Communications from the Oxford Mineralogical Laboratory.

On the constitution of the mineral Arsenates and Phosphates.

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Part I.—*Chalcophyllite.*

THIS mineral was originally described as a hydrated copper-arsenate. Analyses of copper-arsenate are given as far back as 1801 by Vauquelin (*Journ. des Mines*, 1801, X. 562), and by Chenevix in the *Philosophical Transactions* (for 1801); but at this early date the analyses seem to refer partly to chalcophyllite and partly to olivenite.

Subsequently analyses have been published by Hermann, Damour and Church –(1) Hermann, *Journ. prakt. Chem.* 1844, XXXIII. 294; (2) Damour, *Ann. Chem. Phys.* 1845, XIII. 413; (3) Church, *Journ. Chem. Soc.*, 1870, VIII, 168.

	As_2O_5	P_2O_5	CuO	H_2O	Al_2O_3	FeO	
Hermann	17·51	undet.	44·45	31·19	3·93	2·92	=100
Damour (i)	19·35	1·29	52·92	23·94	1·80	—	= 99·3
,, (ii)	21·27	1·56	52·30	22·58	2·13	—	= 99·84
Church	15·54	—	46·1	(31·75)	5·97	—	= 99·4

From the last analysis Church deduced the formula—

$$8CuO.Al_2O_3.As_2O_5.24H_2O \text{ (or } 25H_2O).$$

In Hermann's and Damour's analyses the water was determined by loss of weight on heating the mineral, but this method is not satisfactory, as there is always the risk of minerals of this class losing arsenic on ignition. Church only estimated the water by difference. It therefore seemed advisable to make a fresh analysis of this mineral, especially with a view to estimating the water directly.

Though the exact locality of the mineral used for analysis is uncertain, the specimens were undoubtedly old Cornish specimens, and consisted of fine pale emerald-green crystals implanted on massive cuprite, and associated with quartz and traces of malachite and chessylite.

The portion taken for analysis was very carefully picked under the microscope, and consisted entirely of clear crystals, free from any inclusions except a few minute black specks which were visible in some of the crystals.

Although the mineral loses nearly 18 per cent. of water at 100 C., no change in its optical properties was observed when the crystals were heated on a sheet of mica supported over the stage of a polarising microscope until a considerable temperature was reached, when they suddenly became opaque and cracked. Under these circumstances they appeared nearly black, but when examined in sufficiently thin flakes they were seen to be yellow and devoid of double refraction. No further change was produced when the fragments were immersed in water.

A qualitative analysis was made to see if iron or phosphoric acid were present, but neither of these substances was found.

Analysis.

The water was determined by heating a weighed portion of the mineral in a porcelain boat in a hard glass tube, and collecting the water given off in a weighed calcium chloride tube.

To prevent any arsenious oxide from passing over with the water, a layer of about two inches of a mixture of lead oxide and dioxide was interposed between the boat and the calcium chloride tube. This layer was heated by means of a broad luminous flame kept about 1 inch below the tube, and it has been found that in this way all arsenic is kept back while the water passes over.

With regard to the rest of the analysis, the arsenic acid was reduced with sulphurous acid, and the copper and arsenic precipitated together in a strongly acid solution with sulphuretted hydrogen. The arsenic sulphide was dissolved out as far as possible by sodium sulphide, and the copper was redissolved and reprecipitated in one case as oxide, and in the other as sulphide, and weighed as such.

The alumina was estimated in the filtrate from the copper and arsenic by evaporating and precipitating with ammonia.

The arsenic acid was estimated in a separate portion by direct precipitation with magnesia mixture, a small quantity of tartaric acid having been added to prevent the simultaneous precipitation of alumina or copper. The percentages thus found from the analysis showed a deficit of about 7 per cent.; it was then found that sulphuric acid is present as a constituent of this mineral in such a proportion as exactly to account for the deficit. It is remarkable that this constituent has been entirely overlooked by previous analysts.

The analytical numbers are as follows:—

$$\left.\begin{array}{l}\cdot 2192 \text{ grm. lost at 100 C. } \cdot 0393 \text{ grm. } H_2O = 17\cdot 93\ \% \\ \text{and gave further on ignition } \cdot 0233 \text{ ,, } H_2O = 10\cdot 63\ \%\end{array}\right\} 28\cdot 56\ \%\ H_2O$$

·2271 grm.	gave	·0643	H_2O	corresponding to	28·31	%	H_2O
·2003	,,	·0559	H_2O	,,	27·91	,,	H_2O
·3436	,,	·1582	CuO	,,	46·04	,,	CuO
		·0163	Al_2O_3	,,	4.74	,,	Al_2O_3
·2632	,,	·1206	Cu_2S	,,	45·82	,,	CuO
		·0125	Al_2O_3	,,	4.74	,,	Al_2O_3
·2828	,,	·0559	$Mg_2As_2O_7$	,,	14·66	,,	As_2O_5
·2409	,,	·0463	$Mg_2As_2O_7$	,,	14·26	,,	As_2O_5
·3652	,,	·0759	$BaSO_4$	,,	7·13	,,	SO_3
·2423	,,	·0491	$BaSO_4$	,,	6·96	,,	SO_3

Taking the mean of these results the following numbers are obtained :—

(Water lost at 100 C., 17·93.)

Total H_2O	28·26
CuO	45·93
Al_2O_3	4·74
As_2O_5	14·46
SO_3	7·04
	100·43

It seems impossible to deduce a simple formula for the mineral from these numbers, which give the following molecular ratios for the different constituents :—

H_2O	1·57
CuO	·58
Al_2O_3	·046
As_2O_5	·062
SO_3	·088

It is therefore desirable that further analyses of chalcophyllite from some other localities should be made, with a view to finding variations in the proportions of some of the constituents which might throw light on the true constitution of this mineral.

The specimens of chalcophyllite used in the preceding investigation were from the mineral collection in the Oxford University Museum, and the analyses were made in the laboratory of the Mineralogical Department.