ART. XLV.—*The Chemical Composition of Bornite and its Relation to Other Sulpho-Minerals*;* by E. H. KRAUS and J. P. GOLDSBERRY, with one text-figure.

Introduction.

IN September, 1912, the Mineralogical Laboratory of the University of Michigan purchased from the Ward's Natural Science Establishment of Rochester, N. Y., four specimens consisting of well-developed crystals or crystal aggregates of bornite from Bristol, Connecticut. The material was a part of an old collection which had recently come into the possession of this firm. As crystallized bornite is very rare, it was thought advisable to study this material first crystallographically, and then chemically, even though some of the crystals would have to be sacrificed, in order to determine whether or not some light might be thrown upon the question of the composition of this mineral.

Crystallography.

Crystals of bornite from Bristol, Connecticut, have already been studied, and according to Dana† the following forms and combinations noted: (100), (110); (111), (110), (100); and (111), (110), (211). On the four specimens at our disposal all of these forms, with the exception of the octahedron (111) were observed, and in addition the following were also noted: (221), (322), (433), (411), (522), (533), and (833). Of these (221), (433), (411), (522), and (833) are not listed by Goldschmidt‡ and, hence, are to be considered as new forms for bornite. As will be shown later all of these forms, with the possible exception of (411), are to be considered as well established.

Specimen 1.—This is a portion of an extremely well-developed crystal, but only the faces of one octant are present. The greatest length of the specimen measured about 2·5^{cm}. The observed forms are d(110), t(221), and i(211). Although the faces are not all of a uniform size d(110) predominates. One face of i(211) is the largest on the crystal, the other two being of intermediate sizes. Two of the faces of t(221) appear as small triangles, the third as a narrow plane between i and d. Fig. 1 shows the sizes and distribution of the various faces. All planes are striated, and the orientation of these striations,

* Read before the Geological Society of America at the Princeton meeting, January 1, 1914.

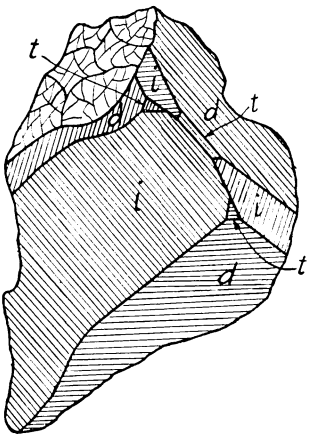
† System of Mineralogy, 5th edition, 45, 1868.

‡ Atlas der Krystallformen, 1913, I (text), 248.

as shown in fig. 1, indicates the symmetry of the hexoctahedral (holohedral) class of the cubic system. The lower portion of this crystal was subsequently sacrificed for the chemical analysis.

Specimen 2.—The following forms were noted: (100), (211), (322), (433), (522), and (533). The faces were not nearly as well developed as on specimen 1. Due to an oscillatory development of the various forms, tetragonal pyramids were built up on the faces of the cube, whereas trigonal pyramids

FIG. 1.



were formed on the corners of the same. The cube faces are the largest on the crystal, the others being usually quite small. The faces of the cube were dull and gave rather poor reflections. The signals obtained from the faces of the other forms were, however, sufficiently good to establish their identity. Some of the faces of the tetragonal trisoctahedrons were striated as shown in fig. 1.

Specimen 3.—This is a small crystal aggregate about 1·25^{cm} in length. The individual crystals showed the following forms: (100), (211), (322), (433), (522), and (533). Of the various forms, which were developed, those of the cube are the largest.

Specimen 4.—This was a crystal aggregate measuring several centimeters in length and made up of small, well developed cubes. The entire specimen was sacrificed for the chemical investigation.

In general there was a close agreement between the averages of the observed readings and the calculated values for the different angles, as is shown in the following table:

	Observed	Calculated
(110) : (101)	60°15′	60°
(110) : (112)	30 2	30
(110) : (221)	19 40	19 28′
(211) : (121)	33 43	33 34
(322) : (232)	19 41	19 45
(411) : (141)	60 28	60
(433) : (343)	13 45	15 56
(522) : (252)	43 15	43 21
(533) : (353)	25 4	24 55

Of the new forms for bornite (221), (433), (411), (522), and (833), only (411) should be considered as doubtful. The identification of this form is based upon only one measurement, the observed angle differing from the calculated by 28 minutes. The values for all the other angles, given in the table, are the averages of from two to eight readings.

*Earlier Interpretations of the Chemical Composition.**

For over one hundred years the chemical composition of bornite has been the subject of much discussion among mineralogists. Based upon the results of the earliest analyses of this mineral, Hisinger, Phillips, and Berzelius assumed bornite to be a mixture of the sulphides of copper and iron, as follows: $2Cu_2S + FeS$. Plattner in 1839 analyzed specimens of bornite from five different localities and concluded that the composition of crystallized bornite should be expressed by the formula $3Cu_2S + Fe_2S_3$. He, however, considered massive bornite as being variable in character, that is, a mixture of bornite of the above composition with chalcopyrite and chalcocite. In 1840 Schaffgotsch concluded that the composition of massive bornite could be best indicated by varying combinations of Fe_2S_3 and Cu_2S, thus one Fe_2S_3 with either 3, 5 or $9Cu_2S$. A little later, in 1841, Rammelsberg considered $Fe_2S_3.3Cu_2S$ as the correct formula, but assumed the admixture of varying amounts of Cu_2S in some varieties. In 1851 Forbes thought the composition of bornite should be represented by the following three mixtures: $CuS + 2Cu_2S$, $CuS + Cu_2S$, or $2CuS + Cu_2S$. Forbes, however, assumed that iron partially replaced copper.

By heating varying quantities of Cu_2O, CuO, and Fe_2O_3 in a current of H_2S at a temperature of about 200° C., Doelter,† in 1885, obtained small cubical crystals which he thought were bornite. The analyses, however, did not lead to any of the

* This summary is based largely upon Hintze's résumé, Handbuch der Mineralogie, I, p. 905, where references to the original contributions may be found.

† Zeitschr. Kryst., xi, 36, 1886.

then recognized formulas for bornite. Doelter, therefore, concluded that bornite could be considered as an isomorphous mixture of Cu_2S, CuS, and Fe_2S_3, in varying proportions.

Rammelsberg revised his earlier ideas in 1895 and gave as the general formula $p\ Cu_2S.q\ CuS.r\ FeS$, in which the relationship of the metals to the sulphur could vary greatly. Rammelsberg further considered the composition of crystallized bornite as $Cu_2S.CuS.FeS = Cu_3FeS_3$, but to some varieties he assigned the formula $Cu_{10}Fe_2S_8$.

Groth* in 1898 interpreted bornite as Cu_3FeS_3, and placed it in a group with chalcopyrite, $CuFeS_2$, and barnhardtite, $Cu_4Fe_2S_5$. These three minerals were thought to be derivatives of $Fe(SH)_3$. More recently Harrington,† in 1903, analyzed some crystallized bornite from Bristol, Connecticut, obtained from the Brush Collection of minerals of Yale University, and concluded from the results of the analysis of this and other material, and also from a study of previous analyses, that the chemical composition of bornite is best indicated by the formula $Cu_{10}Fe_2S_8$ or Cu_5FeS_4.

Chemical Investigations.

Inasmuch as crystallized bornite is exceptionally scarce it was thought advisable to use some of the material for an analysis, and accordingly all of specimen 4 and a portion of specimen 1 were sacrificed for this purpose. Specimen 4 consisted of an aggregate of cubical crystals. These were covered with a dark-colored coating which was thoroughly removed before the material was crushed for the analysis. The material from specimen 1 was the lower portion of the crystal represented by fig. 1, and was entirely free from any superficial coating. The material was, as far as could be determined by the ordinary methods, homogeneous in every respect. This was later substantiated by a careful metallographic study of specimen 1.

Sulphur was determined by oxidation to the sulphate with sodium peroxide and precipitation as $BaSO_4$. The copper was determined electrolytically, and the iron volumetrically by oxidation with potassium permanganate. The specific gravity of specimen 1 was determined as 5·086 at ordinary temperatures. The results of the analysis are as follows:

	I	II	Average	Ratios	
Copper	65·42%	65·91%	65·665%	1·03296	12·000
Iron	9·74	9·67	9·705	0·17377	2·019
Sulphur	24·79	24·51	24·650	0·76863	8·927
			100·020		

* Tabellarische Uebersicht der Mineralien, 4th edition, 29.
† This Journal, xvi, 151–154, 1903.

The above analysis leads to the formula $Cu_{12}Fe_2S_9$. This formula differs materially from the one, $Cu_{10}Fe_2S_8$, derived by Harrington from an analysis of crystallized bornite from this same locality, namely Bristol, Connecticut.

Inasmuch as we were confident that our material was well crystallized and homogeneous, and the methods of analysis could not be questioned, it was thought desirable to obtain and analyze some of the material used by Harrington for his analysis. Through the courtesy of Professor W. E. Ford a sufficient amount of bornite from specimen No. 805 of the Brush Collection of minerals of Yale University was placed at our disposal. This material was from the same specimen from which Harrington obtained his material. That the two analyses agree very closely is clearly shown by the following comparison:

	Harrington			Kraus and Goldsberry		
		Ratios			Ratios	
Copper...	63·24%	0·9948	10·000	63·18%	0·9939	10·000
Iron	11·20	0·2005	2·016	11·38	0·2038	2·051
Sulphur ..	25·54	0·7964	8·005	25·43	0·7929	7·978
	99·98			99·99		

Since our analysis of this material agrees very closely with that made by Harrington and both lead to the formula $Cu_{10}Fe_2S_8$, we are confronted by the fact that here is a mineral, specimens of which from a single locality show a variable composition. It should be stated at this point that the material used by Harrington, and also by us in checking his analysis, was from a large specimen a portion of which is very well crystallized. Harrington had determined the specific gravity of this material to be 5·072. It will also be noted that this value is somewhat lower than that obtained by us on our material from Bristol, Connecticut, namely 5·086.

Metallographic Investigation.

In order to be certain that the material used for these analyses was homogeneous, surfaces were ground at random on our specimen No. 1 and on one of the larger fragments used for the check analysis of the Harrington material. This metallographic investigation was carried out on specimen No. 1 subsequent to the making of the analysis leading to $Cu_{12}Fe_2S_9$, but on the Harrington material before the analysis was begun. The surfaces were polished and examined under a metallographic microscope with magnifications of 85, 135, 200, and about 400 diameters without revealing the presence of any in-

clusions or admixtures. The surfaces showed absolute homogeneity, which was further confirmed by etching with nitrohydrochloric acid.

Interpretation of the Chemical Data.

It is now clearly evident that the material investigated consisted, in the cases referred to, of crystallized bornite, was homogeneous, possessed different specific gravities, and showed marked differences in chemical composition. That the analyses of crystallized bornite made by earlier investigators had also led to the formula $Cu_6Fe_2S_6$ must be emphasized here. We, thus, have three formulas which may be used to express the composition of the mineral we usually call bornite, namely $Cu_6Fe_2S_6$, $Cu_{10}Fe_2S_8$, and $Cu_{12}Fe_2S_9$. It is, therefore, necessary to determine how this great variation in composition can be explained most satisfactorily.

With this in mind the various analyses of bornite and chalcocite, as listed by Hintze,* were calculated for the possible formulas they might yield. The analyses of chalcocite were included in this study because it was found that one of them leads directly to the formula $Cu_6Fe_2S_6$, the one very commonly accepted for bornite. Another reason for including chalcocite is the fact that this mineral usually contains iron in varying amounts and, when massive, may resemble in many ways some bornites. Of the various analyses considered, it was found that thirty-eight lead quite directly to definite formulas. The following table shows the various formulas which resulted, arranged in order of increasing copper content. The number of analyses yielding these formulas is indicated in each case, and where possible the specific gravity is also given. It will be noted that by adding to the list the compound Fe_2S_3, not as yet found in nature, chalcopyrite, barnhardtite, and chalcocite, a most interesting series from Fe_2S_3 to Cu_2S can be arranged.

Name of mineral	Specific gravity	Formula	Number of analyses
		Fe_2S_3	
Chalcopyrite	4·2	$Cu_2Fe_2S_4$	
Barnhardtite	4·521	$Cu_4Fe_2S_5$	
Bornite	4·9	$Cu_6Fe_2S_6$	4
"	----	$Cu_8Fe_2S_7$†	3
"	5·072	$Cu_{10}Fe_2S_8$	17
"	5·086	$Cu_{12}Fe_2S_9$	4

* Loc. cit., pp. 914–916 and 537–538.

† This conforms to the formula generally accepted for tetrahedrite, see page 549. Some cupriferous tetrahedrites possess specific gravities slightly over 5 ; Dana, System of Mineralogy, 1892, 6th edition, pp. 139–140.

Bornite	5·248	$Cu_{14}Fe_2S_{10}$	5
"	----	$Cu_{16}Fe_2S_{11}$	2
"	----	$Cu_{18}Fe_2S_{12}$	1
:	:	:	
"	----	$Cu_{34}Fe_2S_{20}$	1
:	:	:	
"	----	$Cu_{40}Fe_2S_{23}$	1
:	:	:	
"	----	$Cu_{76}Fe_2S_{41}$	1
:	:	:	
Chalcocite	5·51	Cu_2S	

It appears then that there is here a regular progression in the chemical composition, by the addition of Cu_2S, from the end member Fe_2S_3, through to chalcocite, the other end member. The specific gravities, as far as determined, seem also to show a steady increase from the lower value to the highest, namely to that of chalcocite. Furthermore, the composition of any member of the series can be expressed by the general formula $Cu_xFe_2S_y$, where $y = \frac{x}{2} + 3$.

The criticism may be raised that the evidence for the existence of some of the compounds included in the above list is not sufficient, especially for those having large molecules. Further, that there is no positive evidence that the material used for analysis was always homogeneous, not having been examined metallographically. In reply to these criticisms, it may be stated that there are many sulpho-minerals the chemical compositions of which have not been questioned and which have not been studied metallographically. In fact, there are few minerals which have been investigated in this way. Also, there is no doubt in our minds but that the analysts in each case endeavored to get as homogeneous material as possible, and that $Cu_{18}Fe_2S_{12}$, for example, with but only one analysis at present as a basis, must, nevertheless, be considered as a definite compound, being analogous in composition to the well-established polybasite, $Ag_{18}Sb_2S_{12}$. The composition of many minerals is based upon more meager evidence than this, for example, that of prolectite. Although this mineral has never been analyzed, $Mg[Mg(F,OH)]_2SiO_4$ is assumed as its formula since its elements of crystallization are such as to place the mineral in the humite group.* This question of the composition of the various members of the above series will be discussed again.

There are few crystallographic data at present available with

*Groth, loc. cit., 119–120; Sjögren, Bull. G. Inst., Upsala, 1892, 1, 40, also 1894, 2, 99; Dana, loc. cit., 1st Appendix, 1899, 55; Doelter, Handbuch der Mineralchemie, 1913, II, 313–324.

respect to the various members of this series, but from what is known the crystallization of the various members may be interpreted as being either cubic or pseudo-cubic. The members, commonly called bornite, from $Cu_6Fe_2S_6$ to $Cu_{12}Fe_2S_9$ are known to belong to the cubic system. Chalcopyrite, $Cu_2Fe_2S_4$, is tetragonal, but pseudo-cubic, as is clearly indicated by its elements of crystallization: $a : c = 1 : 0{\cdot}9856$. Chalcocite, Cu_2S, is recognized as orthorhombic, $a : b : c = 0{\cdot}5822 : 1 : 0{\cdot}9702$, being the axial ratio given. If, however, the length of the a axis be doubled, and this does not cause serious difficulty with the resulting indices, we obtain $a : b : c = 1{\cdot}1644 : 0{\cdot}9702$, clearly indicating a pseudo-cubic character. Generally chalcocite is interpreted as pseudo-hexagonal on account of the value of the prism angle being 60°25′. It should, however, be pointed out that the rhombic dodecahedron of the cubic system also possesses angles of 60° and may accordingly be held so as to show an hexagonal development. In fact, beginners in crystallography often make this mistake when endeavoring to orient the rhombic dodecahedron. Furthermore, Groth* points out that Cu_2S may also be cubic. According to him the cubic modification is formed at high temperatures and on cooling passes over into the orthorhombic.

It, therefore, appears that from the crystallographic standpoint the relationships between the various members of this series are in accord with the conception of a regular progression in the chemical composition. In order to test this, the meager data concerning specific gravities and crystallization of the members of the series have been made use of in calculating the topical axes. In doing this barnhardtite has been assumed to be cubic. The specific gravity of chalcocite is that of some crystallized material from Cornwall, England, and was recently determined in this laboratory. The elements of crystallization used for chalcopyrite and chalcocite are those given above.

In determining the values of M, the molecular weight, and V, the equivalent volume, Fe_2S_3 and Cu_2S were interpreted as the end members of the series, and the various intermediate members as transition products. Hence, if the regular molecular weights be assigned to Fe_2S_3 and Cu_2S, those for chalcopyrite, barnhardtite, and so forth, are to be obtained by assuming the composition of chalcopyrite, $Cu_2Fe_2S_4$, to be $Cu_2S.Fe_2S_3$, that is the molecular weight of chalcopyrite may be placed equal to the sum of one-half of the molecular weights of each of the end members, namely 183·56. In a similar manner the weights of the other intermediate members of the series were obtained.

* Chemische Krystallographie, i, 135, 1906.

Name of Mineral	Composition	Molecular Weight, M	Specific Gravity	Equivalent Volume, V	χ	ψ	ω
----------	Fe_2S_3	207·91	----	-----	-----	-----	-----
Chalcopyrite	$Cu_2Fe_2S_4$	183·56	4·2	43·705	3·5407	3·5407	3·4897
Barnhardtite	$Cu_4Fe_2S_5$	175·44	4·521	38·806	3·3856	3·3856	3·3856
Bornite	$Cu_6Fe_2S_6$	171·39	4·9	34·977	3·2704	3·2704	3·2704
"	$Cu_8Fe_2S_7$	168·95	----	-----	-----	-----	-----
"	$Cu_{10}Fe_2S_8$	167·33	5·072	32·989	3·2072	3·2072	3·2072
"	$Cu_{12}Fe_2S_9$	166·17	5·086	32·672	3·1950	3·1950	3·1950
"	$Cu_{14}Fe_2S_{10}$	165·40	5·248	31·516	3·1587	3·1587	3·1587
"	$Cu_{16}Fe_2S_{11}$	164·62	----	-----	-----	-----	-----
"	$Cu_{18}Fe_2S_{12}$	164·08	----	-----	-----	-----	-----
	:	:					
Chalcocite	Cu_2S	159·21	5·51	28·895	3·4302	2·9466	2·8586

This table shows that the topical axes, which take into consideration not only the elements of crystallization, but also the chemical composition, as expressed by the molecular weights and the specific gravities, show striking similarities. Of the three axes, two, ψ and ω, vary quite regularly from their maximum values for $Cu_2Fe_2S_4$ to their minimum for Cu_2S. In the case of χ, there is a steady decrease down to $Cu_{14}Fe_2S_{10}$, the last intermediate member for which the axes can be calculated, and then an increase to Cu_2S. This change involves passing from the cubic to the orthorhombic system. These relationships are perhaps brought out a little more clearly in the following, where χ', ψ', and ω' are the values obtained when the topical axis, ψ, corresponding to the b axis of chalcocite, is taken as the unit for the whole series.

		χ'	ψ'	ω'
----------	Fe_2S_3	-----	-----	-----
Chalcopyrite ---	$Cu_2Fe_2S_4$	1·2016	1·2016	1·1843
Barnhardtite ---	$Cu_4Fe_2S_5$	1·1490	1·1490	1·1490
Bornite --------	$Cu_6Fe_2S_6$	1·1099	1·1099	1·1099
" --------	$Cu_8Fe_2S_7$	-----	-----	-----
" --------	$Cu_{10}Fe_2S_8$	1·0884	1·0884	1·0884
" --------	$Cu_{12}Fe_2S_9$	1·0843	1·0843	1·0843
" --------	$Cu_{14}Fe_2S_{10}$	1·0720	1·0720	1·0720
" --------	$Cu_{16}Fe_2S_{11}$	-----	-----	-----
" --------	$Cu_{18}Fe_2S_{12}$	-----	-----	-----
:	:			
Chalcocite------	Cu_2S	1·1644	1·0000	0·9702

The topical axes show, therefore, progressive changes which, as far as can be determined from the very meager data concerning the specific gravities available at present, are fully in

accord with what should be expected from the progressive changes which have been assumed in the chemical composition.

Relation of the Minerals of the Fe_2S_3–Cu_2S Series to Other Sulpho-Minerals.

The general formula $Cu_xFe_2S_y$, given above, page 545, for the Fe_2S_3–Cu_2S series, may be further generalized so as to read $M'_xR'''_2S_y$, where again $y = \frac{x}{2} + 3$. Here M′ is principally copper, silver, or lead, more rarely zinc, tin, mercury, thallium, or bivalent iron, copper, cobalt or nickel. R‴ may be ferric iron, arsenic, antimony, bismuth, or trivalent chromium, nickel, or cobalt. Sulphur is sometimes partially replaced by selenium. With $M'_xR'''_2S_y$ as a basis, it is now possible to arrange a list of sulpho-minerals which show conclusively that the compositions given for the various members of the Fe_2S_3–Cu_2S series, page 544, correspond directly to those of well-established minerals. In this list the formulas are in nearly every case those recognized by Groth.*

General Formula $M'_xR'''_2S_y$, where $y = \frac{x}{2} + 3$.

Chalcopyrite	**$Cu_2Fe_2S_4$**
Lorandite	$TlAsS_2$
Miargyrite	$AgSbS_2$
Wolfsbergite	$CuSbS_2$
Emplectite	$CuBiS_2$
Scleroclase (Sartorite)	$PbAs_2S_4$
Zinckenite	$PbSb_2S_4$
Andorite	$(Pb,Ag_2)Sb_2S_4$
Galenobismutite	$PbBi_2S_4$
Alaskaite	$(Pb,Ag_2,Cu_2)Bi_2S_4$
Seleniferous Galenobismutite	$PbBi_2(S,Se)_4$
Daubreelite	$Fe''Cr_2S_4$
Linnæite	$(Ni,Co)''(Ni,Co)'''_2S_4$
Barracanite	$Cu''Fe_2S_4$
Carrollite	$Cu''Co_2S_4$
Barnhardtite	**$Cu_4Fe_2S_5$**
Dufrenoysite	$Pb_2As_2S_5$
Jamesonite	$Pb_2Sb_2S_5$
Kobellite	$Pb_2(Bi,Sb)_2S_5$
Cosalite	$Pb_2Bi_2S_5$

* Tabellarische Uebersicht der Mineralien, 4th edition, 1898, also the French translation with corrections and additions by Joukowsky and Pearce, 1904.

Schapbachite	$(Pb,Ag_2)_2Bi_2S_5$
Sychnodymite	$(Cu,Co,Ni)_2Co_2S_5$
Polydymite	$Ni_2Ni_2S_5$
Bornite	$\mathbf{Cu_6Fe_2S_6}$
Proustite	$Ag_6As_2S_6$
Pyrargyrite	$Ag_6Sb_2S_6$
Xanthoconite	$Ag_6As_2S_6$
Pyrostilpnite	$Ag_6Sb_2S_6$
Seligmannite	$Pb_2Cu_2As_2S_6$
Bournonite	$Pb_2Cu_2Sb_2S_6$
Aikinite	$Pb_2Cu_2Bi_2S_6$
Guitermanite	$Pb_3As_2S_6$
Lillianite	$Pb_3Bi_2S_6$
Bornite	$\mathbf{Cu_8Fe_2S_7}$
Tetrahedrite	$M'_5R'''_2S_7$*
$M' = Cu,Ag,Hg$	
$M'' = Fe,Zn$	
$R''' = As,Sb$	
Jordanite	$Pb_4As_2S_7$
Meneghinite	$Pb_4Sb_2S_7$
Bornite	$\mathbf{Cu_{10}Fe_2S_8}$
Stephanite	$Ag_{10}Sb_2S_8$
Geocronite	$Pb_5Sb_2S_8$
Bornite	$\mathbf{Cu_{12}Fe_2S_9}$
Kilbrickenite	$Pb_6Sb_2S_9$
Beegerite	$Pb_6Bi_2S_9$
Bornite	$\mathbf{Cu_{14}Fe_2S_{10}}$
Bornite	$\mathbf{Cu_{16}Fe_2S_{11}}$
Pearceite†	$(Ag,Cu)_{16}As_2S_{11}$
Polybasite†	$(Ag,Cu)_{16}Sb_2S_{11}$
Plumbostannite‡	$Pb_2(Fe,Zn)_2Sn_2Sb_2S_{11}$
Bornite	$\mathbf{Cu_{18}Fe_2S_{12}}$
Pearceite†	$(Ag,Cu)_{18}As_2S_{12}$
Polybasite†	$(Ag,Cu)_{18}Sb_2S_{12}$
Franckeite‡	$Pb_5Sn_2Sb_2S_{12}$
Polyargyrite	$Ag_{24}Sb_2S_{15}$
Bornite	$\mathbf{Cu_{34}Fe_2S_{20}}$
Cylindrite‡	$Pb_6Sn_6Sb_2S_{21}$
Bornite	$\mathbf{Cu_{40}Fe_2S_{23}}$

* This older, simpler, and generally accepted formula is retained for the present classification, even though Kretschmer has recently (Zeitschr. Kryst., xlviii, 484-513, 1910) suggested a more complex one, namely $xM'_9R'''_3S_9 + M''_6R'''_2S_9$. If $M'_9R'''_3S_9$ be written in its simpler form, $M'_6R'''_2S_6$, it will be noted that both of these components correspond to well-known minerals in the above list.

† Penfield (this Journal, xliv, 17, 1892) gave $Ag_{18}R'''_2S_{12}$ as the general formula for these minerals. Van Horn and Cook have, however, recently suggested $Ag_{16}R'''_2S_{11}$ (ibid., xxxi, 518, 1911, and xxxii, 40). Unquestionably both formulas hold good, the conditions being analogous to what is now shown to be the case for bornite with its varying composition, belonging as it does to the Fe_2S_3–Cu_2S series. Pearceite and polybasite are accordingly to be interpreted as being members of two similar series, namely, As_2S_3–Ag_2S and Sb_2S_3–Ag_2S.

‡ In these minerals tin is considered as being basic in character.

It is thus seen that many of the rarer minerals with complex molecules fall into this series. The chemical composition of some of these has generally, heretofore, been considered rather doubtful. Thus, to cite but one example, polyargyrite, $Ag_{24}Sb_2S_{15}$, has always been placed in a class by itself, but it now appears that its composition is such as to conform to the general formula of this series.

Other Series of Sulpho-Minerals.

(1) The klaprotholite group shows the general formula $M'_xR'''_4S_y$ where $y=\frac{x}{2}+6$. These minerals are:

Klaprotholite	$Cu_6Bi_4S_9$
Rathite	$Pb_3As_4S_9$
(Binnite)	
Warrenite	$Pb_3Sb_4S_9$
Schirmerite	$(Ag_2,Pb)_3Bi_4S_9$
Boulangerite	$Pb_5Sb_4S_{11}$
Diaphorite	$(Pb,Ag_2)_5Sb_4S_{11}$
Freieslebenite	$(Pb,Ag_2)_5Sb_4S_{11}$

(2) Baumhauerite, $Pb_4As_6S_{13}$, has a composition which may be expressed by the general formula $M'_xR'''_6S_y$, where $y=\frac{x}{2}+9$. This is the only mineral of this type thus far noted.

(3) The composition of plagionite, $Pb_5Sb_8S_{17}$, may be written to conform to the formula $M'_xR'''_8S_y$, where $y=\frac{x}{2}+12$. Plagionite is the only member of this series thus far observed.

(4) The series of sulpho-stannates possesses the general formula $M'_xR'^{v}_2S_y$, where $y=\frac{x}{2}+4$. M′ may be silver, univalent copper, or bivalent iron; R'^{v} is either tin or germanium. The minerals of this series are:

Stannite	$Cu_4Fe_2Sn_2S_8$
Canfieldite	$Ag_{16}(Sn,Ge)_2S_{12}$
Argyrodite	$Ag_{16}Ge_2S_{12}$

(5) The series of minerals in which arsenic, antimony, vanadium are interpreted as having valencies of five conform to the formula $M'_xR^{v}_2S_y$, where $y=\frac{x}{2}+5$. The series is as follows:

Enargite	$Cu_6As_2S_8$
Luzonite	$Cu_6As_2S_8$
Famatinite	$Cu_6Sb_2S_8$
Sulvanite	$Cu_6V_2S_8$
Epigenite	$Cu''_4Fe''_3As_2S_{12}$

It is thus evident that all the important sulpho-minerals listed by Groth, with the exception of the sternbergite series, can be made to conform to some one of the above simple general formulas. In the case of the sternbergite minerals it is very doubtful whether these are to be considered as independent species. We are strongly of the opinion that Groth is right when he intimates that sternbergite, argyropyrite, frieseite, and argentopyrite are probably only argentiferous pyrites.

The compositions of the various sulpho-minerals may therefore be referred to the following six general formulas:

$$M'_xR'''_2S_y, \text{ where } y = \frac{x}{2} + 3. \quad (1)$$

$$M'_xR'''_4S_y, \text{ where } y = \frac{x}{2} + 6. \quad (2)$$

$$M'_xR'''_6S_y, \text{ where } y = \frac{x}{2} + 9. \quad (3)$$

$$M'_xR'''_8S_y, \text{ where } y = \frac{x}{2} + 12. \quad (4)$$

$$M'_xR'^v_2S_y, \text{ where } y = \frac{x}{2} + 4. \quad (5)$$

$$M'_xR^v_2S_y, \text{ where } y = \frac{x}{2} + 5. \quad (6)$$

Some Morphotropic-genetic Series.

As a result of the foregoing considerations, it is now desirable to arrange and study the various progressive chemical series into which the sulpho-minerals may be classified. Several of the more important series of minerals with the general formula $M'_xR'''_2S_y$, where $y = \frac{x}{2} + 3$, are the following:

As_2S_3–PbS Series

		Specific gravity
Orpiment	As_2S_3	3·5
Sartorite	$PbAs_2S_4$	5·39
Dufrenoysite	$Pb_2As_2S_5$	5·56
Guitermanite	$Pb_3As_2S_6$	5·94
Jordanite	$Pb_4As_2S_7$	6·393
:	:	
Galena	PbS	7·45

Sb_2S_3–PbS Series

		Specific gravity
Stibnite	Sb_2S_3	5·32
Zinckenite	$PbSb_2S_4$	5·4
Jamesonite	$Pb_2Sb_2S_5$	5·57
:	:	
Meneghinite	$Pb_4Sb_2S_7$	6·399
Geocronite	$Pb_5Sb_2S_8$	6·3—6·45
Kilbrickenite	$Pb_6Sb_2S_9$	6·4
:	:	
Galena	PbS	7·45

Sb_2S_3–Ag_2S Series

		Specific gravity
Stibnite	Sb_2S_3	5·32
Miargyrite	$Ag_2Sb_2S_4$	5·18—5·3
:	:	
Pyrargyrite	$Ag_6Sb_2S_6$	5·85
:	:	
Stephanite	$Ag_{10}Sb_2S_8$	6·25
:	:	
Polybasite	$Ag_{16}Sb_2S_{11}$	6·067
Polybasite	$Ag_{18}Sb_2S_{12}$	6·33
:	:	
Polyargyrite	$Ag_{24}Sb_2S_{15}$	6·974
:	:	
Argentite	Ag_2S	7·3

Bi_2S_3–PbS Series

		Specific gravity
Bismuthinite	Bi_2S_3	6·5
Galenobismutite	$PbBi_2S_4$	6·88—7·14
Cosalite	$Pb_2Bi_2S_5$	6·39—6·75
Lillianite	$Pb_3Bi_2S_6$	6·7
:	:	
Beegerite	$Pb_6Bi_2S_9$	7·273
:	:	
Galena	PbS	7·45

Bi_2S_3–Cu_2S Series

		Specific gravity
Bismuthinite	Bi_2S_3	6·4—6·8
Emplectite	$Cu_2Bi_2S_4$	6·3—6·5
:	:	
Chalcocite	Cu_2S	5·51

A preliminary survey of several of these series shows that some very interesting relationships can be pointed out, for with but few exceptions the crystallization of the various members

can be interpreted as cubic or pseudo-cubic. Heretofore these minerals have been treated chiefly from the standpoint of isomorphism, but unquestionably a new study of the crystallography of the above groups will show that they are to be considered as morphotropic series, as has been shown for the Fe_2S_3–Cu_2S series. These relationships will be reported upon in detail later.

The arrangement of minerals into series of the above character is, we believe, fully justified not only by what was shown to hold good for the Fe_2S_3–Cu_2S series, but also by the characteristic methods of occurrence and association of the members of these series. This classification* of the sulpho-minerals will undoubtedly be of some service to economic geologists in studying the origin and formation of some ore deposits, for it is reasonable to assume that the members of each series were formed in many instances by the interaction of solutions of the various members, especially of the end members, or by solutions upon the solid phases of some of them.

Mineralogical Laboratory,
University of Michigan,
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*Somewhat similar classifications are to be found in Tschermak's Mineralogie, 6th edition, 1905, 416–422; see also Spencer, Economic Geology, viii, 638, 1913, and Clarke's Data of Geochemistry, Bulletin 491, U. S. G. S., 2d Edition, 1911, 623, 628, 630, and 652.