved to sacrifice a portion of the crystal for chemical analysis. A preliminary examination of a few minute fragments showed that the substance was insoluble in concentrated hydrochloric acid, and infusible before the blowpipe, to whose flame it imparted no colour. Heated in a microcosmic salt bead it gave a skeleton of silica. For the purposes of a combined qualitative and quantitative analysis, ·1128 gram, placed in a platinum boat, was heated to dull redness in a current of dry air in a glass tube. Water was deposited on the tube, and the boat lost ·0097 gram. That the loss of weight of the substance was entirely due to the expulsion of water was proved by collecting the latter in a small weighed tube containing sulphuric acid.

The contents of the platinum boat were next transferred to a platinum crucible and heated to bright redness; as no further change of weight took place, sodium carbonate was added, and the substance fused till decomposition was complete. The fused mass was brought into solution in hydrochloric acid, and the silica separated by evaporation to dryness in the ordinary way. The crucible in which the fusion was conducted was found to have undergone no change of weight.

The solution from which the silica had been separated was next treated with hydrogen sulphide, when quite unexpectedly a yellow precipitate began to form. This was filtered off and found to possess the properties of tin disulphide. It was converted into oxide and weighed. From the oxide the metal was obtained by reducing with potassium cyanide, and proved to be tin by the ordinary tests.

The solution from which the tin had been removed was treated with nitric acid, ammonium chloride and ammonia, and a small precipitate of ferric hydroxide obtained. On proceeding with the analysis, calcium was found to be present. It was precipitated as oxalate, and weighed as oxide. The latter proved on spectroscopic examination to be free from barium and strontium. Magnesium could not be detected, nor could any potassium be found in the residue. As the glass tube in which the substance was originally heated showed no trace of etching, fluorine was judged to be probably absent, and a small fragment of the crystal tested for boron gave a negative result.

The results of this analysis are stated in column I of the table below; and as will be seen from the numbers there given, no less than 27 per cent. of the substance was left unaccounted for.

It seemed at the time possible that this deficiency was due to the presence of sodium, which could not be estimated in the first analysis, and it was therefore considered advisable to sacrifice another portion of the crystal for a second determination.

For this purpose ·1111 gram was heated to expel water, and then distilled with pure aqueous solution of hydrofluoric acid in a platinum apparatus constructed by Messrs. Johnson and Matthey, according to the designs given by Prof. Story-Maskelyne,[1] whose instructions were carefully followed in every detail. The silica was weighed as potassium silicofluoride, and no tin could be detected in the distillate.

The apparatus, which appeared to be quite tight at the beginning of the experiment, leaked a little towards the end, and a loss of silica occurred, which, though slight in itself, was sufficient to make a serious difference in the percentage found, owing to the very small amount of material available for analysis. On bringing the contents of the platinum still into solution, and passing in hydrogen sulphide, it was at once remarked that the precipitate of tin disulphide was much larger than that obtained in the first analysis, and when converted into oxide was found to amount to 33·3 per cent. The quantity of iron obtained in this analysis was quite insignificant, the calcium oxide agreed well with that obtained before, and only a little sodium could be detected in the residue.

The numerical data are as follows:—

	Analysis I.	Analysis II.
Weight of substance taken	·1128	·1111
„ H_2O expelled	·0097	·0095
„ SiO_2 obtained	·0486	—
„ K_2SiF_6 „	—	·1606
„ SnO_2 „	·0066	·0370
„ CaO „	·0152	·0149
„ Fe_2O_3 „	·0021	·0008
„ Na_2SO_4 „	—	·0032

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[1] *Phil. Trans. Roy. Soc.* 1870, CLX, 191.

These numbers lead to the percentages given in columns I and II respectively.

	I.	II.	III.	IV.	V.
SiO_2	43·1	39·4	43·1	÷ 60 = ·72	42·65
SnO_2	5·85	33·3	33·3	÷ 150 = ·22	35·55
CaO	13·5	13·4	13·45	÷ 56 = ·24	13·27
H_2O	8·6	8·55	8·6	÷ 18 = ·48	8·53
Fe_2O_3	1·9	·7	—		—
Na_2O	—	1·3	—		—
	72·95	96·65	98·45		100·00
Loss	27·05	3·35			

On looking at the results given above under columns I and II it will be seen that the determinations of water and calcium oxide agree closely. There can be no doubt that of the two silica estimations, that under I is the most trustworthy; the analysis proceeded perfectly smoothly, and the result may be accepted with confidence. On the other hand, the first tin determination has no quantitative value, for the solution containing it was evaporated several times with hydrochloric acid to ensure the separation of the silica, and, as is well known, stannic chloride is volatile under these conditions; moreover, the actual mass present being so small, a comparatively insignificant loss of material is sufficient to wholly vitiate the result. The major part of the iron, if not indeed the whole of it, I am inclined to attribute to external impurity, for the air of the mineralogical laboratory is unfortunately liable to be contaminated with the dust from rusty iron to a quite exceptional extent. It is not easy to decide whether in the circumstances the small amount of sodium obtained is to be considered an essential constituent of the mineral or not.

If, as seems permissible, we accept the numbers given in column III as representing correctly the percentage composition of the mineral, and from them attempt to calculate a formula, we obtain for the atomic ratios the values in column IV, and from these we see that

$$CaO : SnO_2 : SiO_2 : H_2O = 1 : 1 : 3 : 2$$

—very nearly. The formula is therefore $CaO,SnO_2,3SiO_2,2H_2O$.

The percentage composition corresponding to this formula is given in column V, and on comparing the theoretical numbers with the analytical results we find satisfactory agreement in the case of the calcium oxide, the water and the silica, the quantity of stannic oxide being alone deficient. The composition can only finally be settled when more material is available and new analyses can be made on larger quantities, but for the present we are, I believe, justified in assigning to stokesite the empirical formula $H_4CaSnSi_3O_{11}$.

Minerals containing stannic oxide and silica have been described by Breithaupt,[1] Bischof,[2] Tschermak,[3] and Collins.[4] The material analysed by these authors was massive, and its homogeneity open to doubt. Stokesite appears therefore to be the first example of a well crystallised definite compound containing silica and stannic oxide as essential constituents.

When we come to consider the constitution of this mineral, we see that several views may be held, the choice between many possible formulæ depending on the part assigned to the tin and to the hydrogen. Analogy may help us here, for catapleiite, a mineral of similar chemical composition, $H_4Na_2ZrSi_3O_{11}$, has been variously regarded; viz. as a hydrated metasilicate $Na_2Zr(SiO_3)_3.2H_2O$ by Rammelsberg;[5] as a basic meta-silicate $H_2Na_2[Zr(OH)_2]\ [SiO_3]_3$ by Brögger;[6] as a compound of an ortho- and meta-silicate $Na_2SiO_3.H_4Zr(SiO_4)_2$ by Dana;[7] and lastly as an acid salt of a tetrasilicic acid $H_4Na_2(Si,Zr)_4O_{11}$ by Groth.[8] According to the first three of these authors the zirconium is regarded as a base; whilst by Groth it is taken to replace silicon. Again, while Rammelsberg regards the water as water of crystallisation, the other authors look upon the hydrogen as part of the acid. Exactly similar formulæ may be written for stokesite when Zr is replaced by Sn, and Na_2 by Ca; and if the zirconium in catapleiite is playing the part of a metal, we have an equal right to assign the same part to tin in stokesite. If the hydrogen is present as water of crystallisation, we must either adopt the metasilicate formula, and regard the tin as metallic in function, or else look upon the compound as a derivative of a tetrasilicic acid, and write the formula thus: $Ca(SiSn)_4O_9.2H_2O$—a less plausible hypothesis.

In order to obtain, if possible, a clue to the most probable formula, a determination was made of the water driven off at different temperatures from the second portion of material analysed. The mineral remained

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[1] Breithaupt, *Pogg. Ann.* 1846, LXIX, 435.

[2] Bischof, *Jahrbuch f. Mineralogie*, 1854, 346; 1855, 841.

[3] Tschermak, *Sitz. Ber. d. k. Ak. d. Wiss.* Wien, 1864, XLIX (i), 330.

[4] Collins, *Min. Mag.* 1882, IV, 8, 109, 115.

[5] Rammelsberg, *Mineralchemie*, 2nd Suppl. 1895, p. 450.

[6] Brögger, *Zeits. f. Kryst.* 1890, XVI, 458.

[7] Dana, *Mineralogy*, 1892, p. 413.

[8] Groth, *Uebersicht der Mineralien*, 1898, p. 159.

unchanged at 100° C., heated to 220° C. it lost 1·9 per cent., at 350° C. the loss amounted to 6 per cent., and the rest of the water was given off between 350° C. and dull redness. From these numbers we may conclude that the water is not all present as water of crystallisation. The behaviour of catapleiite is strikingly similar,[1] and apophyllite, according to Hersch,[2] does much the same. In the latter case some of the hydrogen is believed to be present as water of crystallisation, the rest as acid hydrogen; and on looking at stokesite from this point of view we can regard it as an acid meta-disilicate, $H_2(Sn,Si)_2O_5,Ca(SnSi)_2O_5,H_2O$, or as $H_2CaSnSi_3O_{10}.H_2O$, a derivative of trisilicic acid. Lastly, if we conclude from the results above that no water of crystallisation is present, we may represent it either as a compound of a disilicate and an ortho-silicate, $H_4CaSi_2O_7,SnSiO_4$; or as $H_4Ca(SnSi)_4O_{11}$, a salt of a tetrasilicic acid; the latter view having perhaps the most to recommend it.

5. *Locality.*

The specimen is described in the catalogue of the Carne Collection as from Roscommon Cliff, St. Just. This cliff descends somewhat abruptly into the sea very nearly due west of Trewellard. On a hurried visit to the neighbourhood I was shown axinite *in situ* in several places on the cliffs, especially at "The Crowns," at Botallack Head, and near the bottom of Roscommon Cliff. A comparison of the matrix of stokesite with the axinite specimens from this district leaves no room for doubting that the locality given in the catalogue is correct.

A careful examination of the axinites in the collection at the British Museum and in the museums at Penzance, Camborne, Redruth and Truro, has unfortunately failed to bring to light any more specimens of this interesting mineral.

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[1] Brögger, *loc. cit.*, p. 457, found that catapleiite lost 1·66 per cent. at 220° C. and 7·1 per cent. at 270° C. out of a total percentage of 9·25.

[2] Hersch, *Inaug. Diss.*, Zürich, 1887, 26.