XVI.—*On some Hydrated Cupric Oxysulphates from Cornwall.*

By A. H. CHURCH.

Lyellite.—Not very long after his announcement of “Langite” as a new mineral species from Cornwall, Prof. Maskelyne pointed out a second copper compound, from the same locality, as distinct. This species he termed “Lyellite.” Three months later, M. Pisani gave an analysis of the same mineral; it will be found in the *Comptes Rendus*, of Nov. 14th, 1864. M. Pisani re-names the mineral “Devilline,” and deduces for it the formula :—

I purpose to employ the name *Lyellite*, as having priority.

I have received from Mr. Talling a portion of the same specimen of lyellite as that analysed by M. Pisani, and have submitted it to analysis. It is unnecessary to repeat in detail the physical and chemical characters of this new species of Prof. Maskelyne's; it will suffice to say here that the analysis of this mineral presents

some peculiar difficulties. For, intermixed with the true lyellite, which occurs in concretionary crusts of a very pale bluish white tint, and satiny lustre, is a darker blue mineral, apparently langite. This impurity occurs in layers, and is irregularly distributed in the whiter mineral; these layers are sometimes in the direction of the radiation, sometimes across it. Fortunately the blue mineral, being in loosely coherent masses of minute crystals, may be almost completely removed by breaking the mineral into small fragments, and carefully brushing these with a fine sable pencil. In this way my specimen was prepared for analysis, but it was not *quite* pure even then. I believe the only impurity was the blue mineral, and assuming this, as is most probable, to be langite, the discrepancies between the theoretical and experimental percentages are explained. Lyellite contains copper, calcium, a sulphate, and the elements of water. It contains also a minute trace of iron, so minute as to give no distinct reaction when a few grains of the mineral in solution were tested with potassic ferri-cyanide; and even after oxidation, the ferro-cyanide gave a faint blue coloration only.

The following are the results of the analysis of lyellite:—

·3245	gramme	lost <i>in vacuo</i>	·002	gramme	H ₂ O
·3225	„	gave	·184	„	BaSO ₄
·3225	„	„	·045	„	CaCO ₃
·3225	„	„	·165	„	CuO

These numbers correspond to the following percentages:—

Hygroscopic water	·62	per cent.
SO ₃	23·50	„
CaO.	7·81	„
CuO.	51·13	„

I have said that M. Pisani proposes for this mineral the formula—

We have, however, seen that it contains no iron, and the results of my analysis, which agree closely with those obtained by M. Pisani, correspond to a slightly modified formula. Annexed are the theoretical and experimental percentages.

Theory. ($\text{CuCa}_2\text{SO}_4 \cdot 3\text{CuH}_2\text{O}_2$, 3aq.)		Experiment.	
		Pisani.	Church.
4CuO	318 49·53	51·01	51·13
CaO	56 8·72	7·90	7·81
2SO ₃	160 24·90	23·65	23·50
6H ₂ O	108 16·95	16·60	16·88 (by diff.)
	<hr/> 642 100·00	<hr/> 99·16	<hr/> 0·68 (impurities).
		<hr/> FeO 2·77	<hr/> 100·00
		<hr/> 101·93	

It will be observed that the cupric oxide is in excess, while the calcium-oxide and sulphuric anhydride are deficient; the assumed admixture of the lyellite with a mineral evidently (from its deeper blue tint) richer in copper, will account for all these discrepancies—a very small percentage of langite would in fact produce this result.

Brochantite.—A mineral which appears to have the chemical characters of brochantite has been lately found in Cornwall. M. Pisani announced this discovery in the *Comptes Rendus* for Nov. 28th, 1864. Several formulæ have been proposed for the native and the artificial brochantites, but it has been remarked that this basic sulphate oscillated between—

my analysis points in the same direction; it suggests, however, the intermediate formula—

Before giving the analytical results, it may be stated that the brochantite often accompanies langite, the latter mineral being then seen as a scattered blue crust upon the dark green or emerald-green brochantite. I fear that the crystals in my specimens are too small and confused for accurate measurement. They are transparent, and occur in groups of slender wedges, tapering towards either extremity. Two of the boundaries of each crystal appear curved. Since my preliminary note on Cornish brochantite appeared in the *Chemical News* (Feb. 10th, 1865), this mineral has been described, under the name of Waringtonite, by Professor Maskelyne; it is unnecessary, therefore, to repeat here the physical characters of the substance; I will merely give the analytical results and the formula they

suggest. It ought to be stated that the utmost care was taken to obtain a homogeneous sample for analysis.

The brochantite occurs upon decomposing elvan, but immediately underneath the cupric crust, a considerable quantity of ferric oxide occurs. An impure cupreous wad also occasionally accompanies the brochantite.

6.73 grains lost	·07 grains at 260° C.
5.17 „ gave	·03 „ insoluble residue
5.17 „ „	2.85 „ BaSO ₄
6.73 „ „	4.62 „ CuO
5.17 „ „	3.51 „ CuO.

Before the mineral was submitted to analysis, it was placed over oil of vitriol *in vacuo*; but by this treatment it suffered no appreciable loss. Below are given the percentage numbers deduced from the foregoing analyses. In the first column the percentages are those deduced directly; in the second column the calculations have been made, after subtraction of the water lost at a temperature not exceeding 260° C.,* and of the insoluble matter:—

CuO.....	68.27	69.32
SO ₃	18.93	19.24
H ₂ O.....	11.18	11.44
H ₂ O lost below 260°	1.04	
Insoluble matter.....	·58	100.00
	<hr/>	
	100.00	

The formula 2CuSO₄.5CuH₂O₂, requires percentages closely corresponding with those deduced from the analyses:—

	Theory.	Experiment.
CuO.....	69.00	69.32
SO ₃	19.84	19.24
H ₂ O.....	11.16	11.44

The differences, it will be observed, all lie in the direction of the probable experimental errors. In an analysis not recorded above, 6.73 grains of the mineral gave 3.39 grains of BaSO₄; this corresponds to 17.3 per cent. of SO₃. But with the lower estimate of the SO₃, the *total* percentage of water in the mineral, calculated by difference, amounts to no more than 13.48; in the second analysis it is only 12.6. These numbers exclude the formula CuSO₄.3CuH₂O₂.aq., which demands 15.34 p.c. H₂O, as the following comparisons show. It must be remembered that the

* Some specimens lose nothing at this temperature.

mineral under review loses sulphuric acid as well as water when heated sufficiently to deprive it of all water; the water in it is retained even at 260°—270°C.

	Theory.			Experiment.		
	I. CuSO ₄ 3CuH ₂ O ₂ .	II. CuSO ₄ 3CuH ₂ O ₂ aq.	III. 2CuSO ₄ 5CuH ₂ O ₂ .	I. Pisani.	II. Maskelyne.	III. Church.
CuO ..	70·36	67·62	69·00	70·06	68·24	69·32
SO ₃ ..	17·70	17·04	19·84	17·52	16·73	19·24
H ₂ O ..	11·94	15·34	11·16	13·42	14·64	11·44

Collating the recent with the older analyses of Brochantite,* there seems some ground for the opinion that at least two substances, chemically distinct, have been included under one name. If such be the case, Prof. Maskelyne's Waringtonite might be separated chemically as well as crystallographically from Brochantite, although his proposed formula (II. above) is negatived by both of my analyses, and as well as by those of M. Pisani. One hesitates, indeed, between the formulæ I. and III., but it is possible that M. Pisani may not have analysed the true wedge-shaped crystals of so-called Waringtonite, but the commoner form of Brochantite occurring in the same locality.

For the analysis of the variety or species Waringtonite, I am indebted to my assistant, Mr. R. Warington, junior.

Langite.—According to M. Pisani, langite has the formula CuSO₄·3CuH₂O₂. aq., the very expression assigned to Waringtonite by Prof. Maskelyne. My own results confirm those of M. Pisani. A few words are necessary as to the material submitted to analysis.

Langite appears both in minute prismatic crystals of a fine blue colour, and also as a foliated crystalline mass. The latter form is the more abundant, and having freed some specimens of it from a few imbedded crystals of the deeper colour, I submitted them to analysis, with the following results:—

a.	{	1·024	gramme	lost in vacuo	·004	gramme	H ₂ O
Air	{	1·024	„	gave	·691	„	CuO
dried.	{	1·024	„	„	·501	„	BaSO ₄
b.	{	14·09	grains	lost at 100° C	·12	grains	H ₂ O
Vacuum	{	14·09	„	below redness	2·29	„	H ₂ O
dried.	{	14·09	„	gave	6·86	„	BaSO ₄

* Rammelsberg's *Mineralchemie* (1860), p. 268.

$\left. \begin{array}{l} c. \\ \text{Dried at} \\ 100^{\circ} \text{C.} \end{array} \right\} \begin{array}{l} 12.3 \text{ grains gave} \\ \\ \end{array} \qquad \begin{array}{l} 8.35 \text{ grains CuO} \end{array}$

I made the analyses of *a*; *b* and *c* were analysed by Mr. Warington. The following are the percentages deduced from the several analyses, calculating the results on the vacuum-dried substance, and also on the substance as dried at 100°C. :—

		Dried <i>in vacuo</i> .		Dried at 100°C.
		A. H. C.	R. W.	R. W.
CuO	..	67.48	67.31	67.88
SO ₃	..	16.79	16.72	16.88
H ₂ O	..	15.73	16.25	15.53
		<hr/> 100.00	<hr/> 100.28	<hr/> 100.29

These numbers correspond very closely with those required by the formula $\text{CuSO}_4.3\text{CuH}_2\text{O. aq.}$:—

					Mean (vacuum dried).
4CuO	..	318	=	67.65	67.40
SO ₃	..	80	=	17.02	16.76
4H ₂ O	..	72	=	15.33	15.89
		<hr/> 470		<hr/> 100.00	<hr/> 100.05

The results of independent analyses by M. Pisani, Mr. Warington, and myself, are so exactly accordant, that there cannot be the slightest doubt that the blue foliæ said to be langite are definite in composition, and that the formula expressing the composition of the mineral is $\text{CuSO}_4.3\text{CuH}_2\text{O}_2.\text{aq.}$ All the slight differences between the theoretical and experimental percentages lie in the direction of the several probable errors; and the loss of water *in vacuo* amounting to no more than .39 per cent., it cannot be said that the mineral has been altered by the method of desiccation adopted. The total amount of impurities in the mineral was found by experiment to be very insignificant, yet, if allowance had been made for it, a still closer coincidence between theory and experiment would have been shown.

It is scarcely necessary to add that all the analyses recorded in the present paper were performed with the greatest care; the reagents were pure, and the methods known to be trustworthy.