

*Communications from the Oxford Mineralogical Laboratory.*  
*On the constitution of the natural Arsenates and Phosphates.*

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PART II.—*Pharmacosiderite.*

THIS mineral, which until now has been regarded as a hydrated arsenate of iron, was mentioned as far back as 1790 by Proust and also by other mineralogists about the same time. In 1801 Chenevix (*Phil. Trans.* 1801, 220) gave an analysis of an arsenate of iron, but it differs very much in composition from pharmacosiderite in that it contained 9 per cent. of copper. Probably it was not a pure specimen of this mineral. Vauquelin also published an analysis of an iron arsenate which was probably pharmacosiderite (Brongniart, *Traité de Min.*, 1807, II. 182), since he describes it as crystallising in cubes. He gave the following numbers:—

$\text{Fe}_2\text{O}_3$	...	= 48	per cent.
$\text{As}_2\text{O}_5$	...	= 18 to 20	„
$\text{H}_2\text{O}$	...	= 32	„
$\text{CaCO}_3$	...	= 2	„

Neither of the above analyses referred to is satisfactory, as at that early date exact analytical methods of separating iron and arsenic acid were not known.

Berzelius (*Akad. Handl. Stockholm*, 1824, 354) published an analysis of pharmacosiderite, giving the following numbers:—

$\text{As}_2\text{O}_5$	...	= 37.82	per cent.
$\text{P}_2\text{O}_5$	...	= 2.53	„
$\text{Fe}_2\text{O}_3$	...	= 39.20	„
$\text{CuO}$	...	= .65	„
$\text{H}_2\text{O}$	...	= 18.61	„
Residue	...	= 1.76	„
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		100.57	„

This corresponds approximately to the formula  $4\text{Fe}_2\text{O}_3 \cdot 3\text{As}_2\text{O}_5 \cdot 15\text{H}_2\text{O}$ , for which the following are the percentages:—

$\text{As}_2\text{O}_5$	...	= 48.1
$\text{Fe}_2\text{O}_3$	...	= 40.0
$\text{H}_2\text{O}$	...	= 16.9

Since this analysis was not altogether satisfactory, and a simple formula cannot be readily deduced from the numbers, it seemed desirable to make a further analysis of the mineral.

The specimens taken for this purpose were from the mineral collection in the Oxford University Museum. They were certainly old Cornish specimens.

Green crystals were chosen as far as possible, as they seemed to be the purest and least altered, and the portion taken for analysis was carefully picked out under the microscope. An examination of some very fresh-looking brown crystals on one specimen showed that the brown colour was only due to surface alteration, since on crushing them they could be seen under the microscope to be nearly all green, with thin flakes of the brown material.

The specific gravity of the material analysed was found to be 2.798; the determination was made by means of a diffusion column of benzene and methylene iodide, by comparing the depths at which the mineral and beads of known specific gravity remained suspended.

The crystals analysed all showed the usual weak birefringence of pharmacosiderite, and a banded structure parallel to the cube faces was clearly visible between crossed nicols.

The following curious property of this mineral was observed.

On letting a good sized crystal stand for a few minutes in a solution of ammonia, the whole crystal became red, and afterwards, even when it was powdered as fine as possible, no green fragments could be seen remaining even in the middle of the crystal. The transparency of the crystal was not in the least degree affected by this treatment, neither were the optical characters altered. On allowing such a red crystal to stand in dilute hydrochloric acid for the same time, the green colour was restored to the whole crystal.

This experiment seems to show that the crystal is permeable to such liquids, though no pores are visible.

With regard to the water in pharmacosiderite, there is no doubt that some of it is only very loosely held. Experiments were made to ascertain the effect of different degrees of heat upon the crystals.

First the loss of weight of the mineral was determined, when finely powdered and subjected to a current of dry air; then the loss of weight

at 100° C.; and the loss of weight at about 180° C., at which temperature the crystals begin to turn brown.

Finally the total water was determined by igniting a weighed quantity of the mineral and weighing the water liberated.

The apparatus used was similar to that employed in the analysis of chalcophyllite (*Min. Mag.* 1899, XII. 121), a mixture of lead oxide and dioxide being used to retain the arsenic.

With regard to the rest of the analysis, the arsenic acid was estimated either by precipitation as sulphide and oxidation of the latter to arsenic acid by means of fuming nitric acid, and finally by precipitation as magnesium ammonium arsenate, or else by precipitation together with phosphoric acid directly, as the magnesium ammonium salt, in the presence of sufficient ammonium tartrate to prevent simultaneous precipitation of the iron. The iron and phosphoric acid were precipitated by ammonia when the arsenic had been removed as sulphide. They were then weighed together, and the phosphoric acid was afterwards separated from the iron by the molybdate method and thus estimated, its weight being then deducted from the combined weights of iron and phosphoric acid.

Since the colour of the crystals might suggest the presence of ferrous iron as a constituent of the mineral, some experiments were made in which a portion was dissolved in dilute sulphuric acid in an atmosphere of carbonic acid gas, and the solution tested with very dilute solution of potassium permanganate. Only two or three drops at most were decolourised by about half a gram of the mineral, so that only the merest traces of ferrous iron can be present.

#### *Preliminary Analyses (I and II).*

After making two analyses by these methods, a considerable deficit was noticed, and a more complete qualitative analysis revealed the presence of a small quantity of potash. This constituent was estimated in two separate portions as potassium platonic chloride. The first estimation was made on material from one of the specimens used in the previous analyses, but it is not certain to which it belongs, as it was picked from some fragments that had been kept from the previous analyses. The second determination of potash had to be made from another specimen altogether, of which there was not sufficient to make a complete analysis. The deficit was at first regarded as only due to experimental errors, and so most of the material at hand had been sacrificed for the other estimations; but the existence of potash was established in all the Cornish

specimens examined, and on p. 157 will be found a complete determination of all the constituents from a single specimen.

The analytical numbers are as follows :—

*Estimation of Water.*

·2749 gram lost in dry air	·0044 gram H <sub>2</sub> O,	corresponding to 1·60 %
·2749            ,,   at 100° C.	·0268            ,,            ,,	9·75   ,,
·3198            ,,   in dry air	·0027            ,,            ,,	·84   ,,
·3198            ,,   at 100° C.	·0816            ,,            ,,	9·88   ,,
·3990            ,,   at 186° C.	·0571            ,,            ,,	14·81   ,,
·2216            ,,   at 180° C.	·0826            ,,            ,,	14·71   ,,
·3990            gave on ignition	·0784            ,,            ,,	19·65   ,,
·2069            ,,   on ignition	·0402            ,,            ,,	19·42   ,,

The above determinations were made on different specimens.

The next two analyses (I and II) were made on portions of two specimens respectively.

*Estimation of remaining constituents.*

I.

·2715 gram lost in dry air	·0022 gram H <sub>2</sub> O	corresponding to ·81 % H <sub>2</sub> O
·2715            ,,   at 150°	·0367            H <sub>2</sub> O	13·52   ,, H <sub>2</sub> O
·2715            ,,   on ignition	·0533            H <sub>2</sub> O	19·63   ,, H <sub>2</sub> O
·3136            gave	·1582            Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub>	37·53   ,, As <sub>2</sub> O <sub>5</sub>
·3136            ,,	·0100            Mg <sub>3</sub> F <sub>2</sub> O <sub>7</sub>	2·04   ,, P <sub>2</sub> O <sub>5</sub>
·3136            ,,	·1232            Fe <sub>2</sub> O <sub>3</sub>	39·29   ,, Fe <sub>2</sub> O <sub>3</sub>

II.

·3603 gram gave	·1398 gram Fe <sub>2</sub> O <sub>3</sub>	corresponding to 38·81 % Fe <sub>2</sub> O <sub>3</sub>
·3603            ,,	·0113            Mg <sub>3</sub> F <sub>2</sub> O <sub>7</sub>	2·06   ,, P <sub>2</sub> O <sub>5</sub>
·3027            ,,	·1504            Mg <sub>3</sub> As <sub>2</sub> O <sub>7</sub>	36·85   ,, As <sub>2</sub> O <sub>5</sub>

*Estimation of potash (a) on material used in the preceding analyses ;*

*(b) on new material.*

(a) ·6082 gram gave	·1288 gram (KCl) <sub>2</sub> ·PtCl <sub>4</sub>	corresponding to 4·12 K <sub>2</sub> O
(b) ·3136            ,,	·0434            (KCl) <sub>2</sub> ·PtCl <sub>4</sub>	2·68 K <sub>2</sub> O

In Analysis II the proportion of water was not estimated, since it was abundantly clear from the preceding three determinations that the percentage of water is constant.

The following are the numbers obtained from the preceding analyses:—

	I.	...	II.	...	Mean result of water estimations.		
Total H <sub>2</sub> O	19·63	...	[19·63]	...	Total water	...	19·63
As <sub>2</sub> O <sub>5</sub>	37·53	...	36·85	...	Water lost at about		
P <sub>2</sub> O <sub>5</sub>	2·04	...	2·06	...	130°	...	14·18
Fe <sub>2</sub> O <sub>3</sub>	39·29	...	38·81	...			
	<hr/>		<hr/>				
	98·49		97·85				
Deficit ...	1·51	...	2·65	...			
	<hr/>		<hr/>				
	100·00		100·00				

Since the deficit in these two analyses differs considerably, and since the percentages of potash determined directly in two different specimens are not at all in accordance, it is fair to assume that this constituent is very variable, and in fact two specimens from Königsberg, Hungary, were examined, and found to contain only a trace of potash.

If we consider the water contained in this mineral, it seems impossible to regard any of it as accidental, since while slight variations occur in the percentages under the varying conditions of the above experiments, the total amount seems to remain constant; and in the case where one sample lost more than another in a current of dry air, it lost less at 100° C., so that these results probably depend partly on the fineness of division of the powdered substance.

Nor does the exact percentage of water lost at 100° C. appear to have much significance, since the crystals hardly alter in appearance at this stage.

A real change, however, seems to begin to take place at 130°, as at this point the crystal liberates sufficient water to lose its transparency and green colour. It therefore seems that the percentage of water lost at about 130° should be taken into account in deducing a formula for this mineral.

#### *Complete Analysis (III).*

A subsequent and complete analysis of pharmacosiderite made on another Cornish specimen showed it to contain a slightly higher percentage of potash than any of the previously examined specimens.

The percentage of water was somewhat lower in this sample than in the others, which is remarkable, as it seemed to be constant in the three former determinations. The numbers obtained were as follows:—

## III.

·3398	gram gave	·1702	$Mg_2As_2O_7$	=	37·16	per cent.	$As_2O_5$
·3347	„	·0631	$H_2O$	=	18·85	„	$H_2O$
·3347	„	·1258	$Fe_2O_3$	=	37·58	„	$Fe_2O_3$
·3347	„	·0063	$Mg_2P_2O_7$	=	1·20	„	$P_2O_5$
·3243	„	·0761	$(KCl)_2PtCl_4$	=	4·54	„	$K_2O$
					<hr/>		
					99·93		

In proposing a formula for this mineral it is of course impossible to express in any molecular proportions the ratio between the potash and the iron, since the former is such a variable constituent. It is, however, possible to construct a formula which would express the constitution of the mineral if free from potash altogether, and to make a suggestion as to the part played by the potash.

The formula, which satisfies the ratios between the iron, arsenic acid and water, is  $3Fe_2O_3 \cdot 2As_2O_5 \cdot 18H_2O$ , or  $2FeAsO_4 \cdot Fe(OH)_3 \cdot 5H_2O$ , in which the 5 molecules of water (15·53 per cent.) lost at about  $180^\circ$  are expressed as water of crystallisation. This gives the following percentages :

Total water	...	...	19·94	per cent.
$Fe_2O_3$	...	...	40·88	„
$As_2O_5$	...	...	39·18	„
			<hr/>	
			100·00	

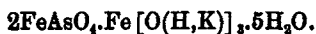
The only way in which the potash can be brought into this formula is by supposing that some of the hydrogen in the hydroxyl groups is replaced by potassium. This would explain why, in the specimen, which contained most potash, all the other constituents showed a smaller percentage. If, on the other hand, the potash be considered to be present as potassium arsenate, forming a double salt with the iron arsenate, the percentage of arsenic acid ought to be higher in those specimens which contain most potash, but it is seen in fact that the ratio of iron, water and arsenic acids remains fairly constant in all cases.

An additional piece of evidence may be adduced in favour of the view that potash is an essential constituent of the Cornish pharmacosiderite, and not merely an impurity, though it may be present only in very small quantities.

While picking out material for the last analysis, it was found that the pharmacosiderite was closely associated with scorodite. Some of the latter was carefully picked out, but was found to be absolutely free from potash. Here then is a case of the two arsenates of iron side by side,

one containing potash in considerable quantity, and the other containing none. It may also be mentioned that one of the Königsberg specimens somewhat differed in crystalline form from the Cornish specimens, owing to the presence of tetrahedron faces; and this difference may possibly be related to the very small percentage of potash which it contained. The other Königsberg specimen, though it appeared to resemble the Cornish crystals in form, was considerably "weathered."

The final result of the above investigation is to propose the following formula as best representing the properties and constitution of pharmacosiderite:—



*Note.*—The presence of potassium was established by means of the microchemical test in all the specimens of pharmacosiderite examined. It is sufficient to immerse a fragment of the mineral in a drop of dilute hydrochloric acid and to add a drop of platinum chloride in order to obtain the characteristic octahedra of potassium platonic chloride.

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