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On the constitution of the natural Arsenates and Phosphates.

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Part III.—*Plumbogummite and Hitchcockite.*

THE present paper deals with the somewhat obscure lead aluminium phosphates, of which the following varieties have hitherto been described :—

(i) The original plumbogummite, a mineral found at Huelgoat in Brittany, and at Nuissière, Dept. Rhône.

(ii) Some varieties of pyromorphite, containing alumina and water as constituents. These pyromorphites occur also at Huelgoat, and are usually quoted in books on Mineralogy as plumbogummite, although Damour, in his original paper on the subject, clearly distinguishes between the true plumbogummite and the aluminous pyromorphites.

(iii) The American mineral, hitchcockite, occurring in the Canton Mines, Georgia.

(iv) A Cumberland mineral, which for some time was mistaken for zinc silicate, but has recently been shown to be a phosphate of lead and aluminium (Miers, *Min. Mag.* 1896, XI, 272).

The want of agreement in the old analyses of plumbogummite, and the possibility of finding some relationship between it and the Cumberland mineral, of which no quantitative results have been published, made it desirable both to repeat the analysis of the former and to make for the first time a complete analysis of the latter.

Finally, a further examination of the American mineral was undertaken, in order to complete the revision of these phosphates.

The present paper is divided into four parts :—

(*a*) A history of previous work.

(*b*) A short account of the analytical methods adopted.

(*c*) The results of the present investigation.

(*d*) Theoretical considerations as to the constitution of the several minerals.

(*a*) *History.*

Plumbogummite was described by Romé de Lisle in 1779 (*Cristallographie*, 1783, III, 399). The first published analysis is by Berzelius (*Ann. des Mines*, 1820 [1], V, 245), and was made on a specimen from Huelgoat. He obtained the following numbers :—

PbO	40·14
Al_2O_3	37·00
H_2O	18·80
SO_3	·20
CaO,MnO,Fe_2O_3	1·80
SiO_2	·60
	98·54

In this analysis phosphoric acid was entirely overlooked, and, as stated by Damour, it was doubtless weighed with the alumina.

In 1835 Dufrénoy published an analysis of plumbogummite from Nuissière, Dept. Rhône (*Ann. des Mines*, 1835 [3], VIII, 243). He regarded the phosphoric acid as an impurity, and appears not to have taken sufficient care to separate it from alumina. His results were :—

SiO_2	2·11
Al_2O_3	34·23
PbO	43·42
P_2O_5	1·89
H_2O	16·14
Loss	2·21
	100·00

In 1840 Damour (*Ann. des Mines*, 1840 [3], XVII, 191) gave a further analysis of plumbogummite from Huelgoat, and also of two pyromorphites from the same locality containing aluminium hydrate.

These analyses were as follows :—

	Plumbogummite.	Aluminiferous pyromorphites.	
		(1)	(2)
$PbCl_2$	2·27	8·24	9·18
P_2O_5	8·06	12·05	15·18
PbO	35·10	62·15	70·85
CaO	·80	—	—
Al_2O_3	34·32	11·05	2·88
H_2O	18·70	6·18	1·24
Fe_2O_3	·20	—	—
SO_3	·30	·20	·40
	99·75	99·92	99·73

From these results Damour suggests that plumbogummite is nothing more than a pyromorphite containing a large quantity of aluminium hydrate.

He criticises Dufrénoy's paper, pointing out that he has in all probability overlooked the greater part of the phosphoric acid.

It seems possible, however, that Damour's method of separating alumina from phosphoric acid was not altogether satisfactory. He fused the mineral with sodium carbonate and nitre, dissolved the mass in water, and after removing any lead remaining in solution by ammonium sulphide, he heated the liquid to boiling, and gradually added excess of pure silica, which, he said, precipitates all the alumina, leaving the phosphoric acid in solution. The separation of these substances by means of ammonium molybdate is probably much more exact.

No analysis of the plumbogummite from Huelgoat or Nuissière has been published since this date.

Hitchcockite has only been described hitherto as occurring in one locality, the Canton Mines, Georgia.

It was first mentioned by Shepard in 1856 (*Rep. Canton Min. Ga.*, 1856). He gave no analysis, but stated that it lost 27 per cent. on ignition. In 1857 Genth (*Am. J. Sci.* 1857, xxiii, 424) published the following analysis of hitchcockite :—

PbO	29·04	per cent.
Al_2O_3	25·54	,,
P_2O_5	18·74	,,
H_2O	20·86	,,
Fe_2O_3	·90	,,
CaO	1·44	,,
CO_2	1·98	,,
Cl	·04	,,
Insoluble Residue	·48	,,
	99·02	

These numbers agree fairly well with the formula $PbO.2Al_2O_3.P_2O_5.9H_2O$, for which the percentage composition is:—

P_2O_5	19·4
Al_2O_3	27·9
PbO	30·5
H_2O	22·2
	100·0

(b) *Analytical Methods.*

The constituents to be determined in these minerals were lead oxide, alumina, phosphoric acid, carbonic acid and water in all cases, while chlorine and a small quantity of sulphuric acid were found in addition in plumbogummite and an accompanying aluminiferous pyromorphite.

The water and carbonic acid were determined by heating to redness a portion of the mineral in a hard glass tube in a current of dry air free from CO_2, and weighing the products in a calcium chloride tube and potash bulbs respectively. The lead was either estimated by precipitation as sulphide from a dilute hydrochloric acid solution, in which case it was re-dissolved, precipitated as carbonate and weighed as oxide, or it was in some cases separated and weighed as sulphate. The alumina in the filtrate from the lead was precipitated with ammonia after separating the phosphoric acid by means of metallic tin in a strong nitric acid solution (Girard's method). The phosphate of tin was dissolved in ammonium sulphide, and the phosphoric acid precipitated by magnesia mixture. This method was not altogether satisfactory, and it was found better to precipitate the alumina and phosphoric acid together with ammonia and weigh them, subsequently deducting the weight of phosphoric acid as found by the molybdate method in a separate portion. In the case of the aluminiferous pyromorphite, where the phosphoric acid was in large excess of the alumina, the precipitate formed when ammonia was added to the filtrate from lead sulphide was weighed and calculated as $AlPO_4$, the residual phosphoric acid in the filtrate being then thrown down by magnesia mixture.

With regard to the estimation of chlorine, it was found best to dissolve the mineral in dilute nitric acid under pressure in a sealed tube, as it was only soluble in the ordinary way by boiling for a long time with strong nitric acid, in which process there might be a considerable loss of chlorine.

(c) *Results of the present investigation.*

(i) The Cumberland mineral.

This mineral occurs apparently only at the old Roughten Gill lead mines, which were worked about thirty years ago in the neighbourhood of Caldbeck, Cumberland.

It varies in colour from a very faint lavender to a beautiful bright smalt blue, and occurs sometimes as a thin crust overlying vein quartz, and sometimes intimately mixed with minute quartz crystals, and constituting the main mass of the vein stuff. The colour is probably due to a small amount of copper which it contains, though in too small a quantity to estimate satisfactorily. It is difficult to separate mechanically the phosphate mineral from intermixed quartz, but since it is readily soluble in strong hydrochloric acid, a chemical separation was easily effected.

The specimen taken for analysis contained about ten per cent. of quartz, but so far as could be seen no other impurity, being quite transparent and free from inclusions. The quartz is visible under the microscope.

The specific gravity was not ascertained owing to the great difficulty in separating sufficient material in an absolutely pure condition.

The following is the result of the analysis :—

·2022	of a gram	gave	·0263 H_2O	=13·01	per cent.	H_2O
·2022	,,	,,	·0064 CO_2	= 3·16	,,	CO_2
·3188	,,	,,	·0388 H_2O	=12·44	,,	H_2O
·3188	,,	,,	·0096 CO_2	= 3·08	,,	CO_2
·3188	,,	,,	·1561 $PbSO_4$	=36·84	,,	PbO
·3041	,,	,,	·1132 PbO	=37·23	,,	PbO
·3041	,,	,,	·0874 Al_2O_3	=28·74	,,	Al_2O_3
·3041	,,	,,	·0892 $Mg_2P_2O_7$	=18·76	,,	P_2O_5
·2396	,,	,,	·0694 $Mg_2P_2O_7$	=18·52	,,	P_2O_5

		I.	II.	III.	IV.	Mean.
H_2O	...	13·01	12·44	—	—	12·73
CO_2	...	3·16	3·08	—	—	3·12
PbO	...	—	36·84	37·23	—	37·03
Al_2O_3	...	—	—	28·74	—	28·74
P_2O_5	...	—	—	18·76	18·52	18·64
						100·26

Traces of copper and arsenic acid were also present. No water was lost by the mineral in dried air or at 100°C.

(ii) Hitchcockite, from Canton Mine, Georgia.

The specimens of this mineral taken for analysis consisted of a very thin whitish crust coating a granular mixture of galena and quartz, with some iron and copper pyrites. It was not found possible to obtain this in as pure a condition for analysis as the previous mineral, and the quantities available were very small. The crystalline material was picked out as carefully as possible under a microscope, but it contained some exceedingly minute black inclusions, which could not be completely removed. The numbers obtained on analysis were as follows:—

·2375	of a gram	gave	·0816	PbO ...	=34·36	per cent.	PbO
·2375	,,	,,	·0700	Al_2O_3 ...	=29·48	,,	Al_2O_3
·3030	,,	,,	·0084	CO_2 ...	= 2·77	,,	CO_2
·3030	,,	,,	·0446	H_2O ...	=14·71	,,	H_2O
·3030	,,	,,	·0025	Insoluble Residue	= ·82	,,	Residue
·3030	,,	,,	·0833	$Mg_2P_2O_7$ ...	=17·58	,,	P_2O_5
					99·72		

(iii) Plumbogummite, from Huelgoat.

The specimen of plumbogummite examined consisted evidently of two sorts of material, one being a dark-brown gum-like substance, transparent, and showing a crystalline structure under the microscope. The second mineral was much lighter coloured, and occurred mostly as a crystalline crust, but some minute crystals of this material, situated in a small cavity, were examined by Professor Miers, and proved to be hexagonal, with angles near those of pyromorphite. Unfortunately these did not occur in sufficient quantity even for a qualitative analysis. Of the two minerals, the first agrees completely in appearance with the published description of the original plumbogummite. In the course of analysis it was found to contain some organic matter, since on heating it turned black and smelt like charred paper. Unfortunately this was not discovered till the last portion was being used for the estimation of carbonic acid and water by the method given above, so that it was impossible to distinguish accurately between the percentage of carbonic acid and water, present as such in the mineral, and the percentage which was due to the oxidation of the organic carbon and hydrogen. So far as could be judged, however, by the difference between the loss of weight of the mineral on heating and the gain of weight of the absorption tubes, the organic matter must have amounted to about one per cent.

The analytical results were as follows :—

(*a*) The dark mineral.

I.

·3540 of a gram	gave ...	·0042 AgCl	= ·29	per cent.	Cl
·3641 ,,	,, ...	·0528 H_2O	=14·50	,,	H_2O
·3641 ,,	,, ...	·0167 CO_2	= 4·59	,,	CO_2
·3641 ,,	,, ...	·1046 $Mg_2P_2O_7$	=18·37	,,	P_2C_5
·3980 ,,	,, ...	·1721 PbO	=43·24	,,	PbO
·3980 ,,	,, ...	·0758 Al_2O_3	=19·04	,,	Al_2O_8
·3797 ,,	lost at 100° C.	·0195 H_2O	= [5·13]	,,	H_2O
			100·03		

II.

·4415 of a gram	gave ...	·0123 $BaSO_4$	= ·96	per cent.	SO_3
·4415 ,,	,, ...	·0028 AgCl	= ·16	,,	Cl
·4415 ,,	,, ...	·1321 $Mg_2P_2O_7$	=19·14	,,	P_2O_5
·4332 ,,	lost at 100° C.	·0208 H_2O	= 4·80	,.	H_2O
·4332 ,,	gave on ignition	·0461 H_2O	=10·64	,,	H_2O
·4332 ,,	,, ,,	·0202 CO_2	= 4·66	,,	CO_2
·4332 ,,	,, ...	·2290 $PbSO_4$	=38·91	,,	PbO
·4332 ,,	,, ...	·0909 Al_2O_3	=20·98	..	Al_2O_3
			100·25		

The percentages in both analyses should doubtless amount to a somewhat higher total, since some of the CO_2 and H_2O is derived from carbon and hydrogen in a lower state of oxidation.

The interpretation of these analyses will be discussed below.

(*b*) The light coloured mineral.

·5621	of a gram	gave	·0025 CO_2	= ·44	per cent.	CO_2	
.5621	,,	,,	·0110 H_2O	= 1·96	,,	H_2O	
·3436	,,	,,	·0322 AgCl	= 2·32	,,	Cl	
·3436	,,	,,	·2609 PbO	=75·93	,,	PbO	
·3436	,,	,,	·0228 $AlPO_4$	= 2·76	,,	Al_2O_3	
				3·86	,,	P_2O_5	17·02
·3436	,,	,,	·0707 $Mg_2P_2O_7$	=13·16	,,	P_2O_5	
·4144	,,	,,	·0278 $AlPO_4$	= 2·80	,,	Al_2O_3	
				3·90	,,	P_2O_5	16·60
·4144	,,	,,	·0823 $Mg_2P_2O_7$	=12·70	,,	P_2O_5	

Calculating the chlorine as lead chloride, and taking the mean of the alumina and phosphoric acid determinations, the numbers are as follows :

CO_2	·44	per cent.
H_2O	1·96	,,
$PbCl_2$	9·11	,,
PbO	68·62	,,
Al_2O_3	2·78	,,
P_2O_5	16·81	,,
	99·72	

(*d*) *Theoretical considerations as to the constitution of the minerals analysed above.*

The analyses of the Cumberland mineral and the American hitchcockite agree sufficiently well to make it more than probable that these two are identical, and their constitution is expressed by a simple formula, viz.—$2PbCO_3.Pb_3(PO_4)_2+6\,[AlPO_4.2Al(OH)_3.H_2O]$, or—

$$5PbO.9Al_2O_3.4P_2O_5.2CO_2.24H_2O.$$

Comparing this formula with the numbers obtained, we get the following table :—

	Calculated.	Cumberland Mineral.	Hitchcockite.
PbO	35·73	37·03	34·36
Al_2O_3	29·41	28·74	29·47
P_2O_5	18·20	18·64	17·58
CO_2	2·82	3·12	2·77
H_2O	13·84	12·73	14·71
	100·00	100·26	98·89

The above analysis of hitchcockite, however, differs considerably from Genth's. Genth found only about 29 per cent. of lead oxide, whereas the present specimen contained 34 per cent. Again, the percentage of water in Genth's mineral was nearly 21 per cent. as compared with 14·7.

This difference may, in the case of the lead, be due to the replacement of lead oxide by lime. The percentage of lime in his analysis was 1·44, which, if calculated into its equivalent of lead oxide, amounts to 5·73 PbO. When this latter number is added to the 29·04 per cent. PbO, it gives a total of 34·77, which approaches the calculated percentage.

With regard to the water, it is just possible that Genth may have estimated it by loss of weight of the mineral on ignition without taking into account the simultaneous loss of carbonic acid. Unfortunately the exact details of the analysis are not given in the published description.

The close resemblance in composition of the Cumberland and American minerals may however be put forward as a point in favour of the correctness of the present analysis of the latter.

In discussing the question of the constitution of plumbogummite, it will be well to compare the present analysis with those previously published.

It will be noticed, firstly, that carbonic acid was entirely overlooked by all previous analysts, and as the percentage of water was in most cases estimated by loss of weight on heating the mineral, the carbonic acid was doubtless included in the number given for water. Dufrénoy, however, determined the water by collecting it in a calcium chloride tube, and he observed that there was a greater loss of weight of the mineral than gain of weight of the absorption tube, and in fact he includes this loss in his published analysis as amounting to 2·21 per cent.

Secondly, the want of agreement in the determinations of alumina and phosphoric acid is very evident, but it seems certain that this was due to inadequate methods of separating these constituents.

Berzelius, indeed, did not observe the presence of phosphoric acid at all. Dufrénoy found only a small quantity, while Damour, who was the first to regard it as an essential constituent of plumbogummite, made use of a method of separation which, as was pointed out above, was probably unsatisfactory.

If, however, the numbers, showing the percentages of (i) lead oxide, (ii) alumina and phosphoric acid, and (iii) water and carbonic acid, are compared, it will be seen that the differences are not great, and such differences as occur in the case of the lead oxide are doubtless due, as in the two present analyses, to varying proportions of pyromorphite present in this mineral.

	Berzelius.	Dufrénoy.	Damour.	Hartley. (i)	Hartley. (ii)
PbO ...	40·14	43·42	36·92	43·24	38·91
$Al_2O_3+P_2O_5$	37·00	36·12	42·32	37·41	40·02
H_2O+CO_2	18·80	18·35	18·70	19·09	20·10

In considering the question of the constitution of plumbogummite, it seemed possible that this substance might be a mixture of pyromorphite and hitchcockite, together with some water held more loosely than in the latter mineral, and a small quantity of organic matter and lead sulphate.

In order to test this view, a calculation was made in which the proportion of pyromorphite corresponding to the chlorine, the water lost at 100° C., and lead sulphate corresponding to the SO_3, were deducted from the total percentages, and the remainder was brought to 100 parts.

The numbers so obtained were as follows :—

		Analysis I.		Analysis II.		Calculated for hitchcockite.
H_2O	...	11·55[1]	...	12·42[1]	...	13·84
CO_2	...	5·66[1]	...	5·44[1]	...	2·82
PbO	...	38·80	...	36·43	...	35·73
Al_2O_3	...	23·48	...	24·49	...	29·41
P_2O_5	...	20·51	...	21·22	...	18·21

The agreement is certainly not good, the ratio of phosphoric acid to alumina being very different.

In favour, however, of this view, it must be remembered that the mineral was not a well-crystallised substance, so that it would not be surprising to find one or more of the constituents out of proportion.

At all events, the above view seems more reasonable than Damour's suggestion, that the mineral is a mixture of aluminium hydrate with pyromorphite.

Much the same view can also be taken of the light-coloured mineral. This latter is clearly pyromorphite in the main, as will be seen by comparing its composition with that of pyromorphite.

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[1] Partly derived from organic matter.

	Light-coloured plumbogummite.	Pyromorphite.
$PbCl_2$	9·11	10·26
PbO	68·62	74·03
P_2O_5	16·81	15·71
Al_2O_3	2·78	
CO_2	·44	
H_2O	1·96	

Deducting pyromorphite from the former mineral, as calculated from the chlorine, the following constituents are left :—

H_2O	1·96
CO_2	·44
PbO	3·08
Al_2O_3	2·78
P_2O_5	2·91

Here, of course, all the errors of analysis fall on this small residue, so that the numbers cannot be expected to agree very closely ; but they are sufficient to prove that, at all events, there is more oxide of lead and phosphoric acid than is required for a simple mixture of pyromorphite and aluminium hydrate.

If Damour's two analyses of so-called aluminiferous pyromorphites are treated in the same way, in both cases some oxide of lead is left over and above that required for pyromorphite and lead sulphate; but in the first analysis it is only a very small proportion, and there is no excess of phosphoric acid—in fact, there is less than that required for pyromorphite as calculated from the chlorine. In the second example, perhaps by chance, the residue agrees very fairly well with the proportions in hitchcockite. The numbers so obtained are :—

	(i)	(ii)
PbO	2·13	3·51
Al_2O_3	11·05	2·88
H_2O	6·1	1·24
P_2O_5	—	1·12

Taking into consideration the fact that these minerals are by no means well-crystallised substances, it seems reasonable to suggest that they may be somewhat impure mixtures of pyromorphite with hitchcockite, and to ascribe to the latter mineral the formula given above, namely :—

$$2PbCO_3.Pb_3(PO_4)_2+6[AlPO_4.2Al(OH)_3.H_2O].$$