

CLASSIFICATION OF MINERALS OF THE TYPE
 $A_3(XO_4)_2 \cdot nH_2O$ (Concluded)

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THE $A_3(XO_4)_2 \cdot 4H_2O$ FAMILY

This family is composed of the triclinic group—parahopeite and anapaite; the monoclinic member—phosphophyllite; and the orthorhombic member—hopeite. The relations between the unit cells of phosphophyllite and hopeite are simple and are given in the description of the former. Parahopeite and anapaite have very similar unit cells, their differences being due solely to the variation in cation content. The relation between the cells of the triclinic members and the monoclinic and orthorhombic members is not clear.

The addition of one or more molecules of water to each crystallizing molecule must be accompanied by a completely new bonding arrangement, for there is no recognizable relation between the unit cells of the members of the various families and there is no single factor of the unit cells which varies with the water variation. Thus it is impossible to relate the unit cells of the various families, although there is a definite relation

between the cell volumes and the number of water molecules.

Within this family the optics vary over a narrow range, and the optic sign changes from positive to negative as the crystal system changes from triclinic to monoclinic and orthorhombic symmetry systems. The hardness varies from about $2\frac{1}{2}$ in hopeite to about $3\frac{3}{4}$ in parahopeite. The specific gravity reflects the cation content and the crystal system. The heavier ions, of course, raise the specific gravity, and the higher symmetry tends to be accompanied by a decrease in specific gravity. The cell volumes in this family increase or decrease with the varying ionic radii of the cations (all of the minerals of the family being phosphates, the anion effect is constant) and with the symmetry, the higher symmetries being accompanied by multiple cell volumes. These multiple volumes, when divided by the number of molecules in the unit cell are actually larger per unit than the comparable lower symmetry cells, which is in conformity with the occurrence of lower densities with higher symmetries.

Parahopeite. The physical and chemical properties of parahopeite were adequately described by Spencer (1908). Spencer made no attempt to give a thorough treatment of the crystallography, but this was done later by Ledoux, Walker, and Wheatley (1919). L. LaForge (private communication), using the measured angles of these authors, calculated somewhat different elements which were more consistent with the majority of their measurements. LaForge's morphological values are given in Table 7.

The only new data developed in the present work are the results of *x*-ray investigations. The value for *a*:*b*, determined by Ledoux, Walker, and Wheatley is actually slightly closer to the $a_0:b_0$ value determined in this study, but the *b*:*c* value of LaForge is decidedly closer to the $b_0:c_0$ *x*-ray value than that of the other authors.

The *x*-ray work consisted of rotation, 0-layer-line, and 1-layer-line pictures about *c*[001] and a 0-layer-line picture about *b*[010]. The measured specific gravity of 3.307 on 21 mg. is practically identical with the value of 3.31 obtained by Spencer, using a pycnometer, on 889 mg.

Anapaite. The crystallography of anapaite (tamanite of Popoff, 1903) has been treated adequately by Palache (1933). One change has been necessitated, however, in order that the *c*-axis might be shorter than either the *a* or *b*-axes, This is brought about by interchanging Palache's *a* and *c*-axes, making his perfect cleavage $a\{100\}$ the $c\{001\}$ in the new setting. The transformation from the setting of Palache to the one adopted here is:

$$00\bar{1}/010/\bar{1}00$$

The cell resulting from this transformation is strictly comparable with that obtained by *x*-ray means.

TABLE 7. DATA OF THE $A_3(XO_4)_2 \cdot 4H_2O$ FAMILY

Mineral	Parahopeite	Anapaite	Phosphophyllite	Hopeite
Composition	$Zn_3(PO_4)_2 \cdot 4H_2O$	$Ca_2Fe(PO_4)_2 \cdot 4H_2O$	$Zn_2(Fe, Mn)(PO_4)_2 \cdot 4H_2O$	$Zn_3(PO_4)_2 \cdot 4H_2O$
Crystal System	Triclinic	Triclinic	Monoclinic	Orthorhombic
Crystal Class	Pinacoidal	Pinacoidal	Prismatic	Dipyramidal
Space Group	$C_2^1 - P\bar{1}$	$C_2^1 - P\bar{1}$	$C_{2h}^2 - P2_1/c$	$D_{2h}^{16} - Pnma$
a_0	5.755	6.41	10.23	10.64
b_0	7.535	6.88	5.08	18.32
c_0	5.292	5.86	10.49	5.03
$a_0 : b_0 : c_0$	0.7638:1:0.7023	0.9317:1:0.8512	2.0138:1:2.0650	0.5808:1:0.2745
α	$93^\circ 17 \frac{1}{2}'$	$101^\circ 34 \frac{1}{2}'$		
β	$91^\circ 55'$	$104^\circ 05 \frac{1}{2}'$		
γ	$91^\circ 19'$	$71^\circ 03 \frac{1}{2}'$	$120^\circ 15'$	
Morphology $a:b:c$	0.7747:1:0.7017	0.9401:1:0.8575	2.026:1:2.079	0.5761:1:0.2741
Cell Volume	228.83	234.86	470.92	980.47
Cell Contents	1 molecule	1 molecule	2 molecules	4 molecules
Sp. G. Meas.	3.307	2.812	3.130	3.04
Sp. G. Calc.	3.304	2.796	3.144	3.08
Cleavages	(010) Good	(001) (010) Perfect Good	(100) (010) (102) Perfect Distinct	(010) (100) (001) Perfect Good Poor
Hardness	3.75	3.5	3.5	2.5-3
Optical Sign	+	+	-	-
$2V$	90° ca.	$53^\circ \pm$	50°	37°
$r:v$	$r < v$	$r > v$ perc.	$r > v$ perc.	
Indices of Refraction	α 1.614 β 1.625 γ 1.637	1.602 1.613 1.649	1.595 1.614 1.616	1.589 1.598 1.599
Locality	Broken Hill, S.W. Rhodesia	Taman Peninsula	Pleystein	Broken Hill, S.W. Rhodesia

The x -ray data, using one of the crystals studied by Palache, were obtained from rotation and 0-layer-line pictures, using the three principal directions of the lattice as rotation axes. Calculation of λ , μ , and ν gave almost identical values with those obtained by Palache, so his values were used in the calculations. The calculated specific gravity (2.796) of pure $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ compares favorably with the measured value (2.812).

The composition of anapaite is practically the same as that of fairfieldite except for the addition of two water molecules to the simplest molecular composition of the latter. Some similarity in other properties might be expected, but the properties in general are much more like those of the other members of the family rather than like those of fairfieldite. Each of the cell edges has been lengthened, but not uniformly. The resultant volume is 37.66 cubic ångströms greater, which gives the volume of one water molecule in the structure as 18.83 cubic ångströms, which is very close to the average value of 19 cubic ångströms derived from Table 1. The best cleavage in both cases is $c\{001\}$, and each has a good cleavage parallel to $b\{010\}$. The hardness does not seem to have been affected, but the specific gravity is notably less. There is a marked change in the optical orientation and a lowering of the indices of refraction.

Messelite. This mineral has been found in only one locality, Messel in Hessen, Germany, associated with dark, carbonaceous material. Crystals are abundant in the material, but they are highly altered and etched. A complete morphological treatment is impossible, since there are but two forms on the crystals, and the large one of these is highly etched on all of the crystals. The only published work on the mineral is the original, short description by Muthmann (1889). He gives the angle between these two forms as 42–43 degrees. My x -ray study proves the angle to be about 46 degrees; the optical goniometer measurements are quite unreliable.

Muthmann's analysis gives $2\frac{1}{2}$ molecules of water in the simplest formula. As the triclinic species of the chemical type have but one molecule to the unit cell and as one-half of a molecule of water is impossible, except statistically, it seemed wise to have another analysis made on the type material. This was done by Mr. F. A. Gonyer with the results given in Table 8.

Gonyer's analysis gives the simplest formula as $\text{Ca}_2(\text{Fe}, \text{Mg})(\text{PO}_4)_2 \cdot 2\frac{1}{4}\text{H}_2\text{O}$. This fits no better into the theory of this paper than Muthmann's formula. The small but notable differences between the two analyses, as shown in columns 1 and 2, would seem to indicate the possibility of considerable variation in composition from sample to sample. That this might well be so is indicated in the discussion which follows.

A powder picture of the material was almost identical with that of

TABLE 8. COMPOSITION OF MESSELITE

	1	2	3	4
P ₂ O ₅	37.72	38.75	.2728	1.000
FeO	15.63	17.27	.2404	0.881
CaO	31.11	29.47	.5255	1.926
MgO	1.45	2.97	.0737	0.270
H ₂ O	12.15	10.89	.6050	2.218
Insol.	1.40	.87		
	99.46	100.22		

1. Analysis by W. Muthmann (1889).
2. Analysis of messelite from Messel in Hessen. Analyst, F. A. Gonyer.
3. Molecular proportions.
4. Molecular proportions with P₂O₅ equal to 1.

collinsite, belonging to the 2H₂O family, but rotation and Weissenberg studies gave an unit cell almost identical with that of anapaite, which belongs to the 4H₂O family. On the Weissenberg pictures were many extraneous spots which did not fit into any projected reciprocal lattice pattern. The specific gravity was between that of collinsite and fairfieldite and much higher than anapaite. The listed indices of refraction were much too high for anapaite and somewhat too high for the fairfieldite group.

The reason for these ambiguities lies in the extensive alteration of the mineral. Under crossed nicols no complete extinction could be obtained due to this alteration except in very limited regions of the crystals. The altered portions had a mean index of 1.66 to 1.67, while the unaltered sections had indices comparable with those of anapaite. Thus, messelite, as analyzed, is composed of two substances, one of which is essentially anapaite, and the other is essentially collinsite.

According to Palache's work on anapaite (1933), $m\{110\}$ (his setting) is the largest form on the crystals. The angle between $m(110)$ and $r(101)$ is 45°29', which is very close to the value of 46° determined by *x*-ray analysis for the angle between the two faces found on messelite. If this correlation be correct, the axis of rotation of the messelite crystal would be equivalent to the $[1\bar{1}\bar{1}]$ axis of anapaite. It is possible to calculate the periodicity along $[1\bar{1}\bar{1}]$ (Wolfe, 1937). The value obtained is 9.81Å as compared with the measured rotation value for messelite of 9.80Å.

When the cell edge lengths for Messelite obtained from pictures with $[1\bar{1}\bar{1}]$ as the rotation axis were transformed to obtain the shortest periodicities in the lattice, the following results were obtained as compared with anapaite.

Messelite	Anapaite
$a_0 = 6.59$	6.41
$b_0 = 6.81$	6.88
$c_0 = 5.76$	5.86
Cell Vol. = 232.5Å	234.9Å

In the crystals used for Weissenberg study the collinsite portions were not oriented relative to the axis of rotation, but the anapaite parts were. Thus, anapaite results were obtained. The extraneous spots observed on the Weissenberg films were no doubt due to the unoriented collinsite material. There was probably seven times as much of this as of the anapaite material, which explains the collinsite powder pictures obtained from messelite. On a sample separated by gravity, a powder picture was obtained which showed very faint lines which could be referred only to anapaite.

All lines of evidence, therefore, point to the fact that messelite is a mixture of an unaltered material, anapaite and an altered material, collinsite. Messelite, therefore, cannot be considered a mineral species.

Phosphophyllite. This mineral, found only near Pleystein in the Oberfalz, Bavaria, has been amply described by Laubmann and Steinmetz (1920), Steinmetz (1926), Palache and Berman (1927), and Kleber (1935).

Palache and Berman chose a different orientation and unit than did the first two authors, the transformation formulae being:

$$\begin{array}{ll} \text{Laubmann and Steinmetz to P. \& B.} & 101/010/\bar{2}00 \\ \text{Palache and Berman to L. \& S.} & 00\bar{1}/020/201 \end{array}$$

One of the crystals studied by Palache and Berman was used for the x-ray investigation, which verified their choice of orientation and unit. Laubmann and Steinmetz chose a pseudo-orthorhombic cell which is directly comparable with the orthorhombic equivalent, hopeite. Peacock (1936) found in the case of roselite, as I do here, that it is incorrect to choose the lattice with the highest pseudo-symmetry if that lattice is multiple.

In phosphophyllite the planes (100) and ($\bar{1}02$) of Palache and Berman are planes of pseudosymmetry in the multiple pseudo-orthorhombic lattice of Laubmann and Steinmetz, but not in the simple lattice. According to the French school of twinning, these two planes should act as twin planes in the crystal. The following discussion of the twinning will show that this is the case.

Twinning on the plane (100) has been noted by all authors working on the mineral as being very common. In the Friedel sense this twin law would be a case of twinning by pseudorecticular merohedry with an index of 2 and an obliquity of $0^\circ 37'$.

Kleber (1935) has described an additional twin law, which I have verified and identified on type material. The twin law is actually defined by the plane $\alpha\{\bar{1}02\}$; this is not in accord with Kleber. He states that the twin plane is normal to the c -axis, and that the twin axis is normal to $a(100)$. The twin plane $\alpha\{\bar{1}02\}$ is inclined $0^\circ 27'$ to the plane normal to the c -axis. This results in a re-entrant of $0^\circ 54'$ between the twinned (100) faces, which is the angle defined by Kleber.

The index of this twin is also 2, and the obliquity is $0^\circ 27'$. Thus, we see that the two planes which are planes of pseudosymmetry in the multiple lattice do become the twin planes of the simple lattice.

Although the lattice of Laubmann and Steinmetz discloses the pseudosymmetry best, it is not the simplest lattice, and the indices of the forms referred to it, as has been shown by Palache and Berman, are more complex than when referred to the simple lattice.

The Relations of Phosphophyllite to Hopeite. The compositions of phosphophyllite and hopeite are quite similar, and some simple geometrical relations might be expected between them. Such is the case. The correlation of key forms is given below.

Phosphophyllite		Hopeite
100	=	020
010	=	001
001	=	110
$\bar{1}02$	=	200

The transformation formulae are:

- (1) Phosphophyllite to Hopeite— $001/201/010$
- (2) Hopeite to Phosphophyllite— $\frac{1}{2}0/001/100$

From the x -ray studies the angle between (100) and (001) is $59^\circ 45'$. The correlative angle in hopeite, according to the above correlations, would be the angle between (010) and (110), which is $59^\circ 51'$. This is excellent agreement. A further check on the correlation may be obtained by transforming the elements of one lattice according to the formula to obtain the elements of the other. If the transformed values are approximately the same as the values actually measured, the correlation is correct.

Transformation formula (1) above gives the following cell edges for hopeite as derived from the structural lattice of phosphophyllite:

$$a_0 = 10.49, b_0 = 17.68, c_0 = 5.08.$$

The values actually obtained for hopeite are:

$$a_0 = 10.64, b_0 = 18.32, c_0 = 5.03.$$

Likewise, from (2) we obtain the following cell edge lengths for phosphophyllite as derived from hopeite:

$$a_0 = 10.59, b_0 = 5.03, c_0 = 10.64.$$

The values actually obtained for phosphophyllite are:

$$a_0 = 10.23, b_0 = 5.08, c_0 = 10.49.$$

It is to be expected that the cleavages of the two minerals should also be closely related. That this is true is demonstrated below.

Cleavages in Phosphophyllite	Cleavages in Hopeite
{100}—perfect	= {010}—perfect
{010}—distinct	= {001}—poor
{102}—distinct	= {100}—good

The angles between the three cleavages in phosphophyllite are practically 90 degrees within the limits of measurement, so they are directly comparable with the three pinacoidal cleavages of hopeite. The ease of cleavage, also, is practically the same for the equivalent faces in the two minerals.

A further relation between phosphophyllite, hopeite, and parahopeite appears in the indices of refraction. As was pointed out earlier, there is a definite relation of cell volume, density, and hardness to the symmetry in similar minerals. The higher the symmetry, the greater the cell volume per unit molecule becomes. With this increase in volume there is a corresponding decrease in density and hardness.

It has long been known that in most substances the mean refractive index is a partial function of the specific gravity. In substances whose chemistry is practically identical, this is especially true. Parahopeite, phosphophyllite, and hopeite are very similar chemically, and thus we may expect that the physical properties will vary directly with the symmetry. This is demonstrated in Table 9, where we see the indices of refraction, $2V$, the specific gravity and the hardness increasing as the symmetry and cell volume decrease.

TABLE 9. RELATION OF PHYSICAL PROPERTIES TO SYMMETRY
IN THE $A_3(XO_4)_2 \cdot 4H_2O$ FAMILY

Mineral	Symmetry	Volume per Unit Molecule	Sp. G.	Hardness	Indices	2V
Hopeite	Orth.	245.12	3.04	2.5-3	{ 1.589 1.598 1.599	37°
Phosphophyllite	Mon.	235.46	3.14	3.5	{ 1.595 1.614 1.616	54°
Parahopeite	Tri.	228.83	3.31	3.75	{ 1.614 1.625 1.637	90°

Hopeite. The relations of hopeite to other members of the family have already been given. The principal problem in regard to hopeite is its symmetry.

Well-developed natural crystals of hopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$, were first studied by Spencer (1908) on specimens from Broken Hill, S.W. Rhodesia. He figured several crystals which showed hemimorphic symmetry (Fig. 3, after Spencer), but stated that this hemimorphism was not a regular character and intimated that the phenomenon was fortuitous.

On other crystals from the same locality Ungemach (1910) noted that not only was the plane (010) of Spencer not a symmetry plane, as might be inferred from Spencer's figures, but that (001) of Spencer was, also, not a plane of symmetry. This led Ungemach to the conclusion that hopeite showed monoclinic symmetry. Further study, however, convinced him that the mineral was orthorhombic in all respects, save in its form development. He was, thus, led to postulate a "33rd crystal class," one which possessed but one plane of symmetry but was orthorhombic in all other respects. To differentiate this class of symmetry from the similar monoclinic classes, Ungemach chose a new setting in which the symmetry plane became horizontal. He went further in suggesting that a 34th symmetry class might similarly exist in the tetragonal system.

Three excellent specimens in the Harvard collection from S.W. Rhodesia were available for examination. With these I have corroborated the work of Spencer and Ungemach as to the appearance of the mineral, and demonstrated that hopeite is orthorhombic-dipyramidal, as concluded by Spencer, and does not represent a supposedly new symmetry type, as proposed by Ungemach.

In order to determine the symmetry, the crystals were studied morphologically, physically, and by *x*-ray methods. If Ungemach's analysis of the morphology were correct, disphenoidal symmetry is mandatory. The nature of the derivation of the 32 crystal classes excludes the 33rd which he postulated. Therefore, if hopeite were orthorhombic and if two of the normal symmetry planes were absent, the symmetry class would necessarily be disphenoidal, the third symmetry plane being only apparent or induced by twinning. That Ungemach's determinative crystals, however, must have been accidents of growth is shown below.

No new forms were noted on the several crystals measured. The purpose of the morphological investigation was to fix the symmetry, and to this end most of the crystals on the three specimens were studied, special attention being paid to form development and etching.

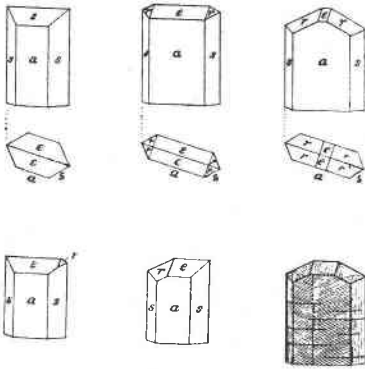


FIG. 3. Hopeite—after Spencer.

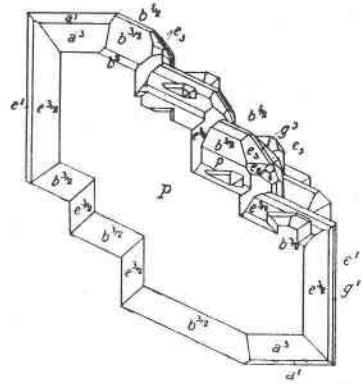


FIG. 4. Hopeite—after Ungemach.

The author is in agreement with Spencer that the symmetry evinced by the crystals is entirely irregular and fortuitous. On some the development is disphenoidal, on others, hemimorphic, and on still others, holohedral. Spencer (Fig. 3) shows the hemimorphic character of some as well as the holohedral character of others. Ungemach (Fig. 4, after Ungemach) depicts a crystal with but one plane of symmetry, but this is really the exception rather than the rule.

In Fig. 5, five crystals are shown which demonstrate the lack of uniformity in development. If any one crystal were used as a basis, the symmetry might be made triclinic-pedal, orthorhombic-pyramidal, orthorhombic-disphenoidal, or orthorhombic-dipyramidal. Such irregularity of growth must be due to the conditions existing at the time of crystallization and not to any lower symmetry of the crystals. Thus, on morphological grounds, alone, it seems that Spencer's decision for holohedry is correct.

Ungemach mentioned one of Spencer's figures (Fig. 3—bottom right) in which the markings of the crystal seem to indicate a twinning by merohedry. If this were truly twinning, a hemimorphic symmetry is indicated. Ungemach did not observe a similar phenomenon. Several of the crystals examined in this study, however, showed quadrilateral etch figures on the same plane ((010), new setting). Due to the stepped nature of this face, the etching was frequently interrupted, giving the impression of an irregular suture separating the two parts of the crystal. Wherever the

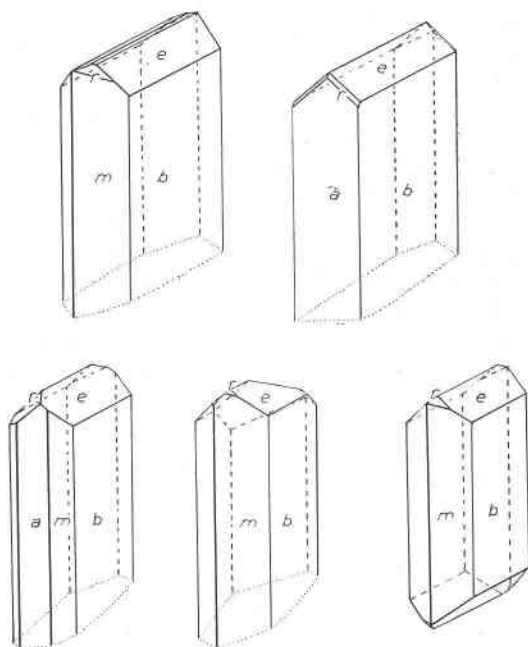


FIG. 5. Hopeite, Broken Hill, S.W. Rhodesia

etching occurred on a smooth, continuous surface, complete quadrilateral etch figures could be observed. The sutures were generally more irregular than that figured by Spencer, but it seems probable that both cases represent the same phenomenon and should not be ascribed to twinning.

Crystals which apparently possessed symmetry lower than holohedry, similar to or identical with those shown in Fig. 5, were tested for piezoelectrical properties with negative results. The instrument used was the same one which demonstrated so conclusively the piezoelectric nature of Hurlbut's (1938) parahilgardite. These tests were conducted in the Cruft Research Laboratory of Harvard University by Professor Pierce, who very graciously gave of his time and equipment for the experiment.

These tests, though not conclusive in themselves, add weight to the conclusion that hopeite is holohedral, the irregular development being a habit variation.

The *x*-ray study of hopeite included the taking of rotation, 0-layer-line, and 1-layer-line Weissenberg pictures about the [001] and about the [100] axes (new setting). From these the lengths of the cell edges were obtained: $a_0 = 10.64$, $b_0 = 18.32$, $c_0 = 5.03$ Å; yielding $a_0:b_0:c_0 = 0.5808:1:0.2745$; $M_0 = 1833.0 = 4 \text{ Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; theoretical specific gravity = 3.08.

The following spectral omissions were noted on the photographs:

- (a) $0kl$ with $k+l$, even
- (b) $h k 0$ with h , even
- (c) $h 0 0$ with h , even
- (d) $0 k 0$ with k , even
- (e) $0 0 l$ with l , even

(c), (d), and (e) are special cases of (a) and (b). Two space groups, only, are possible: $Pnma-D_{2h}^{16}$ or $Pna-C_{2v}^9$, the first being a space group of the dipyramidal, and the second of the pyramidal symmetry class. The first one is correct if (010), (100) of Spencer and (001) of Ungemach, is a plane of symmetry. This is the one plane of symmetry which Ungemach considered to be present, and, in Spencer's figures and in those of the author (Fig. 3), there can be little doubt that this is a symmetry plane in the majority of cases. Thus the space group is fixed as $Pnma-D_{2h}^{16}$, and the symmetry class automatically becomes orthorhombic-dipyramidal. This is conclusive evidence.

The axial ratio determined roentgenographically, $a_0:b_0:c_0 = 0.5808:1:0.2745$, is approximately equal to $b:3a:c$ of Spencer. The interchange of a and b is necessitated by the requirements of the conventional orthorhombic setting in which b is greater than a . The transformation from Spencer's orientation to the structural orientation is: 010/300/001. Ungemach recognized the need of multiplying a by three, but, in order to make the one plane of symmetry horizontal, he interchanged a and c of Spencer or b and c of the structural lattice. The transformation from Ungemach's orientation to the one adopted in this paper is 010/001/100.

The relation of the transformed elements of Spencer and of Ungemach to those obtained by *x*-ray analysis is given below:

$b:3a:c$	Spencer	0.5761:1:0.2741
$b:c:a$	Ungemach	0.5754:1:0.2745
$a:b:c$	<i>x</i> -ray	0.5808:1:0.2745

The following optical properties were obtained, using matched liquids (measured on the minimum deviation goniometer):

$X = a$	1.589	Bx (-) negative
$Y = c$	1.598	$2V = 37^\circ$
$Z = b$	1.599	

These measurements were made on a single crystal which contained both the α and β varieties of hopeite as described by Spencer. The Weissenberg photographs showed no trace of inhomogeneity, however, and no successful attempt was made to separate the two. Although there seem to be two modifications of hopeite, none of the physical evidence obtained in this investigation demonstrates the existence of two species.

The 3.04 value for the specific gravity of hopeite obtained by Spencer using 1.035 grams of material in a pycnometer was duplicated in this study on a crystal weighing 0.012 grams.

Trichalcite— $Cu_3(AsO_4)_2 \cdot 5H_2O$?. Trichalcite occurs in thin pseudohexagonal plates. Data concerning the mineral are very scarce, there being very little recorded on the crystallography and no specific gravity. The one analysis by R. Hermann (1858) on material from Turginsk in the Urals shows considerable divergence from the theoretical composition of the above formula.

Some of the Turginsk material was kindly supplied for this study by W. F. Foshag from the U. S. National Museum collection.

The mineral was easily recognized but showed little promise for fruitful research. There was not sufficient material to obtain a specific gravity. The optical properties checked those given in the literature.

Inasmuch as the composition is not certain, it seemed advisable to make a Weissenberg study to gain some idea as to the probability of the assigned formula. The orientation of a plate for study proved difficult, but after two attempts a crystal gave satisfactory results, which are listed in Table 10. It was impossible to determine the space group with the data obtainable. Rotation, 0-layer-line, and 1-layer-line pictures with [100] as the axis of rotation were used in the calculations. The value for b_0 may be 1 per cent in error.

It would be better perhaps to orient b_0 as the c -axis, since this is the pseudohexagonal axis of the morphology and was made c by Shannon (1922), who observed the three forms $c\{001\}$, $b\{010\}$, and $m\{110\}$. If the convention of $b > a > c$ be followed, the forms of Shannon must be transformed by the formula 010/001/100, making them:

Shannon	Wolfe
$c\{001\}$	$b\{010\}$
$b\{010\}$	$a\{100\}$
$m\{110\}$	$d\{101\}$

The ever-present twinning on the old $m(110)$ will, in the new orientation, be defined by the twin plane $d(101)$. Shannon noted that his prism angle was about 60 degrees. Using the x -ray values, the equivalent angle in the new orientation, (101) to (100) , is $61^{\circ}41\frac{1}{2}'$.

TABLE 10. DATA ON TRICALCITE

$a_0=10.34$	
$b_0=26.9$	$a_0:b_0:c_0=0.384:1:0.207$
$c_0=5.57$	
$V_0=1549.3 \text{ \AA}^3$	

The cell volume is 1549.3 \AA^3 . The orthorhombic minerals of the chemical type have four molecules to the unit cell. If we suppose that this is true for trichalcite, the volume per unit molecule would be 387.3 \AA^3 . Turning to Table 1, we see that the average volume per unit molecule in the $8\text{H}_2\text{O}$ family is only about 309 \AA^3 . Thus, trichalcite, with only $5\text{H}_2\text{O}$, should have a smaller volume, if it is to harmonize with the theory of this classification. As it is actually larger, it seems reasonable to assume that the formula given is incorrect and that it probably does not belong to the type. Further study must await a new analysis.

THE $\text{A}_3(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$ FAMILY

This family of minerals under the name of the *vivianite group* has long been recognized as being interrelated. Most of the relations are well established, and for many of the species within the family, no additional data are required. Barth (1937) has completed the x -ray work on vivianite, bobierrite, erythrite, and annabergite. He has also summarized most of the pertinent data relative to the entire family.

It has been necessary, then, for the purposes of this classification, to examine only those minerals of the family which he has not treated. These include symplecite, köttigite, and hörnesite. All of the data concerning the other minerals which are given in Table 11, except for Barth's x -ray data, have been checked.

This family has long been considered to represent an isomorphous series. The discovery made during the course of this research that symplecite is triclinic requires, however, that the family be considered iso-dimorphous with triclinic and monoclinic groups.

Choice of Unit Cell. Barth has shown that the morphological elements of the family which are commonly given do not represent what he considers the true unit cell, but this supposed unit of Barth is not in the generally accepted orientation because it is body-centered. He has suggested that the morphological elements be retained, as there is an increase in complexity of indices when the known forms are referred to his so-called

true cell. In giving his x -ray elements, therefore, he has retained the orientation of morphology while giving the correct cell edge lengths in that position.

Actually, this orientation is the one that would be chosen conventionally, as it produces a face-centered lattice. It seems wise, then, to retain this orientation, and it also seems wise to describe the morphology in terms of the true lattice rather than in terms of the traditional morphological lattice. The reason for this last statement is as follows. The form indices referred to the traditional morphological unit do not reflect the fact that the basic lattice is a centered one. Donnay (1937 and other references) has convincingly suggested that the elements chosen to describe a mineral should actually portray not only the crystal class but also the space group. This is logical and especially sound in formulating a satisfactory classification.

Inasmuch as no great complexity is introduced when the forms are referred to the base-centered cell and inasmuch as such a reference gives form indices which are compatible with the centered lattice, I believe that it would be better to use the base-centered cell for descriptive purposes in the future. The transformation, morphological lattice to base-centered lattice, is:

$$100/010/00\frac{1}{2}$$

Optical Properties. It is to be expected that members of this family will show similar optical properties with variation compatible with the change in cation and anion content. That this is clearly so is shown in Table 11, the data for which have been obtained, after checking, from the tabulations of Ulrich (1926), Larsen and Berman (1934), and Barth (1937). The optics of köttigite as given in Table 11 are new and will be discussed under that mineral.

Chemistry. The minerals of the family are arsenates or phosphates with 8 molecules of water of hydration and with Fe, Ni, Co, Zn, or Mg acting as cations. Theoretically, a considerable amount of isomorphous replacement is possible, as these ions have similar radii. Actually, but little has been noted. This lack is probably due in part to the paucity of analyses that have been made. At present the various minerals of the family represent almost pure members, there being but one cation listed in the formula of each.

Symplesite-Fe₃(AsO₄)₂·8H₂O. The crystallography of this mineral has been treated by Krenner (1886). He chose a lattice and cell which were monoclinic and directly comparable with the other members of the family. The x -ray investigation carried out in conjunction with this work, however, demonstrates that the lattice is not monoclinic as supposed by Krenner, but is triclinic.

TABLE 11. DATA OF THE $As_2(XO_3)_2 \cdot 8H_2O$ FAMILY

Mineral	Synnesite $Fe_3(AsO_3)_2 \cdot 8H_2O$	Vivianite $Fe_3(PO_3)_2 \cdot 8H_2O$	Annabergite $Ni_3(AsO_3)_2 \cdot 8H_2O$	Erythrite $Co_3(AsO_3)_2 \cdot 8H_2O$	Köttigite $Zn_3(AsO_3)_2 \cdot 8H_2O$	Bobierite $Mg_3(PO_3)_2 \cdot 8H_2O$	Hoernesite $Mg_3(AsO_3)_2 \cdot 8H_2O$
Composition	$Fe_3(AsO_3)_2 \cdot 8H_2O$	$Fe_3(PO_3)_2 \cdot 8H_2O$	$Ni_3(AsO_3)_2 \cdot 8H_2O$	$Co_3(AsO_3)_2 \cdot 8H_2O$	$Zn_3(AsO_3)_2 \cdot 8H_2O$	$Mg_3(PO_3)_2 \cdot 8H_2O$	$Mg_3(AsO_3)_2 \cdot 8H_2O$
Crystal	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Crystal Class	Pinacoidal	Prismatic	Prismatic	Prismatic	Prismatic	Prismatic	Prismatic
Space group	$C_2^1 - P1$	$C_{2h}^2 - C2/m$	$C_{2h}^2 - C2/m$	$C_{2h}^2 - C2/m$	$C_{2h}^2 - C2/m$	$C_{2h}^2 - P2_1/c$?
a_0	7.85	10.039	10.122	10.184	10.11	9.946	
b_0	9.39	13.388	13.284	13.340	13.31	27.654	
c_0	4.71	4.687	4.698	4.73	4.70	4.639	
$a_0 : b_0 : c_0$	0.8320:1:0.5027	0.7499:1:0.3501	0.7619:1:0.3537	0.7633:1:0.3546	0.7593:1:0.3531	0.3596:1:0.1668	
α	99°55'			0.7633:1:0.3546			
β	97°22½'	104°18'	104°45'	105°02'	103°50'	104°01'	
γ	105°57½'						
Morphology $a:b:c$	Unsatisfactory	0.7498:1:0.7017	0.7874:1:0.7223	0.7648:1:0.7122			0.7676:1:0.7182
Cell Volume	321.82	610.43	609.84	620.65	613.95	1238.0	
Cell Contents	1 molecule	2 molecules	2 molecules	2 molecules	2 molecules	4 molecules	
Sp. G. Meas.	3.012	2.676	3.07	3.09	3.33		2.73
Sp. G. Calc.	3.022	2.711	3.235	3.182	3.32	2.17	
Cleavages	(110)	(010)	(010)	(010)	(010)	(010)	
Hardness	2.5	1.5-2	2	1.5-2.5	2.5-3		
Optical Sign	—	+	—	+ or —	+	+	+
2V	87°	83°	84°	90°	74°	71°	60°
$r:v$	$r > v$ strong	$r < v$ weak	$r > v$ strong	weak	imperceptible	$r < v$ weak	
Indices of Refraction	1.635	1.579	1.622	1.626	1.622	1.510	1.563
	1.668	1.603	1.658	1.661	1.638	1.520	1.571
	1.702	1.633	1.687	1.699	1.671	1.543	1.596
X	\perp to (110)	b	b	b	b	b	b
Y							
Z							
Locality	Voigtland	to $c=28^\circ$ Monserrat	to $c=30^\circ$ Laurion	to $c=31^\circ$ Schneeberg	to $c=37^\circ$ Schneeberg	to $c=30^\circ$ Mexillones	to $c=31^\circ$ Joachimstal

Rotation, 0-layer-line, and 1-layer-line pictures were taken about the long axis of a single fibrous crystal selected from a radiating aggregate. Reciprocal lattice projections of the 0-layer-line and of the 1-layer-line pictures showed interpenetrating lattices similar to those already described for roselite, the twin plane being equivalent to the symmetry plane of the monoclinic members. As a twin plane cannot be a symmetry plane, it was necessary to conclude that the mineral was triclinic or that the crystal was peculiarly distorted. To make sure that the latter was not the case, an entirely new and complete Weissenberg study was made on another fiber. Identical results were obtained. Thus, it must be concluded that symplectite is triclinic. The relations between the monoclinic cell and the triclinic cell are rather complex, as the old $a\{100\}$ plane becomes (230) in the triclinic orientation. The transformation is: monoclinic to triclinic—

$$\frac{2}{5}\bar{1}0/\frac{2}{5}\bar{1}0/001$$

The elements of Krenner may be transformed to those of the triclinic cell by the formula:

$$\frac{2}{5}\bar{1}0/\frac{2}{5}\bar{1}0/00\frac{1}{2}$$

These elements: $a:b:c=0.7806:1:0.6812$, $\beta=107^\circ 17'$, transformed according to the preceding formula, give the following values for the triclinic cell edges as compared with those obtained by x -ray study:

$$\begin{aligned} a : b : c &= 0.8604 : 1 : 0.4972 \\ a_0 : b_0 : c_0 &= 0.8320 : 1 : 0.5027 \end{aligned}$$

There is a decided discrepancy between the values for a obtained by the two methods, but, as the crystals of symplectite are never very suitable for measurement, the x -ray values are probably better.

As has already been noted, twinning was first observed on the reciprocal lattice projections of the x -ray pictures. An attempt was made to substantiate the x -ray evidence by optical observations. When the flat cleavage face $\{\bar{1}10\}$ [(010) of the monoclinic setting] which is the twin plane, is vertical, twinning is most easily detected. After much manipulation, a few fibers were set in that position and examined. No definite confirmation of the twinning could be found. The extinction of the fibers in this position, however, was never complete, which may or may not be significant. Perhaps better crystals of symplectite will be found, enabling a check to be made on the conclusions drawn from the x -ray analysis.

The measured (3.012) and calculated (3.022) specific gravities are in close agreement, checking the results of the x -ray study.

Vivianite. Vivianite has been thoroughly studied, and only the specific gravity has been determined here. Specimens of the mineral from Leadville, Victoria, and Llallagua were studied and gave 2.687, 2.668, and

2.674 respectively, with an average of 2.676. This is somewhat lower than 2.711, the calculated value obtained by Barth (1937) on material from Monserrat, but, as the three localities gave values close to the average, it seems probable that this average represents the best value for the mineral. The best data concerning the mineral are summarized in Table 11.

Annabergite. Barth (1937) has given the essential facts concerning annabergite, and they are included in Table 11. His calculated value for the specific gravity of material from Laurion, 3.235, is much higher than the measured specific gravity 3.07, which I obtained on material from the same locality. This is no doubt due to the poor material with which he was working, since there was but very poor agreement between the x-ray and morphological axial ratios. Barth (1937) discarded the species cabrerite, which was presumably a magnesium-bearing annabergite, on optical grounds. According to Barth (and logically enough) the indices of refraction of such a mixed mineral should be considerably lower than those of the pure nickel member. As they actually were not, in spite of analyses showing from 6 to 9 per cent of magnesium oxide, Barth concluded that there actually was little or no magnesium present and that there was no need to retain the species. It might be pointed out, however, that the presence of a small amount of magnesium would materially lower the specific gravity—enough, in fact, to explain the wide discrepancy in calculated and measured specific gravities. A reliable new analysis of so-called cabrerite is needed. In spite of Barth's decision to discard the name, it seems best here to retain it as a varietal modifier of annabergite, with the composition $(\text{Ni}, \text{Mg})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$.

Erythrite. Barth's x-ray measurements of erythrite give what are probably the best elements, as crystals thus far observed are too poor to permit accurate measurement. No new research, except for an accurate determination of the specific gravity, has been done here.

Since Barth worked on erythrite from Schneeberg, the specific gravity was determined on material from the same locality. Once more, a wide discrepancy between measured (3.09) and calculated (3.182) values exist, the reason for which is not apparent.

Köttigite. The crystallography of this mineral has never been adequately described. Material for investigation from Schneeberg was kindly loaned by Dr. F. Pough of the American Museum of Natural History. Although crystals are common, most of them are so etched and rounded that a goniometric treatment of them is impossible. One section of the specimen, however, carried a few unetched crystals with a habit like that of annabergite.

A blowpipe test for zinc was positive, indicating the probability that the mineral was köttigite. Optical tests demonstrated that the mineral

could not be erythrite, which resembles it in color. On the other hand, the values for the indices of refraction determined for the mineral were in complete disagreement with those listed by Larsen and Berman for köttigite. Inasmuch as the zinc test was positive and since the newly determined optical properties are in agreement with properties of a zinc member of this family, as inferred from other families of this chemical type, it seems probable that the identification of the mineral as köttigite is correct and that the data derived from it are authentic for the species.

Five crystals were measured on the optical goniometer, the average size of which was 0.5 mm. in largest dimension. The orientation of the crystals was difficult, due to the poor reflections from most of the faces. The same five forms were noted on all of the crystals. These were $b\{010\}$, $a\{100\}$, $m\{110\}$, $n\{201\}$, and $v\{\bar{2}21\}$. All except $n\{201\}$ gave consistent angular readings. This face, however, varied considerably in its position, the ρ angle varying between 40° and 50° approximately, while the calculated angle was $50^\circ 38\frac{1}{2}'$. The variation is due to the considerable amount of etching on the face. As its position most nearly approximates the position of (201) and as such indices conform to the probabilities of form occurrence suggested by the space group and also because the form is a very prominent one, it seems permissible and probably correct to give it the indices suggested above. All of the form indices in Table 12 are derived with reference to the simple, base-centered lattice.

TABLE 12. KÖTTIGITE: ANGLE TABLE

Monoclinic—Prismatic

$a_0:b_0:c_0=0.7593:1:0.3531$; $\beta=104^\circ 30'$; $p_0:q_0:r_0=0.4650:0.3419:1$
 $r_2:p_2:q_2=2.9253:1.3603:1$; $\mu=75^\circ 30'$; $p'_0=0.4803$, $q'_0=0.3531$, $x'=0.2586$

Forms	ϕ	ρ	ϕ_2	ρ_2	C	A
b 010	$0^\circ 00'$	$90^\circ 00'$	—	$0^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$
a 100	90 00	90 00	$0^\circ 00'$	90 00	75 30	—
m 110	53 41	90 00	0 00	53 41	$78\ 21\frac{1}{2}$	36 19
n 201	90 00	$50\ 38\frac{1}{2}$	$39\ 21\frac{1}{2}$	90 00	$36\ 08\frac{1}{2}$	$39\ 38\frac{1}{2}$
v 221	$-44\ 49\frac{1}{2}$	$44\ 52\frac{1}{2}$	54 56	$59\ 58\frac{1}{2}$	$55\ 50\frac{1}{2}$	60 10

Figure 6 shows the typical habit of köttigite from Schneeberg.

Rotation, 0-layer-line, and 1-layer-line pictures were taken with $c[001]$ as the axis of rotation. The rotation and 0-layer-line pictures taken about $b[010]$ were rather unsatisfactory. The determination of β as listed in Table 11 may be as much as 20 minutes in error, as neither the morphological nor the x-ray studies permitted an accurate determination. The cell constants derived from these pictures are given in Table 11 and are very similar to those of annabergite and erythrite, as is to be expected.

The optical properties listed for köttigite in Table 11 are different from those formerly given for the species. They were measured with sodium light.

The measured specific gravity (3.33) in Table 11 compares favorably with the calculated one (3.32). The hardness conforms to earlier descriptions.

Bobierrite. No specimens of bobierrite suitable for study are available at Harvard, but Barth has already made an *x*-ray study of the mineral

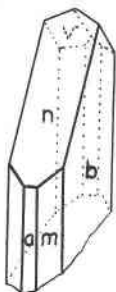


FIG. 6. Köttigite from Schneeberg.

and has shown its relations to the other members of the family. Previously De Schulten (1903) obtained a specific gravity of 2.195 on artificial material, and Lacroix obtained 2.41 on natural material. The calculated value obtained by Barth was 2.169. It is desirable that a trustworthy determination for the natural material be made in order that a significant comparison between the calculated and measured values may be made.

It will be noted that bobierrite, though directly related geometrically and chemically to the $8\text{H}_2\text{O}$ family, belongs to a different space group from that of the other monoclinic members. In fact, the space group here is the same as that of roselite, brandtite, and phosphophyllite, members of the $2\text{H}_2\text{O}$ and $4\text{H}_2\text{O}$ families. The meaning of this is not clear. Strunz and Schroeter (1939) have questioned the place of bobierrite with the rest of the vivianite family because of the different space group. That it might well represent another group in the $8\text{H}_2\text{O}$ family is possible, but it is certainly a member of the family. Without work on better material, it is impossible to be more specific concerning its place in the classification.

Hoernesite. This mineral, the arsenate analogue of bobierrite, has been described crystallographically by Zambonini (1919). The material used was rather unsatisfactory. No other contributions have since been made. Three attempts were made to carry out a Weissenberg study on some very fine fibers of hoernesite from Joachimstal, but the crystals proved too small to give satisfactory diffraction patterns.

The rotation picture gave a value of 6.61 for the translation period of the axis of rotation. This is just half of the value obtained for b_0 on vivianite, annabergite, erythrite and köttigite. The picture is faint, and it is possible that a halving might have escaped detection. The 0-layer-line picture, after 32 kilowatt hours of exposure, showed but 11 reflections, none of which was good. From these, two poor determinations for spacings, 3.14 Å and 3.8 Å, were obtained. If these are considered to be some multiple of the spacings of $a(100)$ and $c(001)$ and if μ be taken to be about 75° (as it is in the other members of the family), some submultiple of the cell volume is obtained by proper multiplication. This volume proves to be 81.6 Å³, which, if multiplied by four, is very similar to the average value for the family. The calculated specific gravity for such a volume is 2.82, which is much higher than any listed values for the mineral. I obtained 2.73 on the Joachimstal material. No further refinement is possible with the material at hand. Actually, the measurements probably mean little.

There is no doubt that hoernesite belongs to the $8H_2O$ family, but the question remains unanswered as to whether its space group conforms to that of bobierrite or to that of the other monoclinic members of the family.

CONCLUSION

The preceding discussion has demonstrated the important part that water of crystallization plays in determining the properties of related minerals. Within any chemical type, where the cation and anion content varies only within prescribed limits, the number of water molecules present in the simplest formula is the controlling factor in the determination of the properties of the minerals and, consequently, of the position of the minerals in the classification.

As the result of this investigation, we may conclude that hydrated minerals should be classified together with their anhydrous analogues in the same type and that the properties of the minerals of any one type will vary in some simple way with the water content in the directions indicated in this paper.

Thus, if we assume the general formula of a type to be $AX \cdot nH_2O$ (where A is the entire cation content and X is the entire anion content), the type will be classified into families on the basis of the change of n in the simplest formula. In the general type formula, n may vary between 0 and an indefinite number.

The anhydrous minerals of the type will be classified as a single family, and all hydrates with different water compositions will be placed in separate families. A more detailed chemical subdivision will often be possible within the types, but, in general, the above method of classification seems sound.

It should be noted that the classification of the hydrated phosphates, arsenates, and vanadates with their anhydrous analogues is a new departure and is counter to the recent classification of Strunz and Schroeter (1939) and earlier classifications, which divide them into water-free and water-containing sections.

The present paper is not the place for a complete classification of these compounds, but such a classification, when made, should be developed along these lines. It is only necessary here that the $A_3(XO_4)_2 \cdot nH_2O$ type be placed in its proper relation to other types containing the (XO_4) radicle as a matter of orientation in the general classification.

Three important chemical types in this category follow.

- (1) $A'B'(XO_4)'' \cdot nH_2O$
- (2) $A_3''(XO_4)'' \cdot nH_2O$
- (3) $A''(XO_4)'' \cdot nH_2O$

Type (1) includes such anhydrous minerals as the triphylite group and such hydrous minerals as dickinsonite and fillowite. Type (2) has been discussed in this paper. In type (3) we find, in the anhydrous family, monazite, xenotime, and pucherite, and, in the hydrated families, the variscite group, koninckite, and others. X-ray diffraction and other evidence indicate that these types are notably different.

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