Hamlinite, Florencite, Plumbogummite (Hitchcockite), Beudantite and Svanbergite, as members of a natural group of minerals.

By G. T. Prior, M.A., F.G.S.,
Assistant in the Mineral Department of the British Museum.

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IN mineralogical literature there appears to be a tendency to over-estimate the degree of exactness attainable in the chemical analysis of minerals. When it is considered how impossible in the majority of cases it is to obtain absolutely pure material for analysis, and how imperfect even in these days are some of the methods of chemical separation employed, for the determination of a formula any great reliance in the figures to the right of the decimal point in the percentages obtained is scarcely justified in the case of analyses made on small amounts (less than half a gram) of material. In such cases also impurities, derived from the reagents and from the glass and porcelain vessels used in the course of a prolonged analysis, become of importance, and in some cases at least may possibly account for the small fractional percentages of lime, iron and alkalies, which, for example, are often seen figuring in analyses of complex niobates.

Some slight protest, therefore, against any over-estimation of the exactness of mineral analysis seems at the present time to be necessary, since otherwise there is danger that simple formulæ may be sometimes unnecessarily rejected in favour of more complex ones agreeing somewhat more closely with the numbers obtained in the analysis, the result of which may be that the mutual relations of analogous species are obscured.

In the case of complex minerals the results of analysis may suggest several formulæ, all of which agree with the numbers obtained within say one per cent. for any of the constituents.

In the choice of a formula, therefore, account must be first taken of the amount of material used in the analysis and of the methods employed,[1] in order to be able to form a judgment of the reliability of the numbers within one per cent.

[1] It is to be regretted that in the published descriptions of mineral analyses these data have been so often omitted.

The possible relationship of the mineral to other species must then receive consideration. The application of such theoretical considerations in the choice of a formula to old analyses made by imperfect methods may have its dangers, since the numbers may be often very wide of the truth. In the case of recent analyses, however, such as those of Hartley on plumbogummite and beudantite (see p. 223), made by modern methods on carefully purified material, we have perfectly suitable material on which to base theories.

In the following note, accordingly, I propose to bring forward some considerations which make it appear probable that these minerals and also svanbergite belong to the same group of aluminium phosphates as hamlinite and florencite.[1]

Plumbogummite (Hitchcockite).

This mineral has hitherto been found only in fibrous radiating aggregates, and not in definite crystals. Hartley, as the result of his analyses (see p. 230) concludes that the hitchcockite from Georgia and from Roughten Gill is a definite mineral, and that probably the original plumbogummite from Huelgoat is an impure mixture of hitchcockite and pyromorphite. It seems reasonable, however, judging from the variations (as much as 2 per cent. in some of the constituents) in the analyses even of hitchcockite alone, to suppose that in none of these fibrous aggregates have we the true species in a pure state.

I would suggest, therefore, that the true species belongs to the same group as hamlinite and florencite, and has the chemical formula

$$2PbO{\cdot}3Al_2O_3{\cdot}2P_2O_5{\cdot}7H_2O$$

analogous to that of hamlinite $2(Sr,Ba)O{\cdot}3Al_2O_3{\cdot}2P_2O_5{\cdot}7H_2O$.

As seen below, the numbers obtained by Hartley in the case of the Roughten Gill mineral show some approach to the theoretical numbers required for this formula.

Thus:—

	Hitchcockite (Roughten Gill).		Calculated for $2PbO{\cdot}3Al_2O_3{\cdot}2P_2O_5{\cdot}7H_2O$
PbO	37·03	...	38·34
Al_2O_3	28·74	...	26·37
P_2O_5	18·64	...	24·44
CO_2	3·12	21·77	
H_2O	12·73	...	10·85
	100·26		100·00

[1] On the mutual relations of florencite and hamlinite, see preceding paper (p. 247).

As regards the physical relations of plumbogummite to hamlinite we have the observation of Bertrand that the mineral is uniaxial and positive, and in accordance with this view in hitchcockite the fibres are positive, and compensate with the quartz wedge across their length. In the case of the paler coloured variety of the French mineral, however, compensation takes place along the length of the fibres, and this observation may have some connection with Hartley's conclusion that the plumbogummite specimens from Huelgoat consist largely of pyromorphite, which is optically negative.

Beudantite.

In the case of this well-crystallised mineral, evidence of its connection with the hamlinite-florencite group is of a more satisfactory character than in the case of plumbogummite.

Instead of Hartley's formula, $4Fe_2O_3 \cdot 3PbO \cdot 3SO_3 \cdot P_2O_5 \cdot 9H_2O$ (see p. 237), I would propose $2PbO \cdot 3Fe_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$, corresponding to that of hamlinite, $2(Sr,Ba)O \cdot 3Al_2O_3 \cdot 2P_2O_5 \cdot 7H_2O$, with one molecule of P_2O_5 replaced by two of $SO_3(S_2O_6)$. This formula may be also written $PbSO_4.FePO_4.Fe_2(OH)_6$ corresponding to hamlinite (regarded as an orthophosphate instead of a pyrophosphate) $SrHPO_4.AlPO_4.Al_2(OH)_6$, with the grouping $SrHPO_4$ replaced by $PbSO_4$ and Al by Fe (see p. 253). The numbers obtained by Hartley agree fairly closely with the theoretical numbers required for the above formula. Thus:—

	Beudantite (Hartley).	Calculated for $2PbO \cdot 3Fe_2O_3 \cdot P_2O_5 \cdot 2SO_3 \cdot 6H_2O$.	Calculated for $4Fe_2O_3 \cdot 3PbO \cdot 3SO_3 \cdot P_2O_5 \cdot 9H_2O$
PbO ...	32·33	33·37	36·10
CuO ...	1·35	—	—
Fe_2O_3 ...	34·61	35·93	34·51
SO_3 ...	12·72	11·99	12·97
P_2O_5 ...	9·35	10·63	7·67
H_2O ...	8·45	8·08	8·75
	98·81	100·00	100·00

The close crystallographic connection of beudantite, and also of svanbergite, with hamlinite and florencite, is evident from the fact that they all crystallise in the rhombohedral system, and show a fairly perfect basal cleavage, and that corresponding angles, as seen in the following table of measured angles, show only slight variations.

Thus :—

	Hamlinite.	Florencite.	Beudantite.	Svanbergite.
cr =	52° 40′	—	53° 49′	54° 19′
cf =	69 7	—	69 55	70 15
rr' =	87 2	88° 56′	88 42	89 25
ff' =	108 2	108 26	ss'108 51	ss'109 12

Svanbergite.

As seen above, svanbergite is crystallographically very similar both to beudantite and also to hamlinite and florencite.

To what extent the mineral is also chemically analogous is seen from Blomstrand's analysis of a specimen from Westanå, the result of which was as follows :—

		Molecular ratios.	
P_2O	15·70	·1108	or 1·108
SO_3	15·97	·2000	2·000
Al_2O_3	34·95	·3428	3·428
FeO	0·73	·0102	3·303
PbO	3·82	·0172	
MgO	0·24	·0060	
CaO	16·59	·2969	
H_2O	12·21	·6799	6·799
	100·21		

These numbers correspond approximately with a formula —

$$3CaO{\cdot}3Al_2O_3{\cdot}P_2O_5{\cdot}2SO_3{\cdot}6H_2O,$$

which only differs from $2CaO{\cdot}3Al_2O_3{\cdot}P_2O_5{\cdot}2SO{\cdot}6H_2O$ analogous to the beudantite formula by containing 3 molecules of CaO instead of 2. The close agreement with theory, except in this one respect, therefore, suggested the idea that Blomstrand's 16 per cent. of CaO may have been partly made up of SrO or BaO of higher molecular weight.

A chemical examination was accordingly made of a specimen of svanbergite from Westana in the Museum collection. The alkaline earths separated from phosphoric acid and alumina were precipitated by ammonium carbonate; the carbonate was converted into nitrate, which was found to be insoluble in a mixture of alcohol and ether, and to consist almost wholly of the strontium and not of the calcium salt. The chloride gave a good strontium flame in the Bunsen. Examined with the spectroscope the bands in the red were seen to be identical with those given by a strontium salt, while the bright green line characteristic of calcium was only once or twice for an instant just faintly visible.

If in Blomstrand's analysis we replace the calcium by strontium, the numbers and molecular ratios are as follows:—

				Molecular ratios.	
P_2O_5	...	15·70	...	·1108 or	1·108
SO_3	...	15·97	...	·2000	2·000
Al_2O_3	...	34·95	...	·3428	3·428
FeO	...	0·73	...	·0102	1·941
PbO	...	3·82	...	·0172	
MgO	...	0·24	...	·0060	
SrO	...	16·59	...	·1607	
H_2O	...	12·21	...	·6799	6·799
		100·21			

These numbers agree fairly closely with the formula

$$2SrO.3Al_2O_3.P_2O_5.2SO_3.6H_2O,$$

which is analogous to that of hamlinite with one molecule of P_2O_5 replaced by two of SO_3. Svanbergite thus bears a similar relation to hamlinite that beudantite does to plumbogummite.

Summary.

In this note it is suggested that the following minerals belong to a natural group:—

	Formula.	Cryst. System.	rr'. Axial ratio.
Hamlinite.....	$2SrO.3Al_2O_3.2P_2O_5.7H_2O$	Rhombohedral	87°2′ $c=1·1353$
Svanbergite	$2SrO.3Al_2O_3.P_2O_5.2SO_3.6H_2O$	,,	89°25′ $c=1·2063$
Plumbogummite	$2PbO.3Al_2O_3.2P_2O_5.7H_2O$	,,	—
Beudantite.....	$2PbO.3Fe_2O_3.P_2O_5.2SO_3.6H_2O$	,,	88°42′ $c=1·1842$
Florencite	$Ce_2O_3.3Al_2O_3.2P_2O_5.6H_2O$	,,	88·56′ $c=1·1901$

The suggestion that in these minerals such a group as $2SO_3$ or S_2O_6 can replace P_2O_5 without materially affecting the crystalline form is similar to that made by the author in the case of members of the fahlerz group (see this volume, page 203), viz. that 6FeS may replace $3Cu_2S$. If, however, the formula of hamlinite be written in the form

$$SrHPO_4.AlPO_4.Al_2(OH)_6$$

as an ortho- instead of a pyro-phosphate, the grouping $SrHPO_4$ may be considered as replaced in beudantite by $PbSO_4$, in svanbergite by $SrSO_4$, and in florencite by $CePO_4$ without materially affecting the crystalline form. According to this view the most probable formula for florencite would be $CePO_4.AlPO_4.Al_2(OH)_6$: for beudantite, $PbSO_4.FePO_4.Fe_2(OH)_6$; and for svanbergite $SrSO_4.AlPO_4.Al_2(OH)_6$.

It is probable that many of the imperfectly described complex phosphates and arsenates of iron, manganese or aluminium may have a similar type of formula to that of the above group. For many of these complex phosphates new analyses made by modern methods on pure material are required.