

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

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INTRODUCTION

The purpose of this paper is to present a logical classification of the minerals of the chemical type  $A_3(XO_4)_2 \cdot nH_2O$  based upon an investigation of the chemical and physical properties of the various minerals comprising it, together with a determination of the lattice constants.

It has been necessary to make a rather complete study of many minerals which, heretofore, have been imperfectly described. The crystallography, the structural cell with its constants and contents, the specific gravity (measured and calculated), the hardness, the cleavage, and the optical properties have been determined. These properties indicate the position of the minerals in the classification and, likewise, their relations to each other. In some few instances, adequate material was not available, and therefore a thorough study could not be made.

In the discussion of the classification, the extent to which minerals of like chemistry and crystallography are also related in their other properties will be pointed out, since one of the purposes of this study was to discover the extent of such relations. Data derived from the literature have been checked in the course of this work. New data, which have been secured during this research, will be indicated as such. If the data concerning any one mineral are complete or nearly so, only points of question or of interest for the classification are discussed; the remainder of the data is summarized in the tables.

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## PREVIOUS CLASSIFICATIONS

Previous classifications by Dana (1892 and earlier), Hintze (1898–1938), and Doelter (1911–1931) of the minerals considered here, which were based on relatively insufficient data, were necessarily only approximations to an adequate systematic treatment. Aside from some members of the vivianite group, practically all of the mineral descriptions up to the time of publication of the above classifications were faulty in one way or another. With the data since published, plus new data obtained during the course of this investigation, it has been possible to develop a satisfactory classification and an understanding of the relations between the various minerals. Strunz and Schroeter (1939) have recently proposed a complete classification of the phosphates and arsenates, but those authors likewise, were without sufficient data concerning the minerals of this type. Aside from the vivianite group, but few of the minerals described and discussed here are included in their classification.

PROPOSED CLASSIFICATION OF THE CHEMICAL TYPE  $A_3(XO_4)_2 \cdot nH_2O$  $A_3(XO_4)_2 \cdot 2H_2O$  family

## Triclinic group

Collinsite  $Ca_2(Mg, Fe)$   $(PO_4)_2 \cdot 2H_2O$ Fairfieldite  $Ca_2(Mn, Fe)$   $(PO_4)_2 \cdot 2H_2O$ 

## Monoclinic group

Roselite  $Ca_2(Co, Mg)$   $(AsO_4)_2 \cdot 2H_2O$ Brandtite  $Ca_2Mn$   $(AsO_4)_2 \cdot 2H_2O$  $A_3(XO_4)_2 \cdot 3H_2O$  family

## Orthorhombic group

Reddingite  $(Mn_{3/4}, Fe_{1/4})_3$   $(PC_4)_2 \cdot 3H_2O$  $A_3(XO_4)_2 \cdot 4H_2O$  family

## Triclinic group

Parahopeite  $Zn_3$   $(PO_4)_2 \cdot 4H_2O$ Anapaite  $Ca_2Fe$   $(PO_4)_2 \cdot 4H_2O$ Messelite  $Ca_2(Fe, Mg)$   $(PO_4)_2 \cdot 4H_2O$ Stewartite  $Mn_3$   $(PO_4)_2 \cdot 4H_2O ?$ 

## Monoclinic group

Phosphophyllite  $Zn_2(Fe, Mn)$   $(PO_4)_2 \cdot 4H_2O$ 

## Orthorhombic group

Hopeite  $Zn_3$   $(PO_4)_2 \cdot 4H_2O$  $A_3(XO_4)_2 \cdot 5H_2O$  family ?Trichalcite  $Cu_3$   $(AsO_4)_2 \cdot 5H_2O ?$  $A_3(XO_4)_2 \cdot 8H_2O$  family

## Triclinic group

Symplesite  $Fe_3$   $(AsO_4)_2 \cdot 8H_2O$ 

## Monoclinic group

Vivianite  $Fe_3$   $(PO_4)_2 \cdot 8H_2O$ Annabergite  $Ni_3$   $(AsO_4)_2 \cdot 8H_2O$ Erythrite  $Co_3$   $(AsO_4)_2 \cdot 8H_2O$

Köttigite	$Zn_3$	$(AsO_4)_2 \cdot 8H_2O$
Bobierite	$Mg_3$	$(PO_4)_2 \cdot 8H_2O$
Hoernesite	$Mg_3$	$(AsO_4)_2 \cdot 8H_2O$
$A_3(XO_4)_2 \cdot nH_2O$ family		
Amorphous group		
Collophanite	$Ca_3$	$(PO_4)_2 \cdot nH_2O$

#### BASIS OF DIVISION INTO FAMILIES

The major divisions in a chemical type are families, which are grouped together according to the chemical similarity of the members. It is to be expected that the members of any one family will show certain additional similarities in their crystallography and physical properties. Thus, it is essential to choose one variable as the basis of division into families which will result in a grouping which satisfies this expectation.

There are but three variables in the chemistry of the minerals of this type: the cations (Mg, Ca, Mn, Fe, Co, Ni, Cu, and Zn), the radicals ( $PO_4$  and  $AsO_4$ ), and the number of water molecules in the simplest formula. Necessarily, then, any division into families must be based upon one of these. Previous experience and the facts revealed by this study demonstrate that the identity of the cation or cations, though of great importance in the determination of the structure, is of little service for classification, for there is no definite similarity between various minerals containing the same cation, while often minerals in which the cations differ show similar physical and crystallographic properties. Likewise, experience has shown that the radicals in the various minerals tend to affect the unit cell volumes and the crystallographic properties, but certain minerals containing the same radicals do not show sufficiently similar properties to group them together. We must, therefore, examine the role of water in determining the properties and relations of the minerals of this chemical type.

#### THE ROLE OF WATER

Those minerals containing the same number of water molecules show, as will be demonstrated here, certain definite similarities, which are only slightly modified by the cations and the radicals. It would seem, then, that the minerals might be separated into families on the basis of the number of water molecules present.

Of the two kinds of water combinations theoretically possible in these minerals, zeolitic or water of crystallization, the latter is indicated for the following reasons. First, although the water can be driven off at relatively low temperatures (Spencer, 1908, has given rate of dehydration curves for hopeite and parahopeite demonstrating this), the crystal structure becomes immediately unstable, leading to the disintegration of the crys-

tals. Second, there is direct correlation between the cell volume, the physical properties, and the number of water molecules present. Table 1 shows the interrelation of water content, cell volume, specific gravity, and hardness. Allowance must be made for the effect of the cations and radicals upon these properties, especially the volume and density. For all cases the cell volumes have been divided by the number of molecules in the unit cell to make them directly comparable.

TABLE 1. RELATION OF PROPERTIES TO WATER CONTENT

Mineral	Water Content per Unit Cell	Molecules in Unit Cell	Cell Volume per Molecule	G.	Hardness
Collinsite	2H <sub>2</sub> O	1	184.5	2.99	3.5
Fairfieldite	2H <sub>2</sub> O	1	197.2	3.08	3.5
Roselite	4H <sub>2</sub> O	2	197.2	3.695	3.5
Brandtite	4H <sub>2</sub> O	2	201.5	3.67	3.5
<i>Average</i>			195.1		
Reddingite	12H <sub>2</sub> O	4	208.3	3.22	3.5
Parahopeite	4H <sub>2</sub> O	1	228.8	3.31	3.75
Anapaite	4H <sub>2</sub> O	1	234.9	2.81	3.5
Phosphophyllite	8H <sub>2</sub> O	2	235.5	3.19	3.5
Hopeite	16H <sub>2</sub> O	4	245.1	3.04	2.5-3
<i>Average</i>			236.1		
Annabergite	16H <sub>2</sub> O	2	304.9	3.24	2
Vivianite	16H <sub>2</sub> O	2	305.2	2.71	1.5-2
Köttigite	16H <sub>2</sub> O	2	307.0	3.33	2.5-3
Bobierite	32H <sub>2</sub> O	4	309.5	2.17	—
Erythrite	16H <sub>2</sub> O	2	310.2	3.18	1.5-2.5
Symplesite	8H <sub>2</sub> O	1	321.8	3.01	2.5
<i>Average</i>			309.8		

The minerals have been arranged in Table 1 according to their increasing volumes. In spite of the modifying influence of the cations and radicals, it will be seen that there is a periodic increase of approximately 19 cubic Ångstroms for each molecule of water, so that the 4H<sub>2</sub>O family averages approximately 41 cubic Ångstroms more in volume than the 2H<sub>2</sub>O family, and the 8H<sub>2</sub>O family approximately 114 cubic Ångstroms more than the 2H<sub>2</sub>O family.

The cell volume is an inverse function of the specific gravity. Further-

more, as has been shown by Stillwell, Evans, and others, the hardness of minerals is intimately related to water content. In this case, this means that hardness must also be related to cell volume, and this is demonstrated in Table 1.

F. W. Clarke (1874) studied the role of water by a method very similar to the volumetric method given above. He tried to determine whether the molecular volume (molecular weight divided by density) of water of crystallization is a constant quantity, or whether it is different for different salts. He worked on the assumption that the volume of the anhydrous salt remained constant when the salt was hydrated and that the change in molecular volume was due only to the addition of water. If this were true, he expected to find a constant value for the volume of one water molecule in the same type of compound. There was, as far as Clarke knew, no a priori reason why this should be so, but calculations of many quite different species demonstrated that water of crystallization has a fairly constant molecular volume, the average of all of his results being 13.76.

Clarke concludes, "When water unites with an anhydrous salt to become water of crystallization, that water undergoes the entire condensation which ensues, the volume of the salt, itself, remaining unaltered." In the "true hydrates," however, Clarke found no uniformity for the molecular volume of water in combination and concluded that both the salt and the water underwent condensation during combination.

The formula used to obtain the molecular volume,  $M/d = \text{molecular volume}$ , is the same as that for the unit cell volume,  $A_0 M_0 / d_0 = V_0$ , save for the omission of the Avogadro constant,  $A_0$ . Thus, the volume in cubic Ångstroms of one molecule may be obtained from the molecular volume simply by multiplying by the Avogadro constant, 1.6498. The converse is likewise true.

It was noted earlier that the average increase in volume per water molecule was approximately 19 cubic Ångstroms. This, converted into the equivalent molecular volume by the method just outlined, would be equal to 11.52, which is somewhat lower than the 13.76 obtained by Clarke. It must be remembered, however, that no allowance has been made in the figure of 19 cubic Ångstroms for the effect of variation in cations and anions; so the significance of the difference between the two figures may not be great.

A better check might be found in existing *x*-ray work on compounds whose only difference lies in the number of water molecules present. An examination of the literature discloses data on but few of the many possible examples. These are listed below in Table 2. It must be pointed out in connection with this table that the molecular volume of water in

TABLE 2. MOLECULAR VOLUME OF WATER CALCULATED FROM CELL VOLUMES

Compound	Cell Volume	Molecular Content of Unit Cell	Cell Volume Molecular Content	Vol. $1H_2O$	Vol. $1H_2O$	Reference
					$A_0$	
LiCl	135.4	4	33.85	—	—	Ott—1923
LiCl · H <sub>2</sub> O	56.1	1	56.1	22.5	13.48	Ott—1923
NaBr	212.0	4	53.0	—	—	Ott—1924
NaBr · 2H <sub>2</sub> O	405.5	4	101.4	24.2	14.67	Wooster—1932
NaI	269.8	4	67.46	—	—	Wyckoff—1931
NaI · 2H <sub>2</sub> O	217.6	2	108.77	20.65	12.52	Wooster—1932
LiI	216	4	54.0	—	—	Wyckoff—1931
LiI · 3H <sub>2</sub> O	262	2	131.0	25.67	15.56	West—1934
<i>Average</i>					14.05	
CaCrO <sub>4</sub>	335	4	84.0	—	—	Clouse—1932
CaCrO <sub>4</sub> · H <sub>2</sub> O	823.8	8	103.0	19	11.5	Clouse—1932
CaCrO <sub>4</sub> · 2H <sub>2</sub> O	1022.0	8	128.0	22	13.33	Clouse—1932
NiSO <sub>4</sub> · 6H <sub>2</sub> O	845	4	221	—	—	Beevers } Lipson }—1932
NiSO <sub>4</sub> · 7H <sub>2</sub> O	961.5	4	240.4	19.4	11.75	Beevers } Schwartz }—1931
CaSO <sub>4</sub>	318	4	79.5	—	—	Rinne—1925
CaSO <sub>4</sub> · 2H <sub>2</sub> O	984	8	123.0	21.75	13.18	Onorato—1929
<i>Average</i>					12.44	

the strongly polar halides is appreciably higher than in the chromates and sulphates, these last being more nearly comparable with the compounds dealt with here. The average value obtained from the chromates and sulphates alone is 12.44, which is very close to the value of 11.52 obtained earlier for the minerals of this chemical type. This is equivalent to 20.5 cubic Ångstroms, which is well within the limits of experimental error.

Such evidence is practically conclusive that, for the most part, the water present in these minerals is water of crystallization. The molecular volume of water in ice, 19 plus, compared with Clarke's average of 13.76 in the hydrates, indicates a condensation which in all probability takes place due to the bonding effect of the cation or anion, or both, upon the water molecules. That the water is changed in no other way is indicated

by the fact that infra-red adsorption spectra of compounds such as vivianite show the characteristic water lines, which is not true of the minerals containing water of constitution, which show characteristic (OH) lines.

Without vapor pressure dehydration measurements and *x*-ray diffraction data, it is impossible to state exactly how the water is held; it must suffice to say here that the water present is apparently compositional and can, therefore, serve as a basis of classification into families.

#### BASIS OF DIVISION INTO GROUPS

The division of the family into groups based upon similarity of crystal symmetry is a standard procedure. The crystallographic relations within the groups will be discussed in the treatment of each family.

It need only be pointed out that in these minerals the number of molecules in the unit cell of the triclinic species is always one, in the monoclinic species, two (in one case there are four), and in the orthorhombic, always four. This is no doubt due to the fact that the higher symmetries are obtained directly from the lower by a twinning of the lattice, a single plane of reflection producing monoclinic symmetry with a double volume and two planes of reflection producing orthorhombic symmetry with a quadruple volume.

#### SYSTEMATIC TREATMENT OF FAMILIES

##### $A_3(XO_4)_2 \cdot 2H_2O$ Family

This family contains the two triclinic species, fairfieldite, and collinsite and the two monoclinic species, roselite and brandtite. The unit cells of the triclinic and monoclinic species are simply related, *a* and *c* being practically the same, while *b* is doubled in the monoclinic species. As the monoclinic members are arsenates, and the triclinic members are phosphates, most of the physical properties are appreciably different, but the cell volumes are strictly comparable.

The cell edges are similar or multiples of each other. The composition is only variable within certain limits. The ratio of calcium to the sum of the other cations present in each mineral is approximately 2 to 1. In some cases, the percentage of calcium is somewhat below this, but for the most part the composition might well be written  $Ca_2(A)(XO_4)_2 \cdot 2H_2O$ , where A is Fe, Mn, Mg, or Co; and  $(XO)_4$  is  $(PO)_4$  or  $(AsO)_4$ .

This indicates that calcium and the A ions occupy non-equivalent positions in the structure. Consequently, only a limited amount of substitution of A for Ca is possible. This is in conformity with other experience with calcium-containing minerals such as diopside. This might also

TABLE 3. DATA OF THE  $Ca_3(A)(XO_4)_2 \cdot 2H_2O$  FAMILY

Mineral	Collinsite	Fairfieldite	Roselite	Brandtite
Composition	$Ca_2(Mg, Fe)(PO_4)_2 \cdot 2H_2O$	$Ca_2(Mn, Fe)(PO_4)_2 \cdot 2H_2O$	$Ca_2(Co, Mg)(AsO_4)_2 \cdot 2H_2O$	$Ca_2Mn(AsO_4)_2 \cdot 2H_2O$
Crystal System	Triclinic	Triclinic	Monoclinic	Monoclinic
Crystal Class	Pinacoidal ?	Pinacoidal	Prismatic	Prismatic
Space Group	$C_2^1 - P\bar{1}$	$C_2^1 - P\bar{1}$	$C_{2h}^2 - P2_1/c$	$C_{2h}^2 - P2_1/c$
$a_0$	5.70	5.77	5.60	5.65
$b_0$	6.72	6.56	12.80	12.80
$c_0$	5.38	5.47	5.60	5.65
$a_0 : b_0 : c_0$	0.8479:1:0.8002	0.8791:1:0.8331	0.4374:1:0.4374	0.4412:1:0.4412
$\alpha$	96°48½'	102°05'	100°45'	99°30'
$\beta$	107°16½'	108°42½'		
$\gamma$	104°32'	90°05½'		
Morphology $a:b:c$	Unsatisfactory	Unsatisfactory	0.8780:1:1.4398	0.8720:1:0.4475
Cell Volume	184.46	197.2	394.36	403.00
Cell Contents	1 molecule	1 molecule	2 molecules	2 molecules
Sp. G. Meas.	2.992	3.082	3.695	3.671
Sp. G. Calc.	3.04	3.09	3.645	3.700
Cleavages	(001)(010)	(001)(010)(110)	(010)	(010)
Hardness	3.5	3.5	3.5	3.5
Optical Sign	+	+	+	+
2V	80°	86°	60°	23°
$r:v$		$r > v$	$r < v$	$r < v$
Indices	1.632	1.633	pink	1.709
of	1.642	1.641	1.694	1.725
Refraction	1.657	1.652	1.704	1.728
			1.719	1.735
X		$\rho$	to [001] 1°	[010]
Y		120° 60°	[010] to [001], 12-20°	to [001] 8°
Z		-102° 36°		
Locality	Francois Lake	18° 69°	Schneeberg	Pajsberg
		Buckfield		



be expected because of the appreciably greater ionic radius of calcium compared with the other cations in these minerals.

The (AsO<sub>4</sub>) compounds show higher indices of refraction and densities than corresponding (PO)<sub>4</sub> compounds. The hardness and cell volumes are not affected by the radical content and are, consequently, approximately constant.

Table 3 summarizes the data on these minerals.

*Collinsite*.—The original and only description of collinsite was made by Poitevin (1927) on material occurring in phosphorite nodules near François Lake, British Columbia. Included in his description were data on the optical and other physical properties, and the chemistry. As no crystals were found, nothing relative to the crystallography except the angles between the cleavages was given.

The optical and other physical properties listed in Table 3 are those given by Poitevin. The specific gravity, 2.99, measured on the torsion microbalance, however, is slightly higher than the 2.95 given by him.

Poitevin lists four cleavages in the following order of perfection: C<sub>0</sub>, C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and gives the following angles between them:

$$\begin{aligned} C_0 \text{ to } C_1 &= 88^\circ 40' \\ C_1 \text{ to } C_2 &= 108^\circ 00' \text{ or } 72^\circ 00' \\ C_2 \text{ to } C_3 &= 111^\circ 00' \text{ or } 69^\circ 00' \\ C_1 \text{ to } C_3 &= 131^\circ 00' \text{ or } 49^\circ 00' \end{aligned}$$

With these he makes a faulty comparison with roselite angles, and correlates faces which cannot actually be considered to be the same. He correlates C<sub>2</sub>, C<sub>3</sub>, and C<sub>1</sub> of collinsite with *b*(010), *m*(110), and *M*(1 $\bar{1}$ 0) of roselite. It is apparent, however, that these faces in roselite form a distinct zone, while there is no possible means of bringing C<sub>2</sub>, C<sub>3</sub>, and C<sub>1</sub> into the same zone. This is clearly shown by Poitevin (1927, p. 6) in his diagram of the optical orientation relative to the cleavages.

The authenticity of these cleavages is questionable. Six apparently homogeneous fibrous crystals were measured by me, and in no case were the angular relations given by Poitevin observed. The only consistent value obtained was an angle of between 75 and 77 degrees between two fair cleavages. This corresponds to the angle between *c*(001) and *b*(010), 75°30', derived from *x*-ray study. This is comparable with the angle of 77°12' between the same cleavage faces of fairfieldite. The optical orientation of collinsite is given by Poitevin on a Fedorov net with the four cleavages noted by him as reference points. The best cleavage, C<sub>0</sub>, is made polar. If the azimuth to C<sub>1</sub> is taken as 0°00', the following orientation angles are obtained from his plot for three principal directions of the indicatrix:

	$\phi$	$\rho$
X	$-50\frac{1}{2}^\circ$	$50^\circ$
Y	$-173\frac{1}{2}$	58
Z	$72\frac{1}{2}$	58

The value of these figures is doubtful, for they could not be reproduced in this study. Due to the nature of the crystals, it was impossible to obtain a dependable check on the optical orientation, the solution of which will have to await the discovery of better crystals.

Poitevin's formula deduced from an analysis made by E. A. Thompson is  $Ca_2(Mg, Fe)(PO_4)_2 \cdot 2\frac{1}{2}H_2O$ . Inasmuch as the  $x$ -ray study had demonstrated that there could be but one molecule to the unit cell,  $2\frac{1}{2}$  molecules of water were apparently out of the question unless the  $\frac{1}{2}$  molecule represented a statistical average of zeolitic water present. Another analysis appeared desirable. Two grams of hand picked material, which under the microscope appeared to be better than 99% pure collinsite, were analyzed by F. A. Gonyer. A summary of the chemistry of collinsite is given in Table 4.

It will be noted that, instead of there being an excess of water in this case, there is a deficiency. There are other differences between the analyses, but it is only necessary to point out that the new analysis agrees fairly well with the theoretical composition in column 6 of Table 4, and the mineral can be said to definitely belong to the  $Ca_2A(XO_4)_2 \cdot 2H_2O$  family.

The results of the  $x$ -ray work are summarized in Table 3. They were obtained from a slender, prismatic fiber of collinsite. Rotation was around the prism axis, which proved to be  $a[100]$ .

TABLE 4. CHEMISTRY OF COLLINSITE

	1	2	3	4	5	6
P <sub>2</sub> O <sub>5</sub>	39.83	41.13	41.35	.975	1	41.63
CaO	32.18	32.03	32.20	1.92	2	32.87
MgO	6.34	9.31	9.36	.78	$\frac{2}{3}$	7.91
FeO	6.86	7.31	7.35	.34	$\frac{1}{3}$	7.03
H <sub>2</sub> O	12.28	9.69	9.74	1.81	2	10.56
Imp.	2.37	0.37				
Total	99.86	99.84	100.00			100.00

1. Analysis by E. A. Thompson.
2. Analysis by F. A. Gonyer.
3. Analysis by F. A. Gonyer recalculated to 100%.
4. Number of oxides in unit cell: volume = 184.46,  $d = 2.992$ ,  $M_0 = 334.3$ .
5. Theoretical number of oxides:  $M_0 = 341.2$ .
6. Theoretical composition for  $Ca_2(Mg_{2/3}, Fe_{1/3})(PO_4)_2 \cdot 2H_2O$ .

*Fairfieldite*. This mineral was first described by G. J. Brush and E. S. Dana (1879) on material from Branchville, Connecticut. The material was sufficiently good to give a satisfactory analysis and a complete description of the physical properties. The crystallography, according to Dana, was very unsatisfactory. The specific gravity of 3.08, given in Table 3, obtained on the torsion microbalance (all of the specific gravities measured in this work were made on this balance), is somewhat lower than the value of 3.15 given by the original describers but is close to the calculated value of 3.09.

The material used for this study came from Buckfield, Maine. No chemical analysis was made, but powder pictures of this material and of the type material were identical, proving its authenticity. Several crystallized specimens are in the Harvard collection. All of the crystals, however, are highly etched.

I measured 35 crystals, 5 of which were from the type locality; the remainder were from Buckfield. No consistent measurements could be obtained from any of the Branchville material, but all of the Buckfield crystals gave practically the same results.

On every crystal from Buckfield there were three and often four well-defined forms:  $c\{001\}$ —perfect cleavage,  $b\{010\}$ —good cleavage,  $M\{\bar{1}10\}$ —distinct cleavage, and  $P\{\bar{1}\bar{1}1\}$ —highly etched face. The first three gave constant interfacial angles which check well with those calculated from the elements derived from  $x$ -ray study, as is seen below:

	Observed Average	Calculated
(010) to (001)	76°46'	77°12'
(010) to (110)	127°48'	127°56½'
(001) to (110)	83°26'	83°39½'

The observed averages given above are of the readings from all of the crystals measured. The fourth form,  $P(\bar{1}\bar{1}1)$ , gave angular readings which varied as much as 21 degrees and 18 degrees for the  $\phi$  and  $\rho$  values, respectively. Its approximate location and the fact that it occurred on every crystal, however, are sufficient reasons for including this form. The reason for the wide variation in readings is the fact that the faces of this form are always extremely etched and never give a well-defined signal.

The average of the measured angles is compared with the calculated angles below:

	Measured	Calculated
(001) to ( $\bar{1}\bar{1}1$ )	60°	65°55½'
(010) to ( $\bar{1}\bar{1}1$ )	110	119 52
(110) to ( $\bar{1}\bar{1}1$ )	102	94 04

Although there are wide discrepancies between measured and calculated values, no other form with simple indices gives as good readings.

The typical development of the Buckfield fairfieldite crystals is shown in Fig. 1. They are often doubly terminated and show no pronounced tendency to have any particular face attached to the matrix.

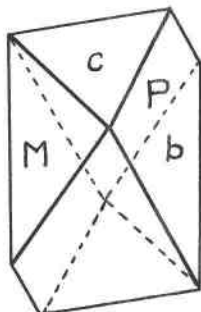


FIG. 1. Fairfieldite from Buckfield.

Table 5 gives the standard angle table and includes, also, the interfacial angle to  $M(\bar{1}\bar{1}0)$ . The front pinacoid was not observed on any of these crystals.

TABLE 5. FAIRFIELDITE: ANGLE TABLE

Triclinic—Pinacoidal

$$a:b:c=0.8791:1:0.8331; \quad \alpha=102^\circ 05', \quad \beta=108^\circ 42\frac{1}{2}', \quad \gamma=90^\circ 05'$$

$$p_0:q_0:r_0=0.9266:0.7891:1; \quad \lambda=77^\circ 12', \quad \mu=70^\circ 50', \quad \nu=85^\circ 45'$$

$$p_0'=1.0032, \quad q_0'=0.8543; \quad x_0'=0.3386, \quad y_0'=0.2399$$

Form	$\phi$	$\rho$	$A$	$B$	$C$	$M$
$c$ 001	$54^\circ 41'$	$22^\circ 32'$	$70^\circ 50'$	$77^\circ 12'$	—	$83^\circ 39\frac{1}{2}'$
$b$ 010	0 00	90 00	85 45	—	$77^\circ 12'$	$127^\circ 56\frac{1}{2}'$
$M$ $\bar{1}\bar{1}0$	$127^\circ 56\frac{1}{2}'$	90 00	$42^\circ 11\frac{1}{2}'$	$127^\circ 56\frac{1}{2}'$	$83^\circ 39\frac{1}{2}'$	—
$P$ $\bar{1}\bar{1}1$	$-136^\circ 08'$	$43^\circ 41\frac{1}{2}'$	$120^\circ 56\frac{1}{2}'$	$119^\circ 52'$	$65^\circ 55\frac{1}{2}'$	$94^\circ 04'$

Brush and Dana have designated the two cleavages as  $b\{010\}$  and  $a\{100\}$ . These become  $c\{001\}$  and  $b\{010\}$  respectively, in the new setting. Due to the very imperfect crystals with which Brush and Dana worked, any further correlation must be but approximate. These authors stated exact measurements were quite impossible, and it seems unwise to try to write a transformation formula which, at best, would be but problematical. It seems likely, however, that their (111) is the equivalent of the strongly etched ( $\bar{1}\bar{1}1$ ) face observed by myself.

The optical orientation referred to the setting in the above angle table is:

Index	$\phi$	$\rho$
X	$120^\circ$	$60^\circ$
Y	$-102^\circ$	$36^\circ$
Z	$18^\circ$	$69^\circ$

This is in essential agreement with that worked out by Berman (1930) on fairfieldite from Poland.

Rotation, 0-layer-line, and 1-layer-line pictures were taken about the [001], [100], and [110] axes. From these the  $x$ -ray data given in Table 3 and the elements in Table 5 were calculated. There is no need to review these calculations here. It is sufficient to point to the excellent agreement between the calculated (3.09) and measured (3.08) specific gravities given in Table 3.

*Roselite and Brandtite.* These two minerals are considered together here because my  $x$ -ray work has proven them to be isostructural, since there is practical coincidence of position and intensities for all spots on the  $x$ -ray pictures.

Similarities and differences between these minerals are shown in Table 3. Differences in optical behavior and specific gravity are easily explained by the differences in composition, the magnesium in the roselite tending to lower the indices of refraction and the specific gravity. It will be noted that two sets of optical data are given for roselite. These are for the "pink" and for the "rose" varieties. The variation in optics, density, and color in the two varieties is, likewise, due to the degree of predominance of magnesium.  $X$ -ray powder pictures of both varieties are identical. For this reason it was not considered necessary to do the Weissenberg work on more than the "pink" one. The amount of magnesium present is insufficient to affect the  $x$ -ray diffraction results.

Aminoff (1919) showed that earlier designations of brandtite as triclinic were in error and made a thorough study of the crystallography, proving the monoclinic symmetry. Later, Peacock (1936) did the same for roselite without cognizance of Aminoff's earlier work on brandtite and obtained strictly comparable results.

No further work on the crystallography of these minerals is necessary except that a transformation formula from the double cells of Aminoff and Peacock must be given. The  $a$ -axis of the unit cell is but half of that given by these earlier workers. The  $x$ -ray pictures of both minerals were excellent, and there seems to be no chance that any halving could have been missed. The transformation formula, then, from Aminoff and Peacock to the structural cell is:  $\frac{1}{2}00/010/001$ .

The  $x$ -ray work on roselite consisted of rotation, 0-layer-line, and 1-layer-line pictures about the  $b[010]$  axis, and rotation and 0-layer-line pictures about the  $c[001]$  axis. A similar set of pictures was taken for brandtite. Peacock noted in his work the almost universal occurrence of twinning in roselite on  $a(100)$ . An apparently single, homogeneous crystal was used for the  $x$ -ray work, but the 0-layer-line and 1-layer-line pictures about  $b[010]$  showed twinning. This twinning was indicated by two in-

terpenetrating lattices with approximate coincidence of one-third of the diffraction spots, which explains the frequency of the twinning. In spite of the halving of the  $a$ -axis, the index of the twin according to the Friedel method of interpretation remains 3 as stated by Peacock (1936). This is due to the presence of a node of the simple lattice in the center of the multiple, pseudo-orthorhombic cell.

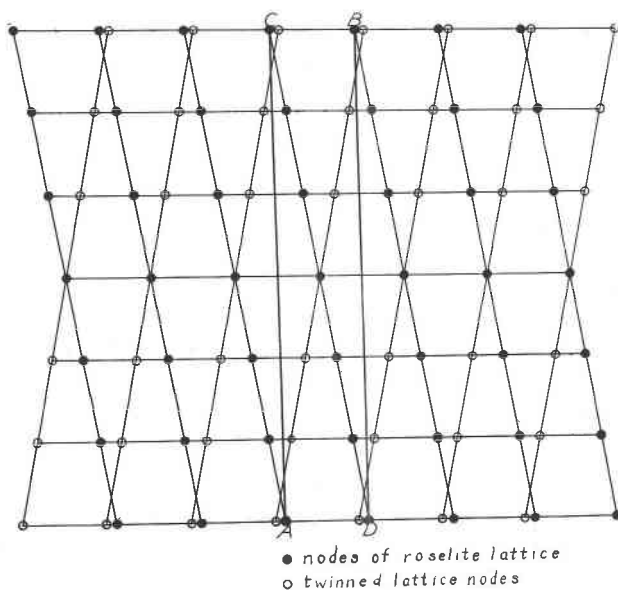


FIG. 2. Twinned lattices of roselite.

Figure 2 shows such a projection with the interpenetrating lattices. That there is an approximate, periodic duplication of the spots in both lattices is apparent. There seems no reason to doubt that it is this duplication which is the physical basis for the twinning. A similar phenomenon was noted in symplectite, which, though triclinic, simulates monoclinic symmetry by a similar twinning of the lattice. An orthorhombic symmetry is simulated in roselite through the twinning of the lattice, as is well shown in Figure 2 by the parallelogram  $ABCD$ .

The space group is fixed by the following determinative reflections, plus the fact that the crystals are holohedral:

$$\begin{aligned} hkl & \text{—all present} \\ h0l & \text{—}l, \text{ even} \\ 0kl & \text{—}k, \text{ even} \end{aligned}$$

Chemically, roselite and brandtite are essentially  $Ca_2A(XO_4)_2 \cdot 2H_2O$  compounds. A in roselite is equivalent to cobalt and magnesium in vary-

ing proportions. As has already been pointed out, the varying amounts of these two are the controlling factors in color, density, and optical variations which have been noted for roselite. The calculated specific gravity given for roselite in Table 3 was derived for a cell containing  $\text{Ca}_4\text{CoMg}(\text{AsO}_4)_4 \cdot 4\text{H}_2\text{O}$ , which is practically the formula obtainable from Winkler's (1877) analysis, the only satisfactory one that has been made of the mineral. The measured specific gravity was made on the "dark rose" variety, which unquestionably carries more cobalt than that in the generalized formula used for calculating the specific gravity. This probably accounts for the discrepancy in values. Specific gravity determinations of the "pink" variety were unreliable due to insufficiently large and homogeneous samples.

A in the brandtite formula is essentially manganese. The calculated specific gravity for brandtite given in Table 3 was derived for a cell containing two molecules of  $\text{CaMn}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$ , which is essentially correct for the analysis made by Lindström (1891).

The slightly larger cell of brandtite is in keeping with the presence of manganese, which has a larger ionic radius than either cobalt or magnesium.

Dana (1892) gives the hardness for brandtite as 5-5.5, which is much greater than the 3.5 of the other minerals of this family. In checking, I found that brandtite would scratch calcite and would not scratch fluorite, making the actual hardness about 3.5.

#### $\text{A}_3(\text{XO}_4)_2 \cdot 3\text{H}_2\text{O}$ FAMILY

*Reddingite.*  $(\text{Mn}_{3/4}\text{Fe}_{1/4})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ . Only one member of this family has thus far been found. This is reddingite with the composition  $(\text{Mn}_{3/4}, \text{Fe}_{1/4})_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$ . There are four of these molecules to the unit cell, yielding  $\text{Mn}_3\text{Fe}_3(\text{PO}_4)_8 \cdot 12\text{H}_2\text{O}$ . This is obtained from the analysis by Gonyer in Berman and Gonyer (1930) on material from Poland, Maine; the same material was used in the *x*-ray investigation.

*X*-ray data were obtained from rotation, 0-layer-line, and 1-layer-line pictures with [010] as the rotation axis, and rotation and 0-layer-line pictures with [100] as the rotation axis. The space group criteria are:

- $hkl$ —all present
- $0kl$ —all present
- $h0l$ —with  $h+l$ , even
- $hk0$ —with  $h$ , even

The mineral is orthorhombic-dipyramidal, and the space group is  $D_{2h}^7 - Pmna$ . Hopeite is the only other orthorhombic mineral in the chemical type. Its space group is  $D_{2h}^{16} - Pnma$ .

The results of the study of reddingite are given in Table 6. The specific

gravity seems to disagree with the general principle that the density should become lower with a higher water content. There is no ambiguity in this case, however, for the cations are iron and manganese, while in the "2H<sub>2</sub>O" family the cation weight was composed principally of the much lighter calcium ion.

TABLE 6. DATA OF THE  $A_3(XO_4)_2 \cdot 3H_2O$  FAMILY

Mineral	Reddingite
Composition	$(Mn_{3/4}Fe_{1/4})_3(PO_4)_2 \cdot 3H_2O$
Crystal System	Orthorhombic
Crystal Class	Dipyramidal
Space Group	$D_{2h}^7-Pmna$
$a_0$	9.52
$b_0$	10.06
$c_0$	8.70
$a_0:b_0:c_0$	0.9463:1:0.8648
Morphology $a:b:c$	0.9428:1:0.8622
Cell Volume	833.2
Cell Contents	4 molecules
Sp. G. Meas.	3.22
Sp. G. Calc.	3.244
Cleavage	{010} poor
Hardness	3-3.5
Optical Sign	+
2V	65°
$r:v$	$r > v$ perc.
Indices of Refraction	$\left. \begin{array}{l} \alpha \\ \beta \\ \gamma \end{array} \right\} \begin{array}{l} 1.655 \\ 1.662 \\ 1.683 \end{array} \begin{array}{l} \text{variable} \\ \text{with} \\ \text{composition} \end{array}$
X	c
Y	b
Z	a
Locality	Poland, Maine

(Part 2 to follow in next issue)