The chemical composition of Lengenbachite.

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LENGENBACHITE is one of the interesting minerals which occur in the dolomite of the Binnenthal, and we owe our knowledge of it, as of many other new species, to the careful investigations conducted in recent years by Mr. R. H. Solly at that remarkable locality. The crystallographic and physical characters, so far as they have proved capable of determination, have been already described by Mr. Solly in the pages of this Magazine (vol. xiv, p. 78). The material which he kindly placed in my hands for chemical examination consisted of cleavage-plates, exhibiting brilliant metallic lustre, and of foliated aggregates of thin greyish-black crystals. Some of the crystals were partially covered with a thin, white incrustation readily removed by boiling dilute hydrochloric acid, a reagent which appeared to be without action on the lengenbachite. After removal of the incrustation, whose nature was not further examined, advantage was taken of the highly perfect cleavage to split the crystals into as thin flakes as possible, in order that minute crystals of iron-pyrites imbedded in the lengenbachite might be picked out. Although this operation was carried out with great care, it seems not unlikely that a little pyrites may have escaped detection and the small quantity of iron subsequently estimated may possibly have been derived from this source. The cleavage-plates were next reduced to fine powder in an agate mortar, a process rendered tedious by the toughness of the laminae, but which was found to be absolutely necessary in order to ensure successful decomposition by chlorine gas.

Specific Gravity.—A careful determination of the specific gravity made on 2·231 gram of the powder, afterwards used for analysis, gave the value 5·85 at 15·5°C. compared with water at 4°C.

Analysis.—For the purpose of quantitative analysis, the substance, which had been found to contain lead, silver, copper, arsenic, antimony, and sulphur, was placed in a porcelain boat and decomposed by a current of chlorine in a glass tube, which was gently heated towards the end of the reaction. The elements contained in the residue and in the distillate were separated and estimated by the usual methods, and during the course of the work a small quantity of iron was found. Sulphur was determined in two independent experiments and control estimations of the arsenic also obtained; owing to an accident, a duplicate determination of the antimony was unfortunately spoilt. The results are exhibited in columns I, II, and III of the table below:—

	I.	II.	III.	Mean.	Atomic ratios.			
Pb ...	57·89	—	—	57·89	0·2798			
Ag ...	5·64	—	—	5·64	0·0522	÷ 2	0·3274	1·761
Cu ...	2·36	—	—	2·36	0·0371			
Fe ...	0·17	—	—	0·17	0·0030			
As ...	(13·29)	13·41	13·52	13·46	0·1795		0·1859	1·000
Sb ...	0·77	—	—	0·77	0·0064			
S ...	—	19·35	19·32	19·33	0·6032		0·6032	3·244
				99·62				

The weights of material used in each of the above analyses were as follows:—analysis I, 0·8750 gram; analysis II, 0·8987 gram; analysis III, 1·2828 gram. The weight of the mixture of chlorides remaining in the porcelain boat after the decomposition by chlorine was finished amounted in analysis I to 0·7933 gram. This weighing affords some check on the accuracy of the subsequent work, for the weight of the mixture of chlorides which should be formed from 0·8750 gram of lengenbachite can be calculated on the assumption that the percentages of lead, silver, copper, and iron given in column I above are correct. On calculation this weight was found to be 0·7938 gram, an agreement which may be considered satisfactory.

Chemical Formula.—The interpretation of the analytical results, though not wholly devoid of difficulty, offers some points of interest. If we assume in the first place that the small quantity of antimony is replacing an equivalent amount of arsenic, and secondly that two atoms of silver or of copper can, in this mineral, play the part of one atom of lead, and if the iron be treated as an essential constituent, then we see from an inspection of the columns headed atomic ratios that Pb : As : S = 1·761 : 1 : 3·244 or 7 : 4 : 13, very nearly. The empirical formula of the mineral is therefore $Pb_7As_4S_{13}$ or, as it may also be written, $7PbS . 2As_2S_3$. Accepting this interpretation, we find that lengenbachite takes its place naturally in the long series of compounds of lead, arsenic, and sulphur, filling a gap between guitermanite and jordanite, just as liveingite, baumhauerite, and rathite find their places between sartorite and dufrenoysite.

$PbS . As_2S_3$,	Sartorite	$2PbS . As_2S_3$,	Dufrenoysite
$5PbS . 4As_2S_3$,	Liveingite	$3PbS . As_2S_3$,	Guitermanite
$4PbS . 3As_2S_3$,	Baumhauerite	$7PbS . 2As_2S_3$,	Lengenbachite
$3PbS . 2As_2S_3$,	Rathite	$4PbS . As_2S_3$,	Jordanite

Another possible interpretation must not, however, be lost sight of. It may be that the number of the lead atoms bears a fixed relation to the number of the atoms of silver and of copper, and a consideration of the ratios lends some support to this view. Thus, if we assume that the iron is present as pyrites, and omit FeS_2 from the calculation, we find that the ratios are as follows:—

$$Pb : (Ag, Cu) : As : S = 0{\cdot}2798 : 0{\cdot}0893 : 0{\cdot}1859 : 0{\cdot}5972$$
$$= 6{\cdot}02 : 1{\cdot}92 : 4 : 12{\cdot}85.$$

A result which leads to the formula

$$Pb_6(Ag, Cu)_2As_4S_{13} \text{ or } 6PbS . (Ag, Cu)_2S . 2As_2S_3.$$

That the ratio $Pb : (Ag, Cu)$ approaches in this case very nearly to three to one is an interesting fact. Whether it is a mere coincidence or whether, on the other hand, it has deeper significance can only be satisfactorily determined when more material is available for analysis. In the meantime the formula

$$6PbS . (\tfrac{3}{5}Ag, \tfrac{2}{5}Cu)_2S . 2As_2S_3$$

has the merit of expressing the analytical results with tolerable exactitude, the corresponding percentage composition being as follows:—

Pb, 58·07; Ag, 6·03; Cu, 2·38; As, 14·03; S, 19·49.

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