Communications from the Oxford Mineralogical Laboratory.

On the constitution of the natural Arsenates and Phosphates.

By E. G. J. Hartley, B.A.

[Read Jan. 23rd, 1900.]

Part IV.—*Beudantite.*

THE constitution of beudantite, which is one of the small group of double sulphates with phosphates or arsenates, has so far not been satisfactorily determined. As will be seen below, the results obtained by several analysts differ so much that it is impossible to deduce any simple formula from them.

Since these differences appear to have arisen mainly from the great difficulty in obtaining the mineral in a pure condition, it has seemed desirable to make a fresh analysis on very carefully purified material, in order to obtain satisfactory evidence as to its true composition.

It is proposed in this paper to give, firstly, a short history of previous work on the subject; secondly, some account of the analytical methods adopted in the present research; thirdly, a description of the specimen of beudantite taken for analysis, and the results obtained, together with some suggestions as to the true composition of this mineral.

(*a*) *History.*

In 1826 Lévy (*Ann. de Phil.* 1826, II, 195) first described beudantite as occurring at Horhausen. With regard to its chemical properties he only mentioned that it contained oxide of lead and oxide of iron, according to Wollaston. Damour (*Ann. Chim. Phys.* 1844, 3 Series, X, p. 73) considered it to be hydrated arsenate of iron (pharmacosiderite), containing some oxide of lead as an impurity.

Percy (*Phil. Mag.* 1850, XXXVII, p. 161) published two analyses of some of Lévy's original specimen from Horhausen. He states that the material in the first of these analyses was decidedly impure, while that used in the second was purified as far as possible with the help of a microscope, but was still not quite free from inclusions.

His results were:

	I.	II.
PbO	24·47	29·52
Fe_2O_3	42·46	37·65
SO_3	12·31	12·35
As_2O_5	9·68	13·60
P_2O_5	1·46	undet.
H_2O	8·49	8·49
	98·87	101·61

Percy did not suggest any formula for beudantite from these numbers. Sandberger (*Pogg. Ann.* 1857, C, 611) described a new variety of beudantite from Dernbach, which contained phosphoric acid in the place of arsenic acid. He quoted analyses by Müller both of this new variety and also of the Horhausen mineral. Müller obtained the following numbers:

	Dernbach.	Horhausen.	Calculated for $PbSO_4.Pb_3(PO_4)_2.3FePO_4.24H_2O$
PbO	26·92	23·43	26·09
Fe_2O_3	44·11	47·28	42·10
SO_3	4·61	1·70	2·34
As_2O_5	trace	12·51	—
P_2O_5	13·22	2·79	16·83
H_2O	11·44	[12·29]	12·62
	100·30	100·00	99·98

In the same year Rammelsberg (*Pogg. Ann.* 1857, C, 581) published an analysis of a specimen of beudantite which had been discovered in the previous year at "Glendone," Co. Cork, by Krantz. He stated that it was only with difficulty soluble in strong hydrochloric acid, in which respect it differed from the Horhausen and Dernbach varieties, both of which, according to Percy and Sandberger, are readily attacked by this solvent. His numbers were:—

		Calcnlated for $4Fe_2O_3.2PbO.3SO_3.P_2O_5.9H_2O$
PbO	24·05	27·37
Fe_2O_3	40·69	39·26
CuO	2·45	—
P_2O_5	8·97	8·71
As_2O_5	·24	—
SO_3	13·76	14·72
H_2O	9·77	9·94
	99·93	100·00

(*b*) *Analytical Methods.*

The constituents to be determined in this case were oxides of lead, copper and iron, phosphoric and sulphuric acids, a trace of arsenic acid and water of crystallisation. For the estimation of the metals a portion of the mineral was dissolved in strong hydrochloric acid, and evaporated with a little sulphuric acid till the whole of the hydrochloric acid was driven off. The lead was then weighed as sulphate. In the filtrate the copper and arsenic were precipitated as sulphides, and the arsenic was separated from the copper by sodium sulphide, the copper being ignited and weighed as oxide. The arsenic was re-precipitated as sulphide and oxidised with fuming nitric acid to arsenic acid; the liquid was evaporated to a small bulk and precipitated with magnesia mixture. The precipitate was, however, too small to be weighed. The filtrate from the copper and arsenic was boiled till all the sulphuretted hydrogen was driven off. The iron was then oxidised with nitric acid, neutralised with ammonium carbonate, and precipitated together with the phosphoric acid by ammonium acetate, the two being weighed together. The phosphoric acid was determined in a separate portion, which was also used for the sulphuric acid estimation. This portion was dissolved in hydrochloric acid, and the chlorides were converted into nitrates by repeated evaporation with nitric acid. A few drops of lead nitrate were added to the liquid, which was evaporated nearly to dryness, and the residue was taken up with water and a little alcohol, the precipitate of lead sulphate being then collected and weighed. The filtrate was evaporated to dryness to remove alcohol, the residue taken up with dilute nitric acid, and the phosphoric acid was estimated by the molybdate method and weighed as magnesium pyrophosphate.

With regard to the water, preliminary experiments showed that none was lost either in a current of dry air or at 100° C.

The total water was therefore determined by heating a portion of the mineral, weighed into a porcelain boat, in a hard glass tube connected with a weighed calcium chloride tube, a current of dry air being slowly drawn through the apparatus. In order to prevent any arsenic or sulphur trioxide from passing over into the absorption tube, a heated layer of a mixture of litharge and lead dioxide was interposed between the latter and the boat.

(*c*) *Description of specimen and results of analysis.*

The specimen analysed belonged to the Oxford University Collection, and was obtained by exchange from the British Museum. It was acquired by the British Museum by purchase from Dr. Krantz as from the Glandore Iron Mines, Co. Cork, in the year 1858; but the crystals and the matrix exactly resemble specimens from Dernbach, and do not agree in all respects with the Cork specimens in the British Museum.

The portion taken for analysis was carefully purified under the microscope. It was almost entirely free from inclusions, but a very small amount of quartz escaped notice. This, however, was separated in the course of analysis.

The beudantite occurs in dark green crystals, which present the appearance of nearly black cubes with slightly curved faces. They have a greenish yellow streak, and are pale green when viewed in thin fragments by transmitted light. The crystals line cavities in a jaspery limonite, which is traversed by a little white quartz. The back of the specimen is covered with botryoidal hæmatite converted into limonite.

Results of analysis :—

·5730	of a gram gave	·0032 insoluble residue	= ·56	per cent.	residue
·5730	,, ,,	·2517 $PbSO_4$ ...	=32·33	,,	PbO
·5091	,, ,,	·0430 H_2O ...	= 8·45	,,	H_2O
·5091	,, ,,	·1762 Fe_2O_3 ...	=34·61	,,	Fe_2O_3
·5091	,, ,,	·0069 CuO ...	= 1.35	,,	CuO
·4591	,, ,,	·2211 $PbSO_4$ ...	=12·72	,,	SO_3
·4591	,, ,,	·0671 $Mg_2P_2O_7$ ...	= 9·35	,,	P_2O_5[1]

(*d*) *Discussion of results.*

The numbers obtained agree very closely with those demanded by the formula $3PbSO_4.2FePO_4.6Fe(OH)_3$, or $3PbO.4Fe_2O_3.P_2O_5.3SO_3.9H_2O$.

Comparing the calculated percentages with those obtained by experiment, converting the CuO into its equivalent of PbO and reducing the numbers to 100, we get :—

	Calculated.	Found.
PbO	36·10	35·69
Fe_2O_3	34·51	34·18
SO_3	12·97	12·56
P_2O_5	7·67	9·23
H_2O	8·75	8·34
	100·00	100·00

---

[1] Containing a trace of As_2O_5.

It will be noticed on looking back to the previous analyses that three out of four analysts found about 12 per cent. of SO_3, while Müller alone obtained a much smaller quantity, and since both Müller and Percy analysed the Horhausen variety and obtained such different results, it seems reasonable to assume that the former either made some error in his analysis or else made it on some altogether different mineral.

It remains, therefore, to consider Percy's and Rammelsberg's results. Rammelsberg's numbers agree very well with the formula he suggested, which differs from the present one in having two equivalents of PbO instead of three.

Percy's analysis is more or less intermediate between Rammelsberg's and mine. The numbers obtained in his second analysis made on purified material compared with the numbers calculated from these two formulæ, of course replacing P_2O_5 by As_2O_5, are as follows:—

	Percy.	Calculated for $4Fe_2O_3.2PbO.3SO_3.As_2O_5.9H_2O$ (Rammelsberg)	Calculated for $4Fe_2O_3.3PbO.3SO_3.As_2O_5.9H_2O$ (Hartley)
PbO	29·52	25·96	34·46
Fe_2O_3	37·65	37·25	32·97
As_2O_5	13·60	13·39	11·85
SO_3	12·35	13·97	12·37
H_2O	8·49	9·43	8·35
	101·61	100·00	100·00

In spite of these results, the formula suggested in this paper, which may be written $3(Pb,Cu)SO_4.2Fe(P,As)O_4.6Fe(OH)_3$, seems the most probable, the following points being in its favour :—

(i) The material used was, with the exception of a little quartz, almost absolutely free from visible impurities, and sufficient quantity was available for a reliable analysis.

(ii) The formula is very much simpler than Rammelsberg's, the equivalents of acids and bases corresponding to one another, and the water fitting in with the extra amount of ferric oxide to give the simplest hydrate.

(iii) The higher percentages of iron in previous analyses can easily be accounted for by the fact that the mineral is in many cases closely associated with particles of ferric oxide, which are somewhat difficult to remove.