On Zinc Sulphide replacing Stibnite and Orpiment; Analyses of Stephanite and Polybasite.

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

[Read January 14th, 1890.]

(*a*) Zinc Sulphide replacing Stibnite.

IN a paper in *Zts. f. Kryst.* IX. 186, Professor Laspeyres states that the yellow encrustation upon Felsöbanya stibnite is not cervantite, but a sulphide of zinc, which he determines to be wurtzite, chiefly on the optical ground that a black interference cross was observed between crossed nicols, for the chemical proof based on the solubility in cold concentrated hydrochloric acid can hardly be regarded as very conclusive, considering the fact that he had no true wurtzite with which to make the comparison, but only so-called schalenblende, spiauterite, etc. On this account it seemed desirable to test the solubility of wurtzite in HCl, and accordingly a series of experiments as to the comparative solubility of wurtzite, spiauterite, voltzite and different varieties of blende was made by treating small fragments with cold concentrated HCl, (as was done by Professor Laspeyres) in small tubes, in the mouth of which strips of lead acetate paper were inserted. As far as could be judged by these experiments, the order of solubility was as follows:—

The encrustation: very readily attacked and quickly dissolved.

Voltzite from Joachimsthal and from Geroldseck: attacked at once very readily.

Light-brown botryoidal blende from Wolkenstein, Saxony: attacked at once, almost as readily as voltzite.

So-called ribbon blende from Belgium: freely attacked at once.

Ordinary botryoidal blende from Cornwall: slightly attacked after short time.

Spiauterite from Kapnik, Hungary: slightly attacked after short time.

Wurtzite from Oruro, Bolivia: slightly attacked after some time.

Deep red crystallised blende from Pzribram : scarcely affected at all after standing for several hours.

A qualitative examination of the yellow crust on all the stibnites from Felsöbanya in the Museum collection showed that in all cases it consisted of zinc sulphide very freely soluble in cold concentrated HCl. On one specimen in which the stibnite in radiating groups was associated with a mass of small quartz crystals, the zinc sulphide occurred partly in the usual form as an encrustation on the crystals and partly as an earthy mass of a dull yellowish colour at the root of the crystal. This mass, very different in appearance from the ordinary honey-yellow encrustation, was so thick that ·3901 gramme could be removed for analysis. It was found to contain—

$$\begin{aligned} Zn &= 59{\cdot}22 \text{ p.c.} \\ S &= 27{\cdot}85 \\ Sb &= 2{\cdot}2 \end{aligned}$$

which, assuming that the antimony occurred as oxide, gives for the atomic proportion of zinc to sulphur—

$$\begin{array}{rcl} Zn & : & S \\ {\cdot}911 & : & {\cdot}870 \\ \text{or } 1{\cdot}05 & : & 1 \end{array}$$

The excess of Zn over S may be due to the presence of oxide, but the difference is perhaps hardly sufficient to support the idea suggested by the above table of solubility, that the encrustation is more closely related to voltzite than to wurtzite.

The specific gravity of the mass was 3·44 at 18° C.

In order to discover whether this peculiar encrustation was restricted to stibnite from Felsöbanya, an examination of the deposit on stibnite from other localities in the Museum collection was made, with the result that two new localities may now be added, viz. Estremadura, Spain, and Siegen, Prussia. On all other specimens the encrustation was found to consist of one or more of the oxides of antimony.

The Siegen specimen, which had been described as "antimonglanz passing into valentinite," was remarkable for the thickness of the deposit, which did not, as in Felsöbanya specimens, form a thin coating, but wholly replaced the terminations of the stibnite crystals, which occurred in small radiating groups on brown spar.

A precisely similar encrustation of zinc sulphide was subsequently found coating and partly replacing botryoidal orpiment on a specimen from Felsöbanya.

(*b*) STEPHANITE.

(1) *From Copiapo, Chili.*

The specimen, in size about 5 cm. × 3 cm., without matrix, consists of a group of large stout prisms, with individuals about 15 mm. in length and 20 mm. broad. It was chosen for analysis from its appearance of purity; for, unlike most of the stephanites examined, no pyrargyrite could be detected on it, and when broken into small particles and examined under the microscope by strong transmitted light, the only impurity found consisted of one or two deep red scales of polybasite. The traces of Cu and As found in analysis were no doubt due to this intermixed polybasite. The mineral was decomposed in chlorine, and analysis conducted by methods given in *Min. Mag.* VII. p. 128.

Result of analysis:—

Ag = 68·65
Sb = 15·22
S = 16·02
Cu trace
As trace
99·89

S.G. = 6·26 at 16°C. Weight used in analysis—

For Ag and Sb ... 1·0418 grms.
For S ... ... ·5393 „

The atomic proportions are—

Ag = ·636
Sb = ·127
S = ·500

or approximately	Ag	Sb	S
	5	1	4

which corresponds to the formula now generally adopted for stephanite, $5\,Ag_2S.\,Sb_2S_3$, and not $6\,Ag_3S.\,Sb_2S_3$, as taken by Rose and still given in some text-books.

The following forms have been observed on the specimen by Mr. H. A. Miers:—

c	001	0P
d	201	2P∞
k	101	P̆∞
f	313	P̆3
P	111	P

(2) *From Wheal Boys, Cornwall.*

Only two Cornish specimens of stephanite have hitherto been described, viz. one from Wheal Ludcott by Mr. Davies (*Geol. Mag.* 3, 432), and a large crystal from Wheal Newton by Prof. Lewis (*Zeit. f. Kryst.* VII. p. 575). The present specimen consists of bright prisms attaining a length of 13 mm., on quartz which, in parts is coated with minutely crystalline mispickel.

It was thought that an analysis of the specimen might be of interest, since none had hitherto been made on Cornish stephanite.

Unfortunately for the analysis, the crystals of stephanite were found to be interpenetrated in an extraordinary way with pyrargyrite.

To ordinary observation, even with the aid of a lens, the mineral appeared to be pure, and it was only when examining it in strong sunlight that the red light transmitted through small particles of pyrargyrite could be detected on every freshly-exposed surface.

For the specific gravity determination the mineral was broken into small particles and all visible pyrargyrite separated. This specific gravity cannot altogether represent that of the analysed material, since in the subsequent crushing more pyrargyrite was removed. Each of the small particles was separately flattened out under the pestle, and the intimate nature of the mechanical mixture of the two minerals may be judged by the fact, that when treated in this way few particles were found which did not show thin streaks of red pyrargyrite running through the main mass of the stephanite. The particles containing no pyrargyrite would not have been sufficient for analysis, and so a rough separation of the two minerals had to be made as well as possible on the flattened-out particles. This separation could naturally not be perfect, and accordingly the analysis indicates the presence of pyrargyrite by the low p.c. of Ag and high p.c. of Sb., as compared with analysis (1). Making allowance, however, for this slight admixture with pyrargyrite, the analysis shows that stephanite from Cornwall and stephanite from Copiapo are identical in composition.

Result of analysis :—

Ag = 68·21
Sb = 15·86
S = 15·95
Fe trace

100·02

S.G. = 6·24 at 17°C.

Weight used for Ag and Sb = ·9704 grms.
for S ·5032 ,,

The following remarks on the crystalline form of the two Cornish specimens from Wheal Ludcott and Wheal Boys have been contributed by Mr. H. A. Miers:—"The crystals from Wheal Ludcott on the specimen described by Mr. Davies in 1866 are small bright prisms exhibiting a combination of the forms—

c	001	OP
o	110	∞P
m	113	$\frac{1}{3}$P
h	112	$\frac{1}{2}$P
P	111	P
t	203	$\frac{2}{3}\breve{P}\infty$
k	101	$\breve{P}\infty$
d	201	$2\breve{P}\infty$

and are compound crystals twinned both upon the planes 110 and 310.

The crystals from Wheal Boys are large bright prisms attaining a length of 13 mm. and exhibiting a combination of the forms—

c	001	OP
P	111	P
β	011	$\bar{P}\infty$
h	112	$\frac{1}{2}$P
o	110	∞P
λ	130	$\infty\bar{P}3$
a	100	∞P∞
Γ	731	$7\breve{P}\frac{7}{3}$
d	201	$2\breve{P}\infty$

They are also twinned both upon the planes 110 and 310 and further show the hemimorphic character and twin structure described in *Min. Mag.* Vol. IX. p. 2.

The hemimorphism and the twinning with parallel axes are betrayed by the faces of Γ which occur only on the inner ends of the individuals and lead to unsymmetrical striations on the bright faces of *o*."

(*c*.) POLYBASITE.

From Santa Lucia Mine, Guanaxuato, Mexico.

This specimen consists of a group without matrix, of polysynthetic hexagonal tables about 20 mm. in length and 6 to 10 mm. in thickness. The material was very carefully examined for impurities and enclosed minerals. As before, each particle was separately flattened out under the pestle, but no pyrargyrite or argentite was detected in this way. Whether a little stephanite was mixed with the polybasite it would be impossible to say. The result of this analysis as well as of many of those hitherto published would seem to imply that such may be the case, but owing to the similarity in appearance of the two minerals such a mixture as occurred for instance, in the case of the Cornish stephanite could not be optically detected. In breaking up the crystals slight differences in lustre in different parts were noticed, but otherwise the material appeared to be quite homogeneous, and no mineral which could account for the copper in any other way than as a normal constituent of the polybasite could be discovered.

The only impurity found, consisted of one or two very small particles with bright yellow metallic lustre, which were easily detected and removed owing to their perfect malleability, which caused them to be flattened out under the pestle in the process of crushing the material for analysis. There was very little of this impurity to deal with, little over a milligram, but a chemical examination with the help of the microscope showed, without doubt, that it consisted of an electrum or gold containing a large proportion of silver. Heated to redness in a small glass tube over the Bunsen flame, it suffered no change whatever, but it fused to a bright yellow malleable metallic globule when exposed for some time to the blowpipe-flame in a small porcelain crucible. Repeated evaporations on a watch-glass with nitric acid appeared to have very little effect upon it. It was only by heating in aqua-regia that it lost its metallic appearance, but did not dissolve readily owing to the layer of silver chloride (found to be soluble in ammonia), which protected the metal beneath: however, by rubbing with the rounded end of a glass rod and exposing the fresh surface beneath, sufficient gold was dissolved to give the purple of Cassius very distinctly. A comparative test made upon a pale specimen of electrum rich in silver showed that it behaved in a precisely similar way with respect to acids.

In the analysis the chlorides of silver and copper left after the decomposition of the mineral in chlorine were reduced in hydrogen, and the resulting metals dissolved in nitric acid. The silver was estimated as chloride and the copper as cuprous sulphide. The arsenic was separated from the antimony by Classen's method.

Result of analysis :—

Ag = 68·39
Cu = 5·13
Sb = 10·64
As = 0·50
S = 15·43

100·09

Specific gravity = 6·33 at 15° C.

Weight used in analysis :—

For Ag, &c.	1·0760
S	·5013

The atomic proportions deduced from the analysis are :—

Ag = ·634
Cu = ·081
Sb = ·089
As = ·006
S = ·481

or approximately

Ag, Cu	Sb. As.	S.
7½	1	5

If Rose's formula $9Ag_2S.Sb_2S_3$ be considered the correct one for polybasite, the above result, like many of those hitherto published, would imply that the specimens contained intermixed stephanite. This idea is supported by the fact that in the analysis of Rose, which approximates most nearly to the formula $9Ag_2S.Sb_2S_3$, there is practically no antimony, so that in this case no stephanite could have been present. It would be interesting to learn, if it were possible, in what respects that particular specimen differed from ordinary polybasite, since it might be almost regarded as another species as distinct from polybasite as proustite is from pyrargyrite.

The specific gravity determinations were made with a 3cc. pyknometer provided with a thermometer-stopper and graduated side tube as described in Graham-Otto's text-book.

Results obtained with this little instrument are surprisingly constant. With stopper very slightly greased, when exactly the same course of procedure is pursued in every detail and in the same order, the difference in two weighings seldom exceeds 0·3 mg., if the temperature is kept constant.