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## CRYSTAL CHEMISTRY OF THE PHOSPHATES, ARSE- NATES AND VANADATES OF THE TYPE $A_2XO_4(Z)$

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## I. INTRODUCTION

### 1. STATEMENT OF PROBLEM

This investigation was undertaken to determine the extent to which minerals of a single chemical type are related, and whether their chemical and physical properties permit their arrangement in a simple classification. The chemical type chosen for this research is expressed by the general formula  $A_2XO_4(Z)$ , which assumed no prior knowledge of the atomic structure. Another formula  $(AZ)(AXO_4)$ , in use in current literature, presupposes a clear perception of the structure, which, the writer believes, has not been adequately demonstrated.

### 2. CRITERIA FOR MINERALOGICAL CLASSIFICATION

*A. Chemical Criteria.* The new approach to the crystallochemical classification between species has been here attempted (Berman, 1937). When minerals are assumed to belong to a chemical type, it implies that their crystal structures may be related through similarities in the relative numbers and sizes of the atoms, the type of bonding between them, and their polarization properties (Stillwell, 1938). In simple chemical compounds, these properties are well known, since many structural analyses

have been made (Stillwell, 1938). However, in the type  $A_2XO_4(Z)$ , little is known concerning their structure because of their complexity. Nevertheless, it is possible to recognize certain fundamental structural properties which must belong to all minerals of this type.

The minerals of the type  $A_2XO_4(Z)$  may be divided into two families, one with a general formula  $AAXO_4(Z)$ , the other  $ABXO_4(Z)$ . This implies, in the first formula, that the two  $A$  positions are equivalent and must, therefore, be occupied either by identical atoms or by unlike atoms whose ionic radii are similar in size and may therefore substitute for each other. When these positions are occupied by identical atoms, simpler compounds are formed, e.g. libethenite  $Cu_2PO_4(OH)$  which is typical of a simple salt of this type. If the positions are occupied by different atoms similar in size, a series usually results in which the ratio between the two atoms is variable, e.g. triplite  $(Fe, Mn)_2PO_4(OH)$ .

In this paper, those minerals forming mixed crystals are said to be isomorphous, using the term in its restricted and classical sense (in Ber- man, 1937). Further examples of this relationship will be seen under the discussion of the sarkinite group.

The positions  $AA$ , assumed to be equivalent in the family  $AAXO_4(Z)$ , become non-equivalent in the family  $ABXO_4(Z)$ . The  $AB$  positions are occupied by unlike atoms whose ionic radii are different, and therefore form double salts in which the ratio between these atoms closely approaches 1:1, e.g. adelite  $CaMgAsO_4(OH)$ .

These cation positions  $AA$  or  $AB$  are not necessarily occupied by atoms of equal valence, but the sum of such valences equals four in the phosphates, arsenates, vanadates and sulphates and six in the silicates. This is shown in adelite  $Ca^{++}Mg^{++}AsO_4(OH)$ , durangite  $Na^+Al^{+++}AsO_4(OH)$  and andalusite  $Al^{+++}Al^{+++}SiO_4(O)$ .

The major division within a chemical type is the family, which is again based on chemistry. The individual species comprising the families do not necessarily form isomorphous series with each other, but they are united by ties of similar cell size, cell edge lengths, axial ratios, optical, chemical and physical properties. The minerals whose properties show this similarity may be said to be *homologous*. This term, in mineralogical classifications, should be restricted to the general relationships between families or groups, not to the more intimate relationships between species or series.

The family itself may be further divided into groups and species on the basis of crystallography and other physical properties.

In the classification which is given below, each family  $AAXO_4(Z)$  and  $ABXO_4(Z)$  contains three crystallographic sections, orthorhombic, monoclinic and triclinic. For purposes of clarity and to avoid repetition, the

discussion of the groups and species will be given under their appropriate crystallographic sections. This arrangement of the discussion will also bring out certain relationships between the orthorhombic species which would otherwise be lost.

*B. Crystallographic Criteria.* The general crystallographic constants from the morphology and *x*-ray study must be in simple relation. In many cases the morphological constants do not coincide with the *x*-ray constants. This disagreement may lie in the adopted morphological orientation, in the choice of the unit form or both. When such discrepancies occur, the morphology is changed in this paper to conform to the

TABLE I. CLASSIFICATION OF THE PHOSPHATES, ARSENATES AND VANADATES OF THE CHEMICAL TYPE  $A_2XO_4(Z)$

Family $AAXO_4(Z)$			
Orthorhombic Section			
Libethenite group			
Libethenite	$Cu_2$	$PO_4$	(OH)
Olivenite	$Cu_2$	$AsO_4$	(OH)
Adamite	$Zn_2$	$AsO_4$	(OH)
Monoclinic Section			
Sarkinite group			
Sarkinite	$Mn_2$	$AsO_4$	(OH)
Triplite	$(Mn, Fe)_2$	$PO_4$	(F)
Sarcopsidite	$(Fe, Mn, Ca)_2$	$PO_4$	(F)
Pseudotriplite	$(Fe, Mn)_2$	$PO_4$	(F)
Triploidite	$(Mn, Fe)_2$	$PO_4$	(OH)
Wagnerite	$Mg_2$	$(Ca, P)O_4$	(F)
Triclinic Section			
Tarbuttite	$Zn_2$	$PO_4$	(OH)
Family $ABXO_4(Z)$			
Orthorhombic Section			
Adelite group			
Adelite	$MgCa$	$AsO_4$	(OH, F)
Higginsite	$CuCa$	$AsO_4$	(OH)
Calciovolborthite	$CuCa$	$VO_4$	(OH)
Austinite	$ZnCa$	$AsO_4$	(OH)
Duftite	$CuPb$	$AsO_4$	(OH)
Descloizite	$(Cu, Zn)Pb$	$VO_4$	(OH)
Araeoxen	$ZnPb$	$(V, As)O_4$	(OH)
Pyrobelonite	$MnPb$	$VO_4$	(OH)
Brackebuschite	$PbMn$	$VO_4$	(OH)
Monoclinic Section			
Tilasite	$MgCa$	$AsO_4$	(F, OH)
Durangite	$NaAl$	$AsO_4$	(F)
Herderite	$CaBe$	$PO_4$	(OH, F)
Triclinic Section			
Amblygonite	$(Li, Na)Al$	$PO_4$	(F, OH)

structural crystallography. This change is commonly advantageous since the new morphology usually gives simpler indices. A full discussion of the orientation adopted here will be given later.

These crystallographic constants, when properly adjusted, may then be used as a basis for arranging the species in an orderly manner within their crystallographic sections.

The major criteria for a mineralogical classification have now been given. It is, therefore, advisable at this point, before discussing the details of the data, to present the suggested classification. This is given in Table 1.

This classification may be compared with that of Dana (1892). The major outline of both classifications is essentially the same, since both are based on the same principles. Because Dana did not recognize the family, as used here, his arrangement is somewhat different. This is due in large part to the fact that the new  $x$ -ray technique was not available to him.

The classifications given by Hintze and by Doelter are essentially the same as Dana's with more emphasis placed on chemistry, which accounts for the somewhat different arrangement.

## II. DATA FOR THE TYPE $A_2XO_4(Z)$

### 1. CHEMISTRY

*A. Phosphates, arsenates, vanadates.* No new chemical analyses have been made for this study with the exception of wagnerite, which will be discussed in its proper place. The chemical composition of the members of the type is well known and generally accepted so that a detailed description of each species from this point of view is unnecessary.

*B. Sulphates.* Two sulphates, lanarkite,  $Pb_2SO_5$ , and dolerophanite,  $Cu_2SO_5$ , may be considered as possible members of the chemical type, since their formulae may equally well be written  $Pb_2SO_4(O)$  and  $Cu_2SO_4(O)$ , respectively. The  $x$ -ray examination of these two minerals in conjunction with their chemical and physical properties shows no relationship with the corresponding properties of any members of the type. The study of these minerals has already been published by Richmond and Wolfe (1938, 1939). The following table summarizes these results.

	<i>Lanarkite</i>	<i>Dolerophanite</i>
Comp.	$Pb_2SO_5$	$Cu_2SO_5$
$a_0$	13.73	9.39
$b_0$	5.68	6.30
$c_0$	7.07	7.62
$a_0:b_0:c_0$	2.417:1:1.245; $\beta=116^\circ 13'$	1.490:1:1.209; $\beta=122^\circ 41\frac{1}{2}'$
$V_0$	494	380

	<i>Lanarkite</i>	<i>Dolerophanite</i>
Space Group	$C_{2h}^3-C2/m$	$C_{2h}^3-C2/m$
H	2-2.5	3
D	6.92	4.17
Optics		
X	1.928	1.715
Y	2.007; Y=b	1.820; Y=b
Z	2.036; Z/c=30°	1.880; Z/c=10°

A comparison of these properties with those shown in Table 4 under the tilasite group indicates that the two minerals, lanarkite and dolerophanite, are more nearly related to members of this group than to the other monoclinic minerals. An examination of the powder photographs (Plate I) of these minerals and those of members of the tilasite group shows no similarity.

From the above evidence it may therefore be concluded that lanarkite and dolerophanite are not members of the type.

*C. Silicates.* Three aluminum silicates, andalusite, sillimanite and cyanite, of the composition  $Al_2SiO_5$ , sphene  $CaTiSiO_5$ , and datolite  $CaBSiO_5$  may be considered as possible members of the type.

The aluminum silicates are all closely related to each other, and andalusite and sillimanite are structurally similar to members of the libethinite and adelite groups, respectively. The following table summarizes the results of various investigations (Taylor, 1928; St. Náray Szabo, Taylor and Jackson, 1928; Taylor, 1929).

	<i>Andalusite</i>	<i>Sillimanite</i>	<i>Cyanite</i>
Comp.	$Al_2SiO_4(O)$	$Al_2SiO_4(O)$	$Al_2SiO_4(O)$
$a_0$	7.76	7.43	7.09 $\alpha = 90^\circ 05\frac{1}{2}'$
$b_0$	7.90	7.58	7.72 $\beta = 101^\circ 02'$
$c_0$	5.56	5.74	5.56 $\gamma = 105^\circ 44\frac{1}{2}'$
$a_0:b_0:c_0$	0.982:1:0.703	0.980:1:0.757	0.919:1:0.720
$V_0$	341	323	
No. of Mol.	4	4	4
Space Group	$D_{2h}^{12}-Pnmm$	$D_{2h}^{16}-Pnma$	$C_3^1-PI$
H	7.5	6-7	5-7.25
D	3.16-3.20	3.23-3.24	3.56-3.67
Opt. Orient.	Y=b; Z=a	X=b; Z=c	X= $\sim$ ⊥{001}; Z/c=30°
nX	1.634	1.659	1.712
nY	1.639	1.660	1.720
nZ	1.643	1.680	1.728
Sign	neg.	pos.	pos./neg.

A comparison of these properties with those given in Table 3 shows similarity in the ratio of the cell edge lengths to the libethenite group, but considerable difference in the absolute cell edge lengths which are more

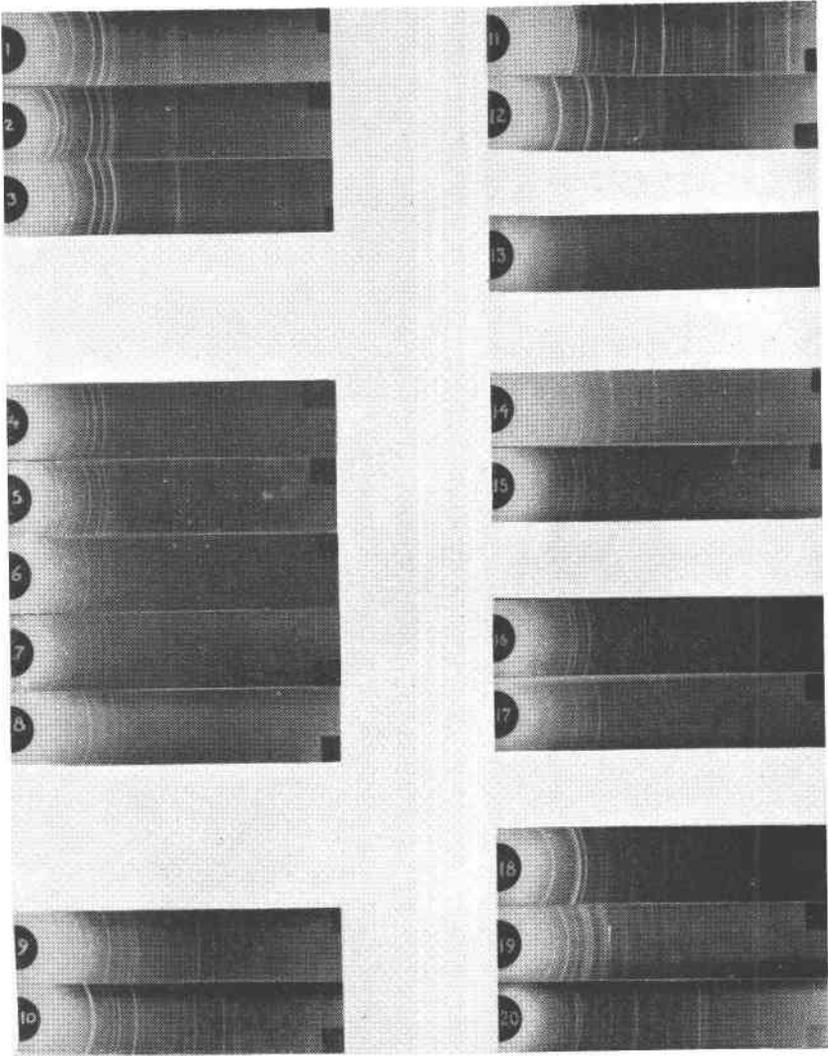


Plate I.

Powder photographs of some of the minerals of the type  $A_2XO_4(Z)$

- |                      |                   |
|----------------------|-------------------|
| 1. Libethenite       | 12. Dolerophanite |
| 2. Olivenite         | 13. Wagnerite     |
| 3. Adamite           | 14. Herderite     |
| 4. Higginsite        | 15. Datolite      |
| 5. Austinite         | 16. Tilasite      |
| 6. Duftite           | 17. Durangite     |
| 7. Descloizite       | 18. Amblygonite   |
| 8. Calciovolborthite | 19. Tarbuttite    |
| 9. Andalusite        | 20. Cyanite       |
| 10. Sillimanite      |                   |
| 11. Lanarkite        |                   |

closely related to some members of the adelite group. On this basis it cannot be assumed that these minerals are homologous with members of either the libethenite or adelite group, but they are related generally to the family  $AAXO_4(Z)$ .<sup>1</sup>

Strunz (1937) has pointed out the relationship of sphene to tilasite and durangite. This relationship is seen in the following table.

	<i>Tilasite</i>	<i>Sphene</i>	<i>Durangite</i>
Comp.	CaMgAsO <sub>4</sub> (F)	CaTiSiO <sub>4</sub> (O)	NaAlAsO <sub>4</sub> (F)
<i>a</i> <sub>0</sub>	7.56	7.43	7.30
<i>b</i> <sub>0</sub>	8.95	8.70	8.46
<i>c</i> <sub>0</sub>	6.66	6.55	6.53
<i>a</i> <sub>0</sub> : <i>b</i> <sub>0</sub> : <i>c</i> <sub>0</sub>	0.839:1:0.750	0.854:1:0.753	0.856:1:0.772
β	120°59'	119°43'	119°22'
<i>V</i> <sub>0</sub>	386	367	352
No. of Mol.	4	4	4
Space Group	<i>C</i> <sub>2h</sub> <sup>6</sup> - <i>C</i> <sub>2</sub> / <i>a</i>	<i>C</i> <sub>2h</sub> <sup>6</sup> - <i>C</i> <sub>2</sub> / <i>a</i>	<i>C</i> <sub>2h</sub> <sup>6</sup> - <i>C</i> <sub>2</sub> / <i>a</i>
H	5	5-5.5	5
D	3.68-3.79	3.4-3.56	3.94-4.03
Opt. Orient.	<i>Z</i> = <i>b</i> ; ext. 30°	<i>Y</i> = <i>b</i> ; <i>Z</i> ∧ <i>c</i> = 51°	<i>Y</i> = <i>b</i> ; <i>Z</i> ∧ <i>c</i> = 65°
<i>n</i> <sub>X</sub>	1.640	1.900	1.634
<i>n</i> <sub>Y</sub>	1.660	1.907	1.673
<i>n</i> <sub>Z</sub>	1.675	2.034	1.685
Sign	neg.	pos.	neg.

The similarity of the properties of the three minerals is striking and illustrates the homologous relationship.

Strunz (1936) has shown the relationship between datolite and herderite. The remarkable similarity between the physical constants is seen in the following table and in the powder photographs of Plate I.

	<i>Datolite</i>	<i>Herderite</i>
Comp.	CaBSiO <sub>4</sub> (OH)	CaBePO <sub>4</sub> (F, OH)
<i>a</i> <sub>0</sub>	9.64	9.80
<i>b</i> <sub>0</sub>	7.62	7.68
<i>c</i> <sub>0</sub>	4.82	4.80
<i>a</i> <sub>0</sub> : <i>b</i> <sub>0</sub> : <i>c</i> <sub>0</sub>	1.266:1:0.633	1.276:1:0.625
β	90°09'	90°06'
<i>V</i> <sub>0</sub>	352	314
No. of Mol.	4	4

<sup>1</sup> Machatschki (1930) states that powder photographs of berzeliite (Na, Ca<sub>2</sub>)Mn<sub>2</sub>As<sub>3</sub>O<sub>12</sub> and calcium garnets are nearly identical. He explains this similarity on the basis of "isomorphism" between *As* and *Si* atoms. This is additional evidence that *Si* behaves in much the same manner as *P*, *As* and *V* in the  $XO_4$  group. It is, therefore, not surprising that the silicates considered here are more or less closely related to the phosphates, arsenates and vanadates of the type.

	<i>Datolite</i>	<i>Herderite</i>
Space Group	$C_{2h}^5 - P2_1/c$	$C_{2h}^5 - P2_1/c$
H	5-5.5	5
D	2.9-3.0	3.0
Opt. Orient.	$Y=b; Z \wedge c = 1-4^\circ$	$Y=b; Z \wedge c = 3\frac{1}{2}^\circ$
$nX$	1.626	1.591
$nY$	1.654	1.611
$nZ$	1.670	1.619
Sign	neg.	neg.

## 2. CRYSTALLOGRAPHY

In order to directly compare the crystallography of each species in the various crystallographic sections and to point out the relationships which exists between them, it is first necessary to reduce the orientation of each species to a comparable setting. This has been accomplished in the orthorhombic section by adopting the conventional setting  $b > a > c$ . In the monoclinic system,  $b$  is fixed by the symmetry, but the other axes are chosen with  $a > c$ .

This orientation, for many of the species, has not been adopted in the original description. These species are therefore reoriented to conform to this convention, and transformation formulae (Donnay in Peacock, 1937) are given from the original to the conventional setting. In the orthorhombic and monoclinic sections these changes, with one exception, involve only an interchange of the axes. These conventions have also been used in the orientation of the unit cell.

The determination of the lattice constants derived from  $x$ -ray study constitutes most of the new data presented here. Therefore, a comprehensive description of the  $x$ -ray crystallography of each species will be given and the relation to the crystal morphology stated.

*A. Orthorhombic Section.* The minerals in this section are nine in number, three belonging to the family  $AAXO_4(Z)$  and six to the family  $ABXO_4(Z)$ .

The crystallography of these minerals as a whole is characterized by similarity of absolute cell edge lengths and axial ratios; on the other hand, there are certain systematic differences in these constants which may be arranged to exhibit a certain definite continuity. This is shown in Table 2, where the arrangement of the species follows very closely a slight differential increase in the lengths of  $a_0$  and  $b_0$ ;  $c_0$  remains constant throughout the entire sequence and shows a maximum difference of only 3%. This systematic change in the absolute cell edge lengths is reflected in a corresponding change in the volume and axial ratios of the unit cell. There is a definite interruption in this continuity between adamite and adelite. This interruption occurs at the transition from simple to double compounds, and is accompanied by an ap-

TABLE 2. SUMMARY OF THE LATTICE CONSTANTS OF THE LIBETHENITE AND ADELITE GROUPS

1		2		3		4		5		6		7		
Composition		Cell edge lengths		Axial Ratio		Vol.		Ionic radii of cations		Ionic sum		$a_0/c_0$		
		$a_0$	$b_0$	$c_0$										
<i>Libethenite Group</i>														
	$\text{Cu}_2\text{PO}_4(\text{OH})$	8.08	8.43	5.90	0.958:1:0.700		401	.80 (Est.)		1.60	1.37			
	$\text{Cu}_2\text{AsO}_4(\text{OH})$	8.16	8.54	5.86	0.955:1:0.686		408	.80		1.60	1.38			
	$\text{Zn}_2\text{AsO}_4(\text{OH})$	8.32	8.54	6.08	0.974:1:0.712		431	.83		1.66	1.37			
<i>Adelite Group</i>														
	$\text{MgCaAsO}_4(\text{OH})$	7.43	8.85	5.88	0.840:1:0.665		387	.78, 1.06		1.84	1.26			
	$\text{CuCaAsO}_4(\text{OH})$	7.42	9.20	5.85	0.806:1:0.636		399	.80, 1.06		1.86	1.26			
	$\text{ZnCaAsO}_4(\text{OH})$	7.43	9.00	5.90	0.826:1:0.656		394	.83, 1.06		1.89	1.26			
	$\text{CuPbAsO}_4(\text{OH})$	7.50	9.12	5.90	0.822:1:0.647		404	.80, 1.32		2.12	1.27			
	$(\text{Cu}, \text{Zn})\text{PbVO}_4(\text{OH})$	7.56	9.39	6.05	0.805:1:0.643		430	.82, 1.32		2.14	1.25			
	$\text{Mn PbVO}_4(\text{OH})$	7.58	9.45	6.09	0.802:1:0.644		451	.91, 1.32		2.23	1.25			

TABLE 3. SUMMARY OF THE CHEMICAL AND PHYSICAL PROPERTIES OF THE LIBETHENITE AND ADELITE GROUPS

		<i>Libethenite Group</i>				<i>Adelite Group</i>	
Mineral Comp.	Libethenite $Cu_2PO_4(OH)$	Olivineite $Cu_2AsO_4(OH)$	Adamite $Zn_2AsO_4(OH)$	Duftsittite $CuPbAsO_4(OH)$	Descloizite $(Cu, Zn)PbVO_4(OH)$	Pyrobelonite $MnPbVO_4(OH)$	
$a_0$	8.08	8.16	8.32	7.50	7.56	7.84	
$b_0$	8.43	8.54	8.54	9.12	9.39	9.45	
$c_0$	5.90	5.86	6.08	5.90	6.05	6.09	
$a_0:b_0:c_0$	0.958:1.0.700	0.955:1.0.686	0.974:1.0.712	0.822:1.0.647	0.805:1.0.643	0.802:1.0.644	
$V_0$	401	408	431	404	432	451	
Ionic Sum	1.60	1.60	1.66	2.12	2.14	2.23	
No. of Mol.	4	4	4	4	4	4	
Space Group	$D_{2h}^{12}-Pnmm$	$D_2^4-P2_12_1$	$D_{2h}^{12}-Pnmm$	$D_{2h}^6-Pnna$	$D_{2h}^{10}-Pnma$	$D_{2h}^{10}-Pnma$	
H	3	3	3.5	3	3.5	3.5	
D	3.6-3.8	4.1-4.4	4.34-4.35	6.19	5.9-6.2	5.38	
Opt. Orient.	$Y=c, X=b$	$Y=c, X=b$	$Y=c, X=b$	—	$Y=b, X=a$	$Y=c, X=a$	
$nX$	1.702	1.772	1.708	2.06	2.185	2.32	
$nY$	1.745	1.810	1.744	2.08	2.265	2.36	
$nZ$	1.789	1.863	1.773	2.09	2.35	2.37	
Sign	Negative	Positive	Negative	Negative	Positive	Negative	
<i>Adelite Group</i>							
Mineral Comp.	Adelite $MgCaAsO_4(OH)$	Higginsite $CuCaAsO_4(OH)$	Austinite $ZnCaAsO_4(OH)$	Duftsittite $CuPbAsO_4(OH)$	Descloizite $(Cu, Zn)PbVO_4(OH)$	Pyrobelonite $MnPbVO_4(OH)$	
$a_0$	7.43	7.42	7.43	7.50	7.56	7.84	
$b_0$	8.85	9.20	9.00	9.12	9.39	9.45	
$c_0$	5.88	5.85	5.90	5.90	6.05	6.09	
$a_0:b_0:c_0$	0.840:1.0.665	0.806:1.0.636	0.826:1.0.656	0.822:1.0.647	0.805:1.0.643	0.802:1.0.644	
$V_0$	387	399	394	404	432	451	
Ionic Sum	1.84	1.86	1.89	2.12	2.14	2.23	
No. of Mol.	4	4	4	4	4	4	
Space Group	—	$D_{2h}^6-Pnmm$	$D_2^4-P2_12_1$	$D_{2h}^6-Pnna$	$D_{2h}^{10}-Pnma$	$D_{2h}^{10}-Pnma$	
H	—	4.5	4	3	3.5	3.5	
D	3.71-3.76	4.33	4.12	6.19	5.9-6.2	5.38	
Opt. Orient.	—	$Y=a, X=b$	$Y=c, X=a$	—	$Y=b, X=a$	$Y=c, X=a$	
$nX$	—	1.800	1.759	2.06	2.185	2.32	
$nY$	1.707	1.836	1.763	2.08	2.265	2.36	
$nZ$	—	1.846	1.783	2.09	2.35	2.37	
Sign	—	Negative	Positive	Negative	Positive	Negative	

preciable change in the absolute cell edge lengths. In the libethenite groups there is an increase of 1–2% in the absolute lengths  $a_0$  and  $b_0$ , but in the transition from the libethenite  $AA(XO_4)Z$  to the adelite group  $AB(XO_4)Z$ ;  $a_0$  decreases 10% and  $b_0$  increases 4%. In the adelite group the orderly increase of about 1% for  $a_0$  and  $b_0$  is again apparent. This break in the sequence between the two groups is also reflected in the change in the ratio of  $a_0:c_0$  from 1.37 to 1.26.

These significant crystallographic and chemical changes are accompanied and, as will be pointed out, are caused by a systematic increase in the sum of the ionic radii of the cations AA or AB.

The orthorhombic section may, therefore, be divided into two groups (Table 2), on the basis of (1) change from simple to double salts, (2) relatively large change in the absolute cell edge lengths and axial ratios, and (3) abrupt change in the sum of the ionic radii of the cations.

The physical properties, hardness and density, vary somewhat, as would be expected from the chemical composition. This variation is shown in Table 3.

The habit of the crystals in the libethenite group is remarkably constant, varying little from short prismatic with simple terminations. The minerals of the adelite group vary from short prismatic to a needle-like habit having a considerably more complex form pattern.

The optical properties of the libethenite group are consistent with each other, but in the adelite group there is no correspondence. This lack of correspondence is due to the fact that optical properties are sensitive to slight chemical changes. In the adelite group, these chemical changes are relatively great. The optical properties are given in Table 3.

(a) LIBETHENITE GROUP. This group is composed of three minerals, libethenite, olivenite and adamite. They are all simple salts  $AAXO_4(Z)$  forming crystals of similar habit and have similar cell edge lengths and an  $a_0:c_0$  ratio of 1.37.

*Libethenite and adamite.* Strunz (1936) determined the lattice constants and space group of libethenite and adamite. These results are:

	<i>Libethenite</i>	<i>Adamite</i>
$a_0$	8.08	8.32
$b_0$	8.43	8.54
$c_0$	5.90	6.08
$a_0:b_0:c_0$	0.958:1:0.700	0.974:1:0.712
$a:b:c$	0.960:1:0.703 (Melczer, 1904)	0.9770:1:0.7124 (morphology) (Ungemach, 1921)
Space Group	$D_{2h}^{12}-Pnm$	$D_{2h}^{12}-Pnm$

Strunz states that these minerals may belong to the space group  $Pm\bar{m}n$  or  $Pmmm$ . His evidence is based on powder photographs and is not sufficient to place them definitely in any one of these space groups.

The cell formula of libethenite is  $4[Cu_2PO_4(OH)]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
CuO	66.42	66.76	0.838	Cu 0.838	7.97	8
P <sub>2</sub> O <sub>5</sub>	29.31	29.46	0.207	P 0.414	3.94	4
H <sub>2</sub> O	3.74	3.78	0.210	H 0.420	3.99	4
	<hr/>	<hr/>		O 2.083	19.82	20
	99.47	100.00				

Specific gravity: measured 3.94, calculated 3.94.

Analysis of libethenite from Coquimbo, Chile; analyst Field (1875).

The cell formula of adamite is  $4[Zn_2AsO_4(OH)]$  determined from the following table:

Analysis	Proportions		No. of atoms per unit cell		
	Molecular	Atomic	Actual	Theory	
ZnO	56.98	0.701	Zn 0.701	7.97	8
As <sub>2</sub> O <sub>5</sub>	39.80	0.181	As 0.362	4.12	4
H <sub>2</sub> O (diff.)	3.22	0.178	H 0.356	4.05	4
	<hr/>		O 1.854	21.10	20
	100.00				

Specific gravity: measured 4.35, calculated 4.39.

Analysis of adamite from Island of Thasos; analyst Rosický (1908).

*Olivenite*. Heritsch (1937) worked out the lattice constants, space groups and structure of olivenite. The writer, working at the same time, agrees with Heritsch's determination of the lattice constants but not with the space group. These constants are:

	Heritsch	Richmond
$a_0$	8.20	8.16
$b_0$	8.62	8.54
$c_0$	5.94	5.86
$a_0:b_0:c_0$	0.963:1:0.689	0.955:1:0.686
$a:b:c$	0.9485:1:0.6810	(morphology)
Space group	$D_{2h}^{12} - Pn\bar{m}$	$D_2^4 - P2_12_12_1$

Transformation Goldschmidt (1897)—Heritsch and Richmond 010/100/001; an interchange of the  $a$ - and  $b$ -axes.

The unit cell of olivenite contains  $4[Cu_2AsO_4(OH)]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
CuO	55.40	55.80	0.703	Cu 0.706	7.65	8
FeO	0.25	0.25	0.003			
As <sub>2</sub> O <sub>5</sub>	40.05	40.35	0.176	As 0.354	3.84	4
P <sub>2</sub> O <sub>5</sub>	0.06	0.06	0.001			
H <sub>2</sub> O	3.39	3.54	0.197	H 0.394	4.28	4
				O 1.788	19.40	20
	99.15	100.00				

Specific gravity: measured 4.378, calculated 4.58.

Analysis of olivenite from American Eagle Mine, Tintic, Utah; analyst Hillebrand (1886).

The writer took Weissenberg photographs about  $c[001]$  and  $a[100]$  and from the various layer-line reciprocal lattice projections determined space group criteria which definitely assigned olivenite to the space group  $D_2^4$ . This is the one symmetry class which has a unique solution with Weissenberg technique. The following reflections were present on the projections:

- ( $hkl$ ) with all present
- ( $h00$ ) with  $h$  even
- ( $0k0$ ) with  $k$  even
- ( $00l$ ) with  $l$  even

This permits of only one space group  $D_2^4$ , which corresponds to the disphenoidal crystal class.

Believing that there should be some morphological evidence of the space group determined from the  $x$ -ray study, specimens of olivenite from Tintic, Utah, were examined for suitable crystals for goniometric measurement. Excellent crystals were found which were terminated by the unit pyramid and several domes.

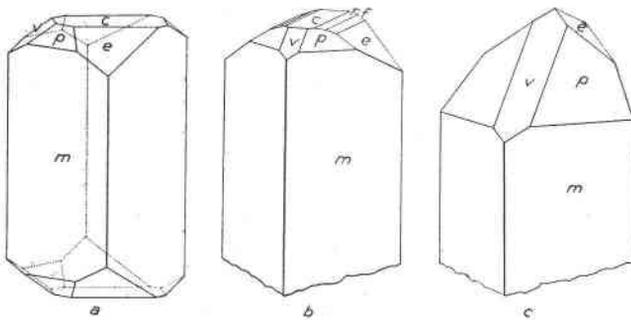


FIG. 1. Crystals of olivenite from Tintic, Utah, illustrating (a) the hemimorphic character of the mineral; (b) a typical habit with the new form  $r\{012\}$ , (c) an unusual habit with strong development of (111) and  $(1\bar{1}1)$ .

The distribution of the faces of the unit pyramid upon the numerous measured crystals indicates that olivenite is hemimorphic about the  $a$ -axis. In order to retain an orientation similar to that of libethenite and adamite, this hemimorphic axis has not been transferred to the conventional  $c$ -axis.

Figure 1*a* shows the usual development of the common forms with the faces (111) and ( $\bar{1}\bar{1}$ ), the only faces of the unit pyramid present; this is regarded as the unit hemipyramid. This condition was found on 25 measured crystals. On two crystals only, shown in Fig. 1*c*, there were, in addition, small faces of the unit negative hemipyramid ( $\bar{1}\bar{1}\bar{1}$ ) and ( $\bar{1}\bar{1}\bar{1}$ ).

With regard to the other terminal forms,  $V\{101\}$  is usually prominent and  $V'\{\bar{1}01\}$  a small face;  $e\{011\}$  and  $e'\{0\bar{1}\bar{1}\}$  are equally developed. One new form,  $r\{012\}$ , occurred on 5 crystals as a small, brilliant face (Fig. 1*b*) and on the gnomonic projection appeared in good position. The following table gives the measured mean, average mean, and calculated  $\phi$  and  $\rho$  of the new form:

Number of faces	Measured mean		Average mean		Calculated	
	$\phi$	$\rho$	$\phi$	$\rho$	$\phi$	$\rho$
7	$-0^\circ08' - +0^\circ08'$	$18^\circ53' - 19^\circ02'$	$-0^\circ01'$	$18^\circ58'$	$0^\circ00'$	$18^\circ48'$

The hemimorphic character of the crystals of olivenite is thus established by the morphology. The distribution of the pyramid planes which would satisfy the disphenoidal symmetry called for by the  $x$ -ray study was not found on a single crystal. However, by analogy with austinite, a member of the adelite group belonging to the space group  $D_2^4$ , there is still further evidence that olivenite is disphenoidal. A comparison of the reciprocal lattice projections of austinite and olivenite shows nearly exact spot-for-spot coincidence, and the morphology of austinite is definitely disphenoidal.

At the present time, therefore, olivenite must be considered disphenoidal on the basis of the  $x$ -ray study. The discrepancy which exists between this study and the morphology must be left for future examination.

(b) ADELITE GROUP. This group contains six minerals, adelite, higginsite, austinite, duftite, descloizite, and pyrobelonite. The group as a whole has similar but increasing cell edge lengths with an  $a_0:c_0$  ratio of 1.26. They are all double salts  $ABXO_4(Z)$ . In general, they are prismatic, varying from a short stubby habit to a needle-like form.

*Adelite*. The original description of adelite by Sjögren (1894) was made on material from Jakobsberg, Sweden. Aminoff (1933) re-examined the type material and found that Sjögren had measured pyroxene crystals, in error, thinking they were adelite. This was proved both by crystallographic data and by powder photographs. Therefore, the crystallograph-

ic data given by Doelter (1914) and Hintze (1931) are not those of adelite but those of a pyroxene.

Aminoff studied anew the morphology of adelite crystals and determined the lattice constants but not the space group. He did not determine all the physical properties shown in Table 3. The orientation of Aminoff's unit cell is not in accordance with the conventional setting adopted here. His lattice constants are:

$$\begin{aligned} a_0 &= 7.43 & a_0 : b_0 : c_0 &= 0.8405 : 1 : 0.665 \\ b_0 &= 8.85 & a : b : c &= 0.8294 : 1 : 0.6650 \text{ (morphology)} \\ c_0 &= 5.88 \end{aligned}$$

Transformation Aminoff-Richmond 010/100/001; an interchange of  $a$ - and  $b$ -axes.

The unit cell formula of adelite is  $4[\text{CaMgAsO}_4(\text{OH},\text{F})]$  determined from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
CaO	23.43	23.46	0.418	Ca 0.418	3.76	4
MgO	17.10	17.12	0.425	Mg 0.425	3.79	4
MnO	4.38	4.38	0.062			
PbO	0.17	0.17	0.000			
P <sub>2</sub> O <sub>5</sub>	3.01	3.01	0.021	P 0.042	4.05	4
As <sub>2</sub> O <sub>5</sub>	47.40	47.40	0.206	As 0.412		
Cl	0.31	0.31	0.001	Cl 0.001	3.98	4
F	1.44	1.44	0.076	F 0.076		
H <sub>2</sub> O	3.33	3.33	0.185	H 0.370		
				O 2.123	18.92	20
	100.57	100.62				
O = Cl <sub>2</sub> + F <sub>2</sub>	.62	.62	0.040			
	99.89	100.00				

Specific gravity: measured 3.80, calculated 3.79.

Analysis of adelite from Långban; analyst R. Blix in Aminoff (1933).

*Higginsite.* The  $x$ -ray study of this mineral was made on a crystal several millimeters in size. Due to the relatively large size of the crystal, the results obtained are only accurate to approximately  $1\frac{1}{2}\%$ .

The constants derived from the measurements and calculations of the Weissenberg photographs give:

$$\begin{aligned} a_0 &= 7.42 & a_0 : b_0 : c_0 &= 0.806 : 1 : 0.636 \\ b_0 &= 9.20 & a : b : c &= 0.8010 : 1 : 0.636 \text{ (morphology)} \\ c_0 &= 5.85 \end{aligned}$$

Transformation Palache-Richmond 010/ $\frac{1}{2}$ 00/001; an interchange of the  $a$ - and  $b$ -axes with the  $b$ -axis halved.

The space group is  $D_{2h}^5$ - $Pm\bar{m}$  determined from the following reflections:

( $hkl$ ) with all present  
 ( $0kl$ ) with all present  
 ( $h0l$ ) with  $h$  even  
 ( $hk0$ ) with all present

The unit cell formula is  $4[\text{CuCaAsO}_4(\text{OH})]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
Cu	28.67	29.83	0.375	Cu 0.375	3.94	4
CaO	20.83	21.67	0.387	Ca 0.387	4.06	4
As <sub>2</sub> O <sub>5</sub>	41.23	42.90	0.187	As 0.374	4.17	4
V <sub>2</sub> O <sub>5</sub>	1.97	2.05	0.011	V 0.022		
H <sub>2</sub> O	3.41	3.55	0.198	H 0.396	4.16	4
Fe <sub>2</sub> O <sub>3</sub>	0.48			O 1.950	20.45	20
MnO	2.84					
Gangue	0.86					
	100.29	100.00				

Specific gravity: measured 4.33, calculated 4.34.

Analysis of higginsite, Bisbee, Arizona; analyst E. V. Shannon (1920).

Palache (in Palache and Shannon, 1920) pointed out the relationship of higginsite to descloizite and olivenite. He recognized the similarity between these minerals on the basis of their axial ratios, but a closer examination of his data in connection with the  $x$ -ray study shows that higginsite is more closely related to descloizite than to olivenite.

The setting chosen by Palache does not conform to the conventional position, and his unit form is not in agreement with that obtained from the  $x$ -ray study. The choice of the unit form derived from the  $x$ -ray study gives simpler indices and is for this reason preferable.

*Austinite*. Staples (1935) described the morphology of austinite and showed its disphenoidal character. The  $x$ -ray study confirmed this symmetry through the reflections on the Weissenberg photographs, which are:

( $hkl$ ) with all present  
 ( $h00$ ) with  $h$  even  
 ( $0k0$ ) with  $k$  even  
 ( $00l$ ) with  $l$  even

The lattice constants derived from the measurements and calculation of the Weissenberg photographs are:

$$\begin{aligned}
 a_0 &= 7.43 & a_0:b_0:c_0 &= 0.826:1:0.656 \\
 b_0 &= 9.00 & a : b : c &= 0.832:1:0.657 \text{ (morphology)} \\
 c_0 &= 5.90
 \end{aligned}$$

Transformation: Staples-Richmond 001/010/100; an interchange of the *a*- and *c*-axes.

The unit cell formula is  $4[\text{CaZnAsO}_4(\text{OH})]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
CaO	19.2	19.57	0.349	Ca 0.349	3.43	4
ZnO	32.5	33.13	0.406	Zn 0.406	3.99	4
As <sub>2</sub> O <sub>3</sub>	42.7	43.54	0.190	As 0.380	3.74	4
P <sub>2</sub> O <sub>5</sub>	0.1	0.10		H 0.412	4.05	4
H <sub>2</sub> O	3.6	3.66	0.206	O 1.911	18.80	20
Residue	2.4					
	100.5	100.00				

Specific gravity: measured, 4.12 (ca); calculated 4.37.

Analysis of austinite from Gold Hill, Utah; analyst R. B. Ellestad (1933).

*Duftite*. The morphology of duftite is unknown because the crystals are poorly developed with faces lacking sufficient luster to give adequate reflections. The habit is prismatic and terminated only by (011).

The lattice constants derived from Weissenberg photographs are:

$$\begin{aligned}
 a_0 &= 7.50 & a_0:b_0:c_0 &= 0.822:1:0.647 \\
 b_0 &= 9.12 & & \text{No morphology} \\
 c_0 &= 5.90
 \end{aligned}$$

This is the first time the axial ratio has been given.

The space group is, tentatively,  $D_{2h}^6\text{-}Pnan$ . The first layer-line photograph about [001] is weak and gives (*hkl*) with *h+k* even, which with reflections from the zero layer-line photographs give inconsistent criteria. If it is assumed that the missing spectra on the first layer-line photograph are due either to the faintness of the film or structural arrangement, the reflections are then as follows and give the above space group:

- (*hkl*) with all present
- (*h0l*) with *h* even
- (*0kl*) with *k+l* even
- (*hk0*) with *h+k* even
- (*00l*) with *l* even
- (*0k0*) with *k* even

The unit cell formula is  $4[\text{CuPbAsO}_4(\text{OH})]$  determined from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
PbO	50.10	50.48	0.226	Pb 0.226	3.62	4
CaO	0.75	0.75	0.013	Ca 0.013		
ZnO	0.46	0.46	0.006	Zn 0.006	3.80	4
CuO	19.32	19.45	0.245	Cu 0.245		
SiO <sub>2</sub>	0.44					
As <sub>2</sub> O <sub>5</sub>	26.01	26.20	0.114	As 0.228	3.45	4
H <sub>2</sub> O	2.65	2.66	0.148	H 0.296	4.08	4
				O 1.208	18.30	20
	99.73	100.00				

Specific gravity: measured 6.19, calculated 6.99.

Analysis of duftite, Tsumeb; analyst, O. Pufahl (1920).

*Descloizite*. The lattice constants and space group of descloizite as given by Bannister (1933) are:

$$\begin{aligned}
 a_0 &= 7.56 & a_0:b_0:c_0 &= 0.805:1:0.643 \\
 b_0 &= 9.39 & a:b:c &= 0.8046:1:0.6367 \text{ (morphology)} \\
 c_0 &= 6.05
 \end{aligned}$$

Transformation: Goldschmidt (1897) and Bannister-Richmond 001/010/100; an interchange of the  $a$ - and  $c$ -axes.

The unit cell formula is  $4[(Cu,Zn)PbVO_4(OH)]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
ZnO	17.56	17.64	0.217	Zn 0.217	3.55	4
CuO	0.40	0.40	0.005	Cu 0.005		
FeO	0.07	0.07	—			
MnO	0.77	0.77	0.011	Mn 0.011	4.21	4
PbO	56.01	56.30	0.252	Pb 0.252		
P <sub>2</sub> O <sub>6</sub>	0.30	0.30	0.002	P 0.004	3.90	4
V <sub>2</sub> O <sub>5</sub>	21.85	21.95	0.120	V 0.240		
H <sub>2</sub> O	2.57	2.57	0.143	H 0.286	4.52	4
Cl	0.27			O 1.238	19.80	20
Insoluble	0.78					
	100.58	100.00				

Specific gravity: measured 6.10, calculated 6.20.

Analysis of descloizite, Sierra de Córdoba, Argentina; analyst Rammelsberg (1880).

*Descloizite series*. Bannister investigated, by powder diffraction photographs, descloizite, mottramite, psittacinite, chileite, eusynchite and deschenite. He states that the photographs are identical and proposes to discard all species names except descloizite and mottramite. He suggests the name descloizite for a mixed crystal of the composition (Cu,Zn)-

$\text{PbVO}_4(\text{OH})$  in which there is less than 10%  $\text{CuO}$  and when this figure is exceeded he proposes the name mottramite.

In this series there is a statistical replacement of  $\text{Cu}$  and  $\text{Zn}$  in one of the non-equivalent positions AB (the other position is occupied by  $\text{Pb}$ ) forming a mixed crystal.

*Pyrobelonite*. The calculations from the Weissenberg photographs give the following lattice constants:

$$\begin{aligned} a_0 &= 7.84 & a_0 : b_0 : c_0 &= 0.802 : 1 : 0.644 \\ b_0 &= 9.45 & a : b : c &= 0.80402 : 1 : 0.65091 \text{ (morphology)} \\ c_0 &= 6.09 \end{aligned}$$

The space group of pyrobelonite is  $D_{2h}^{16}$ -*Pnam* from the following reflections:

$$\begin{aligned} (hkl) &\text{ with all present} \\ (0kl) &\text{ with } k+l \text{ even} \\ (h0l) &\text{ with } h \text{ even} \\ (hk0) &\text{ with all present} \end{aligned}$$

The unit cell formula is  $4[(\text{Mn}, \text{Pb})_2\text{VO}_4(\text{OH})]$  with  $\text{Mn}:\text{Pb}=5:3$  determined from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
$\text{SiO}_2$	0.21					
$\text{PbO}$	48.99	49.51	0.222	Pb 0.222	3.15	3
$\text{MnO}$	25.01	25.26	0.357	Mn 0.357	5.08	5
$\text{FeO}$	0.47	0.47	0.006	Fe 0.006		
$\text{MgO}$	0.60	0.60	0.015	Mg 0.015		
$\text{CaO}$	0.79	0.79	0.014	Ca 0.014	3.21	4
$\text{V}_2\text{O}_5$	20.03	20.26	0.112	V 0.224		
$\text{P}_2\text{O}_5$	0.05	0.05	0.001	P 0.002		
$\text{H}_2\text{O}$	3.02	3.06	0.170	H 0.340	4.83	4
				O 1.569	22.70	20
	99.17	100.00				

Specific gravity: measured 5.377; calculated 5.39.

Analysis of pyrobelonite, Långban; analyst, Mauzelius (1919).

Pyrobelonite is placed provisionally in the family  $\text{ABXO}_4(\text{Z})$ . The ionic radii of  $\text{Mn}$  and  $\text{Pb}$ , 0.91 Å and 1.32 Å respectively, are sufficiently different in their sizes to permit the non-equivalent AB positions to be occupied by  $\text{Mn}$  and  $\text{Pb}$  with a ratio of 1:1. However, the analysis indicates that the ratio of  $\text{Mn}$  and  $\text{Pb}$  is very nearly 5:3.

The preceding table shows that the theoretical number of atoms in the unit cell is in poor agreement with those actually calculated. This is probably due to a poor analysis and the  $\text{Mn}:\text{Pb}$  ratio may then be in

error. The summary of these detailed data, together with the other physical properties, is given in Table 3.

(c) EFFECT OF THE IONS IN THE AA AND AB POSITIONS. The slight systematic changes in the physical properties that occur in the minerals of the libethenite and adelite groups may be explained on the basis of crystal chemistry.

The minerals of the libethenite group (Table 2) are simple compounds with cations  $Cu$  and  $Zn$ , and radicals  $PO_4$ ,  $AsO_4$  and  $OH$ . The ionic radii of  $Cu$  and  $Zn$  are 0.80 Å (estimated) and 0.83 Å, respectively; there are no published values for  $P$  and  $As$ . Since the volumes of the unit cells of libethenite  $Cu_2PO_4(OH)$  and olivenite  $Cu_2AsO_4(OH)$  are nearly identical, it may be assumed that the ionic radii of  $P$  and  $As$  are similar in size. Because the ionic radius of  $Zn$  is greater than that of  $Cu$  and since  $P$  and  $As$  are similar in ionic size, the volume of the  $Zn$  mineral adamite  $Zn_2AsO_4(OH)$  should be larger than that of the  $Cu$  minerals libethenite and olivenite. This is demonstrated from the calculated volumes of libethenite, olivenite and adamite, which are respectively 401 cubic Å, 402 cubic Å and 431 cubic Å.

In both the libethenite and adelite groups the  $c_0$  values are approximately the same and do not show the systematic changes that are found in the  $a_0$  and  $b_0$  values.  $P$  and  $As$  have been shown to possess ionic radii of similar size;  $V$  probably has an ionic radius comparable to  $P$  and  $As$ .

The close relationship between the chemistry and lattice constants of these minerals is also reflected in the similarity of their other physical properties. The specific gravity, hardness, and optical properties are much the same, the greatest variation occurring in the refractive indices (Table 3).

The adelite group affords a better opportunity for examining the effect of the various atoms on the change in lattice constants and physical properties. The minerals composing this group are double salts  $AB(XO_4)Z$  containing cations  $A$  and  $B$  of widely differing ionic radii. Column 5 of Table 2 gives the ionic radii of the cations. It is readily seen that, with the exception of higginsite, there is a progressive increase in the axial ratios, absolute cell edge lengths and volumes from adelite through pyrobelonite (Tables 2 and 3). These increases follow directly from the increased sum of the ionic radii of the cations. The constants of higginsite have a probable error of 1.5%, which would account for the poor agreement with the remaining members of the group.

The lattice constants of adelite, higginsite and austinite should be but slightly different because the sums of the ionic radii of the cation positions ( $Ca$  with  $Mg$  or  $Cu$  or  $Zn$ ) are very nearly identical. As would be

expected, the physical properties of these minerals are similar (Table 3). However, with the introduction of *Pb* and *Mn*, the sums of whose ionic radii are nearly 10% greater than the sums of the ionic radii of the cation pairs above mentioned, the unit cells of duftite, descloizite and pyrobelonite should have lattice constants differing by approximately the same amount. An inspection of Table 3 shows this to be true. It will be noted that the absolute length  $b_0$  is increased greatly with the introduction of *Pb* and *Mn*, indicating that these atoms may be aligned parallel to the  $b$ -axis.

The presence of *Pb* and *Mn* is also reflected in the greatly increased specific gravity and refractive indices of these minerals.

The hardness of the minerals of both the libethenite and adelite groups is remarkably constant. This may be partially explained on the assumption that the intra-atomic spacings, i.e., the distance between the atomic "boundaries," remain the same. This permits the cell volume to increase proportionally to the ionic radii of the cations but allows rupture between atoms to occur with approximately the same ease.

*B. Monoclinic Section.* The minerals which belong to this section are simple  $AAXO_4(Z)$  and double  $ABXO_4(Z)$  salts.

The intimate relationship which exists in the orthorhombic section is not as well defined in the monoclinic species. The systematic changes are not as evident although the general chemical and physical properties unite these minerals and indicate their similarity to other members of the family.

The comparison between species or series is made more easily by adopting the conventional setting  $a_0 > c_0$ . The monoclinic symmetry fixes the position of  $b_0$ . In the sarkinite group, the values of  $b_0$  of sarkinite and triplite are similar; the same is true of triplodite and wagnerite, but in the case of the latter pair  $b_0$  is twice as great as in the former pair.

The relationship between the published morphological setting and the conventional position is correlated by a transformation formula. In all cases but sarkinite, this reorientation involves only an interchange of the  $a$ - and  $c$ -axes.

The physical properties, hardness and density, are quite constant within the various groups, which is to be expected from the similarity of the chemistry.

The optical properties of the minerals within each group are not in close agreement. This is explained by the fact that these properties are sensitive to slight changes in chemical composition. The compositions of the minerals of each group are quite different, so that no close correspondence is to be expected in these properties (Table 4).

TABLE 4. SUMMARY OF THE CHEMICAL AND PHYSICAL PROPERTIES OF THE TILASITE AND SARKINITE GROUPS, AND HERDERITE

Mineral Comp.	Tilasite Group		Durangite NaAlAsO <sub>4</sub> (F)	Herderite CaBePO <sub>4</sub> (F, OH)	Sarkinite Group			
	Tilasite CaMgAsO <sub>4</sub> (F)	Tilasite CaMgAsO <sub>4</sub> (F)			Sarkinite Mn <sub>2</sub> AsO <sub>4</sub> (OH)	Triplite (Mn, Fe) <sub>2</sub> PO <sub>4</sub> (F)	Triplite (Mn, Fe) <sub>2</sub> PO <sub>4</sub> (OH)	Wagnerite Mg <sub>2</sub> (Ca, P)O <sub>4</sub> (F)
<i>a</i> <sub>0</sub>	7.56	7.30		9.80	12.71	12.03	12.24	11.93
<i>b</i> <sub>0</sub>	8.95	8.46		7.68	6.78	6.46	13.35	12.47
<i>c</i> <sub>0</sub>	6.66	6.53		4.80	10.20	10.03	9.88	9.44
<i>a</i> <sub>0</sub> : <i>b</i> <sub>0</sub> : <i>c</i> <sub>0</sub>	0.839:1:0.750	0.856:1:0.772		1.276:1:0.625	1.874:1:1.504	1.862:1:1.553	0.917:1:0.740	0.957:1:0.757
<i>β</i>	120°59'	119°22'		90°06'	108°18'	105°42'	108°14'	108°07'
<i>V</i> <sub>0</sub>	387	352		361	835	751	1535	1334.9
No. of Mol. Space Group	4 5	4 5	$C_{2h}^6-C2/c$	4 5	$C_{2h}^6-P2_1a$ 4-5	$C_{2h}^6-P2_1/a$ 4-5.5	$C_{2h}^6-P2_1/a$ 4.5-5	$C_{2h}^6-P2_1/a$ 5
H	3.68-3.79	3.94-4.03		3.00	4.09-4.32	3.84	3.70	3.07
D	Z = <i>b</i> ; ext. 30°	Y = <i>b</i> ; Z/∧ <i>c</i> = 65°		Y = <i>b</i> ; Z/∧ <i>c</i> = 33°	Y = <i>b</i> ; Z/∧ <i>c</i> = 36°	Y = <i>b</i> ; Z/∧ <i>c</i> = 48°	Y = <i>b</i> ; Z/∧ <i>c</i> = 3°	Y = <i>b</i> ; Z/∧ <i>c</i> = 21°
X	1.640	1.634		1.591	1.793	1.665	1.725	1.569
Y	1.660	1.673		1.611	1.807	1.673	1.726	1.570
Z	1.675	1.685		1.619	1.809	1.682	1.730	1.582
Sign	Negative	Negative		Negative	Negative	Positive	Positive	Positive

The habit is quite uniformly short prismatic with a simple form series, although the elongation is either parallel to the  $c$ - or  $b$ -axes.

(a) TILASITE GROUP. This group contains two minerals, tilasite and durangite, both double salts  $ABXO_4(Z)$  with similar habit, axial ratios and angles, and cell edge lengths. As already pointed out, sphene is homologous with these minerals.

An examination of the lattice constants of tilasite and durangite (Table 4) indicates a rational relationship with adelite and higginsite of the

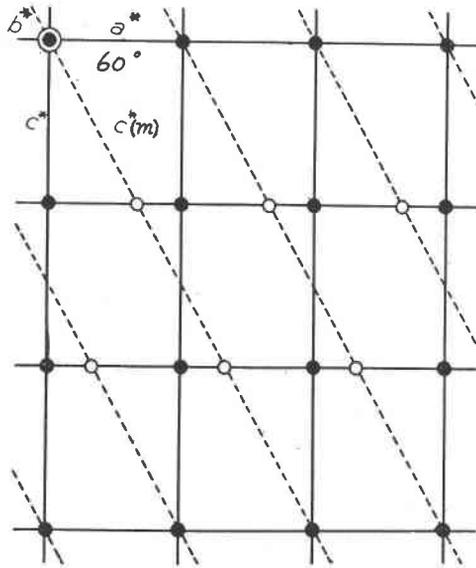


FIG. 2. A reciprocal lattice projection showing the relation of the tilasite group to the minerals of the orthorhombic section.

adelite group. This relationship is shown in Fig. 2. The position of the reciprocal lattice is the second inversion with  $b^*$  vertical. The  $a^*$  and  $b^*$  values of both the adelite and tilasite groups are approximately equal and the tilasite group  $c^*$  is  $[\frac{2}{3}01]$  in the adelite group lattice. In the figure, the tilasite-group reciprocal cell is outlined in dashed lines. The transformation formula of the tilasite-group cell to the adelite-group cell is therefore  $10\frac{2}{3}/010/001$  and from the adelite group to the tilasite group  $10\frac{2}{3}/010/001$ .

*Tilasite.* Strunz (1937) determined the lattice constants and space group of tilasite. In the conventional setting they are:

$$\begin{aligned}
 a_0 &= 7.56 & a_0 : b_0 : c_0 &= 0.839 : 1 : 0.750 ; \beta = 120^\circ 59' \\
 b_0 &= 8.95 & a : b : c &= 0.8454 : 1 : 0.7503 ; \beta = 120^\circ 59\frac{1}{2}' \text{ (morphology)} \\
 c_0 &= 6.66
 \end{aligned}$$

Transformation, Smith and Prior and Strunz-Richmond, 001/0 $\bar{1}$ 0/100; an interchange of the  $a$ - and  $c$ -axes.

Space group  $C_{2h}^6 - C2/c$ .

The cell formula is  $4[\text{CaMgAsO}_4(\text{F})]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
Na <sub>2</sub> O	0.29	0.29	0.005			
MgO	18.22	18.20	0.451	Mg 0.451	3.99	4
CaO	25.32	25.29	0.451	Ca 0.451		
MnO	0.16	0.16	0.002	Mn 0.002	4.02	4
FeO	0.14	0.14	0.002	Fe 0.002		
As <sub>2</sub> O <sub>5</sub>	50.91	50.86	0.221	As 0.442	3.91	4
H <sub>2</sub> O	0.28	0.28		F 0.431	3.83	4
Cl	0.02	0.02		O 1.790	15.82	16
F	8.24	8.23	0.431			
	<hr/>	<hr/>				
	103.58	103.47				
Less O	3.47	3.47				
	<hr/>	<hr/>				
	100.11	100.00				

Specific gravity: measured 3.77; calculated 3.78.

Analysis of tilasite, Långban; analyst Mauzelius (1895).

*Durangite*. Kokkoros (1937) determined the lattice constants and space group of durangite. His data agree well with those obtained by the writer using a crystal of such large size that the accuracy of the resulting data is probably less than that obtained by Kokkoros; for this reason his values are used here.

$$\begin{aligned}
 a_0 &= 7.30 & a_0 : b_0 : c_0 &= 0.856 : 1 : 0.772 ; \beta = 119^\circ 22' \\
 b_0 &= 8.46 & a : b : c &= 0.8532 : 1 : 0.77158 ; \beta = 119^\circ 35' \text{ (morphology)} \\
 c_0 &= 6.53
 \end{aligned}$$

Transformation, Kokkoros and Strunz (1937)—Richmond 001/0 $\bar{1}$ 0/100; an interchange of the  $a$ - and  $c$ -axes.

Space group  $C_{2h}^6 - C2/c$ .

The cell formula is  $4[\text{Na}(\text{Al}, \text{Fe}, \text{Mn})\text{AsO}_4(\text{F})]$  with Al:Fe:Mn = 6:2:1, which is derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
Li <sub>2</sub> O	0.65	0.65	0.022	Li 0.044	4.04	4
Na <sub>2</sub> O	13.06	13.10	0.211	Na 0.422		
Al <sub>2</sub> O <sub>3</sub>	17.19	17.24	0.169	Al 0.338	4.44	4
Mn <sub>2</sub> O <sub>3</sub>	2.08	2.09	0.029	Mn 0.058		
Fe <sub>2</sub> O <sub>3</sub>	9.23	9.26	0.058	Fe 0.116		
As <sub>2</sub> O <sub>5</sub>	53.11	53.20	0.232	As 0.464	4.03	4
F	7.67	7.69	0.405	F 0.405	3.52	4
				O 1.959	17.00	16
	102.99	103.23				
Less O	3.23	3.23				
	99.66	100.00				

Specific gravity: measured 4.07; calculated 4.11.

Analysis of durangite, Durango, Mexico; analyst Hawes (1876).

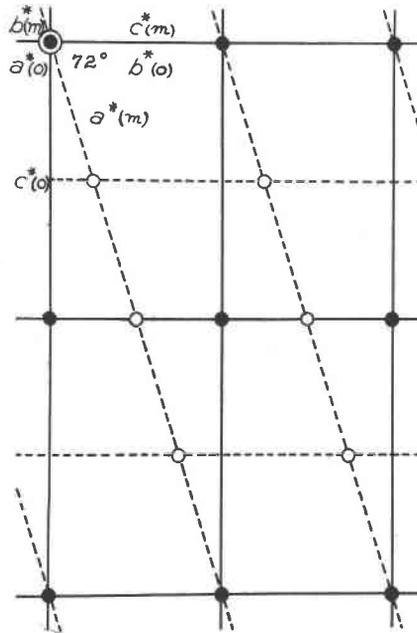


FIG. 3. A reciprocal lattice projection showing the relation of the sarkinite group to the minerals of the orthorhombic section.

(b) SARKINITE GROUP. This group contains four minerals, sarkinite, triplite, triploidite and wagnerite. They are characterized by similar cell edge lengths  $a_0$  and  $b_0$ , with  $b_0$  variable. Their habits vary from prismatic parallel to the  $c$ -axis to prismatic parallel to the  $b$ -axis.

This group is related to the pyrobelonite end of the adelite group. Figure 3 shows the general relationship between the sarkinite and adelite groups; the sarkinite-group cell is outlined by dashes and is projected on the  $a^*-c^*$  plane with  $b^*$  vertical. The adelite-group cell is projected on the  $b^*-c^*$  plane with  $a^*$  vertical. With sarkinite and triplite  $b^*$  is approximately equal to the adelite-group  $a^*$ , while  $b^*$  for triplidite and wagnerite is approximately one-half the adelite-group  $a^*$ . Therefore, the volume of the cell of sarkinite and of triplite must be approximately double that of the orthorhombic cell and contains twice the number of molecules in the unit cell; and the triplidite and wagnerite cells are approximately four times as large and contain four times the molecules in the unit cell. An inspection of Tables 3 and 4 shows this relationship.

The transformation formula from the sarkinite-group cell to the adelite-group cell is  $010/\frac{1}{4}01/\frac{1}{2}00$  and from the adelite-group cell to the sarkinite-group cell  $002/100/01\frac{1}{2}$ .

*Sarkinite*. The  $x$ -ray study was made on an excellent crystal approximately 0.25 mm. in the largest dimension. Rotation and Weissenberg photographs were taken about  $c[001]$  and  $b[010]$ .

A study of the translation distances indicated that the setting adopted by Dana (1892) and Goldschmidt (1897) did not conform to the rule of the three shortest non-coplanar identity periods. If the short diagonal of the morphological cell (in the  $a-c$  plane) is taken as the new  $c$ -axis, all requirements are satisfied. The transformation from Dana and Goldschmidt to Richmond, is therefore,  $\bar{1}0\bar{1}/0\bar{1}0/100$ .

The elements given by Dana and Goldschmidt transformed to the new position are given below with a new angle table of the forms of sarkinite.

TABLE 5. ANGLE TABLE OF THE ACCEPTED FORMS OF SARKINITE

Sarkinite— $Mn_2AsO_4(OH)$							
$a:b:c=1.8642:1:1.5154; \beta=108^\circ 13\frac{1}{2}'$							
$p_0:q_0:r_0=0.8132:1.4393:1; \mu=71^\circ 46\frac{1}{2}'$							
$r_2:p_2:q_2=0.6948:0.5650:1;$							
$p_0'=0.8562, q_0'=1.4393; x_0'=0.3037$							
Form	$\phi$	$\rho$	$\phi_2$	$\rho_2=B$	C	A	
$b$	010	0°00'	90°00'	—	0°00'	90°00'	90°00'
$a$	100	90 00	90 00	0°00'	90 00	71 46 $\frac{1}{2}$	0 00
$p$	120	30 45	90 00	0 00	30 45	80 48	59 15
$o$	011	11 55	55 47	73 06 $\frac{1}{2}$	35 59	54 01	80 10
* $d$	$\bar{1}01$	—90 00	28 55	118 55	90 00	47 08 $\frac{1}{2}$	118 55
$m$	$\bar{1}11$	—21 00	57 02	118 55	38 26 $\frac{1}{2}$	64 59	107 30 $\frac{1}{2}$
$n$	$\bar{4}14$	—56 55 $\frac{1}{2}$	33 24	118 55	72 31	49 33 $\frac{1}{2}$	117 28
$r$	$\bar{1}57$	—28 15 $\frac{1}{2}$	49 24 $\frac{1}{2}$	118 55	48 01	59 38	111 04

\*  $d = a$  (Goldschmidt, 1897)

The lattice constants and space group determined from the Weissenberg photographs are:

$$\begin{aligned} a_0 &= 12.71 & a_0:b_0:c_0 &= 1.874:1:1.504; \beta = 108^\circ 18' \\ b_0 &= 6.78 & a : b : c &= 1.864:1:1.515; \beta = 108^\circ 13\frac{1}{2}' \text{ (morphology)} \\ c_0 &= 10.20 \end{aligned}$$

Transformation Dana (1892) and Goldschmidt (1897)—Richmond  $I\bar{0}I/0I\bar{0}/100$ .

The following reflections give the space group  $C_{2h}^5-C_{21}a$ :

$$\begin{aligned} (hkl) & \text{ with all present} \\ (h0l) & \text{ with } h \text{ even} \\ (0k0) & \text{ with } k \text{ even} \end{aligned}$$

The unit cell contains  $8[\text{Mn}_2\text{AsO}_4(\text{OH})]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
MgO	0.38	0.38	0.001	Mg 0.001	0.02	16
CaO	1.22	1.24	0.022	Ca 0.022	0.47	
MnO	51.92	52.72	0.744	Mn 0.744	15.88	8
As <sub>2</sub> O <sub>5</sub>	41.50	42.14	0.183	As 0.366	7.82	
H <sub>2</sub> O	3.48	3.52	0.195	H 0.390	8.33	8
				O 1.877	40.10	40
	98.50	100.00				

Specific gravity: measured 4.22; calculated 4.21.

Analysis of sarkinite from Pajsberg; analyst Hamberg (1888).

From an examination of analyses of sarkinite there is good evidence that this mineral forms a partial series through the replacement of *As* by *Sb*. In fact, Igelström (1884) gives the name xanthoarsenite to a mineral containing an undetermined percentage of  $\text{Sb}_2\text{O}_5$ .

*Triplite*. The morphology of triplite is unknown, since no measurable crystals have been found. Good cleavage masses are common and may, therefore, be used for *x*-ray examination. A small cleavage fragment was chosen which gave sufficiently good reflections on the cleavage faces to permit the edge between these two cleavages to be oriented as the axis of rotation. These cleavages were assumed to be pinacoidal. Rotation and Weissenberg photographs were taken about what proved to be the  $b[010]$  and  $c[001]$  axes, with the former perpendicular to the best cleavage (010) and the other perpendicular to (001). The results of the measurements and calculations of these photographs give the following lattice constants:

$$\begin{aligned} a_0 &= 12.03 & a_0:b_0:c_0 &= 1.862:1:1.553; \beta = 105^\circ 42' \\ b_0 &= 6.46 & & \text{No morphology.} \\ c_0 &= 10.03 \end{aligned}$$

The space group is  $C_{2h}^5-P2_1/a$  from the following reflections:

( $hkl$ ) with all present  
 ( $h0l$ ) with  $h$  even  
 ( $0k0$ ) with  $k$  even

The unit cell content is  $16[(Mn,Fe)_2PO_4(OH)]$  with Mn:Fe = 8:1 derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
Fe <sub>2</sub> O <sub>3</sub>	0.40	0.40	0.003	Fe''' 0.006	0.10	16
FeO	6.68	6.69	0.093	Fe'' 0.093	1.63	
MnO	53.77	53.80	0.758	Mn 0.758	13.25	
MgO	0.31	0.31	0.008	Mg 0.008	0.14	
CaO	2.17	2.17	0.039	Ca 0.039	0.59	
P <sub>2</sub> O <sub>5</sub>	32.20	32.23	0.227	P 0.454	7.94	8
F	7.58	7.59	0.399	F 0.399	6.98	8
				O 1.841	32.20	32
	103.58	103.19				
Less O	3.19	3.19				
	99.92	100.00				

Specific gravity: measured 3.84; calculated 3.94.

Analysis of triplite from Bagdad, Arizona; analyst F. A. Gonyer (in Hurlbut 1936).

Triplite, as has been shown, represents a series with a varying proportion of Mn:Fe. Minerals, which may be included in this series on the basis of their analyses, are pseudotriplite and sarcopside.

*Triplidite*. A small perfect crystal of triplidite was found in a specimen from Branchville, Connecticut. Rotation and Weissenberg photographs were taken about  $b[010]$  and  $c[001]$ , which gave the following lattice constants:

$$\begin{aligned} a_0 &= 12.24 & a_0:b_0:c_0 &= 0.917:1:0.740 & ; \beta &= 108^\circ 04' \\ b_0 &= 13.35 & a : b : c &= 0.92858:1:0.74627; & \beta &= 108^\circ 14' \\ c_0 &= 9.88 & & & & \text{(morphology)} \end{aligned}$$

Transformation, Dana-Richmond  $100/0\frac{1}{2}0/001$ ; a halving of the  $b$ -axis.

The space group is  $C_{2h}^5-P2_1/a$  from the following reflections:

( $hkl$ ) with all present  
 ( $h0l$ ) with  $h$  even  
 ( $0k0$ ) with  $k$  even

The unit cell formula is  $16 [(Mn, Fe)_2PO_4(OH)]$  with Mn:Fe = 3:1 from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
FeO	14.88	14.90	0.207	Fe } 0.213	7.33	8
CaO	0.33	0.33	0.006	Ca }		
MnO	48.45	48.52	0.684	Mn 0.684	23.56	24
P <sub>2</sub> O <sub>5</sub>	32.11	32.16	0.226	P 0.452	15.56	16
H <sub>2</sub> O	4.08	4.09	0.227	H 0.454	15.63	16
				O 2.274	78.34	80
	99.85	100.00				

Specific gravity: measured 3.697; calculated 3.83.

Analysis of triploidite from Branchville, Connecticut; analyst Penfield (1878).

*Wagnerite* (Cryphiolite). The generally accepted formula of wagnerite was suspected to be in error on the basis of the *x*-ray study. It was found that the unit cell formula was different from that derived from the interpretation of the published analyses. A new analysis was made by F. A. Gonyer of the Harvard Mineralogical Laboratory. The details of the *x*-ray study and a new interpretation of the chemistry are given below.

The lattice constants and chemical composition of wagnerite were determined from portions of the same specimen from the type locality, Werfen, Germany. Rotation and Weissenberg photographs were taken about *c*[001] and *b*[010] axes. The results of the measurements and computations of the photographs give:

$$\begin{aligned}
 a_0 &= 11.93 & a_0 : b_0 : c_0 &= 0.957 : 1 : 0.757 ; \beta = 108^\circ 09' \\
 b_0 &= 12.47 & a : b : c &= 0.9573 : 1 : 0.7530 ; \beta = 108^\circ 07' \text{ (morphology)} \\
 c_0 &= 9.44
 \end{aligned}$$

Transformation, Miller (1879)—Rich 100/0 $\frac{1}{2}$ 0/001; a halving of the *b*-axis.

The halving of the morphological *b*-axis to conform to the absolute cell edge lengths materially simplifies the given indices. It is therefore suggested as the better setting.

The space group is  $C_{2h}^5-P2_1/a$  determined from the following reflections:

$$\begin{aligned}
 (hkl) & \text{ with all present} \\
 (h0l) & \text{ with } h \text{ even} \\
 (0k0) & \text{ with } k \text{ even}
 \end{aligned}$$

The unit cell content was derived from the lattice constants, density (3.153, average of 4 new determinations) and the new analysis. This analysis is similar to many given in the literature, and it is therefore probable that the interpretation of the older analyses has been in error, not the analyses themselves. The older interpretation bracketed the molecular ratio of the whole of the RO constituents as shown below, using Gonyer's analysis as an example.

			Mol. ratio		Atomic ratio	No. of atoms	
MgO	1.178	}	RO	1.283	R	1.283	$2 \times 0.642$
FeO	0.060						
CaO	0.045						
P <sub>2</sub> O <sub>5</sub>	0.283		P <sub>2</sub> O <sub>5</sub>	0.283	P	0.566	$1 \times 0.566$
F	0.500		F	0.500	F	0.500	$1 \times 0.500$
					O	2.448	$4 \times 0.612$

The formula which only approximately fits the atomic ratios is then  $R_2PO_4(F)$ , the generally accepted composition. It is assumed that the unit cell contains 16 molecules of  $R_2PO_4(F)$  by its similarity to tripliodite. The theoretical number of atoms in the cell should then be  $R_{32}$ ,  $P_{16}$ ,  $F_{16}$ ; the actual number found, employing the conventional formula, is  $R_{33.50}$ ,  $P_{14.78}$ ,  $F_{13.05}$ . The agreement is not satisfactory.

Recently Gruner (1938) has shown that in francolite, a carbonate-phosphate, carbon replaces phosphorus. If carbon can replace phosphorus, it is perhaps permissible to consider that calcium can also replace phosphorus. If the latter assumption is made in the case of wagnerite, a formula is obtained which accords fairly well with the unit cell formula. This interpretation is shown in Table 6. Column 8 is the theoretical composition for the suggested formula  $R_{32}(Ca_xP_{16-x}O_{64})F_{16}$ . This formula does not conform exactly to the type formula  $A_2XO_4(Z)$ , which may be generalized to  $R_{32}(Ca_xP_{16-x}O_{64})F_{16-3x}$ . However, when  $x=0$ , we obtain  $16[R_2PO_4(Z)]$ , which conforms to the type formula.

*Cryphiolite* is a name given by Scacchi (1883) to a mineral close to wagnerite in composition but containing 15% CaO. This one analysis was made on 0.07 gram. Zambonini (1910) emphatically states that cryphiolite and wagnerite are identical. An examination of the analyses of wagnerite shows considerable variation in the CaO percentage. It may, therefore, be assumed that cryphiolite is a calcium-rich wagnerite.

TABLE 6. CONTENT OF THE UNIT CELL OF WAGNERITE

	1	2	3	4	5	6	7	8	
MgO	47.56	47.51	1.178	Mg 1.178	} 1.238	31.58	32	49.38	50.50
FeO	4.32	4.32	0.060	Fe 0.060					
CaO	2.53	2.53	0.045	Ca 0.045	0.045	1.15	1		2.20
P <sub>2</sub> O <sub>5</sub>	40.18	40.14	0.283	P 0.566	0.566	14.44	15	43.81	41.70
F	9.51	9.50	0.500	F 0.500	0.500	12.75	13	11.79	9.67
	104.10	104.00		O 2.448	2.448	62.44	64	104.98	104.07
Less O	4.00	4.00	0.250					4.98	4.07
	100.10	100.00						100.00	100.00

Specific gravity: measured 3.153; calculated 3.158.

1. Analysis of wagnerite from Werfen; analyst Gonyer.
2. Analysis calculated to 100%.
3. Molecular proportions.
4. Atomic proportions.
5. Number of atoms in the unit cell.
6. Theoretical number of atoms in the unit cell.
7. Composition of  $Mg_2PO_4F$ .
8. Composition of  $Mg_{32}(Ca, P_{15})O_{64}F_{13}$ .

Strunz (1938) includes cryphiolite as an isotype with durangite, tilasite, and sphene, changing its published orientation to bring out this relationship. This conclusion is not in accord with our findings.

*Herderite*. The lattice constants and space group were determined by Strunz (1936) and are:

$$\begin{aligned} a_0 &= 9.80 & a_0:b_0:c_0 &= 1.276 : 1:0.625 & ; \beta &= 90^\circ 06' \\ b_0 &= 7.68 & a : b : c &= 1.2775:1:0.62457; \beta &= 90^\circ 06' & \text{(morphology)} \\ c_0 &= 4.80 \end{aligned}$$

Space group  $C_{2h}^5 - P2_1/c$ .

Transformation, Durrfeld (1909) and Strunz-Richmond 001/010/300; an interchange of the *a*- and *c*-axes with a tripling of the *c*-axis. Yatskevitch (1935) originally recognized the tripling of the *c*-axis on morphological evidence.

The unit cell formula is  $4[CaBePO_4(F,OH)]$ , with  $OH:F = 1:1$ , from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
CaO	33.67	33.93	0.605	Ca 0.605	3.97	4
BeO	15.51	15.63	0.625	Be 0.625	4.10	4
P <sub>2</sub> O <sub>5</sub>	43.74	44.05	0.310	P 0.620	4.06	4
H <sub>2</sub> O	3.70	3.73	0.207	H 0.414	2.72	4
F	5.27	5.32	0.279	F 0.279	1.83	
				O 2.841	18.62	18
	101.89	102.66				
Less O	2.64	2.66				
	99.25	100.00				

Specific gravity: measured 3.00; calculated 2.96.

Analysis of herderite, Topsham, Maine; analyst Penfield (1886).

Of the monoclinic minerals, herderite shows the least close relation to the orthorhombic minerals. It is probable that herderite is related to the pyrobelonite-end of the adelite group in the following manner.

	<i>Herderite</i>		<i>Pyrobelonite</i>
$a_0$	9.80	$b_0$	9.45
$b_0$	7.68	$a_0$	7.84
$c_0$	4.80	$c_0$	6.09

These are directly comparable since  $\beta$  of herderite is very nearly a right angle ( $90^\circ 06'$ ). The correspondence between the first two terms is reasonably good, but differs considerably in the values for  $c_0$ . This may be due to the differences in size between  $Mn$ ,  $Pb$  ions in the cation positions of pyrobelonite and the  $Ca$  and  $Be$  ions in the cation positions of herderite.

Herderite also represents a series through the interchange of  $F$  and  $OH$ . Two names have been given to members of this series, hydroherderite  $CaBePO_4(OH, F)$ , containing a large percentage of  $H_2O$ , and herderite  $CaBePO_4(F, OH)$ , containing a small percentage of  $F$ .

A summary of the significant physical and chemical properties of the monoclinic minerals is given in Table 4.

*C. Triclinic Section.* There are only two minerals included in this section, amblygonite and tarbuttite. They are not directly comparable but are related to members of other crystallographic sections, as will be shown later.

*Amblygonite.* The  $x$ -ray study was made on a small cleavage fragment of amblygonite from Hebron, Maine. The edge between two cleavages which proved to be  $a(100)$  and  $c(001)$  was set parallel to the axis of rotation, and rotation and Weissenberg photographs were taken about this axis.

The crystal fragment used was polysynthetically twinned ( $\bar{1}01$ ). The interpretation of photographs of such a twin is somewhat more involved than that of a single individual. In this case, the reciprocal lattice projections of the photographs showed two interpenetrating lattices simply related to each other. Values for the translation periods of the axes on the plane of the projections were calculated for each individual, which therefore increased the accuracy of the resulting calculation.

The measurements and calculations of these photographs give the following lattice constants:

$$\begin{array}{ll} a_0 = 4.92 & a_0 : b_0 : c_0 = 0.698 : 1 : 0.699 \\ b_0 = 7.05 & a : b : c = 0.7334 : 1 : 0.7633 \\ c_0 = 4.93 & \alpha = 107^\circ 22', \beta = 97^\circ 27', \gamma = 109^\circ 50' \\ & \alpha = 108^\circ 51', \beta = 97^\circ 48', \gamma = 106^\circ 27' \text{ (morphology)} \end{array}$$

Space group  $C_1^1 - P\bar{1}$ .

The geometrical elements and the lattice constants determined by  $x$ -ray methods are not in close agreement. The morphological elements were made on large coarse crystals, probably with a contact goniometer. The measurements and calculations therefore must be only approximate.

The writer believes that the calculations of the elements as given above, derived from the  $x$ -ray study, are an added refinement to the original work and therefore proposes that these new elements be adopted.

Amblygonite is apparently related to herderite and therefore the pyrobelonite end of the adelite group. The relationship is complex but may be compared through the following reciprocal lattice projection elements:

*Amblygonite*

$$a^* = 0.336$$

$$b^* = 0.257$$

$$c^* = 0.322$$

*Herderite*

$$a^* = 0.157$$

$$b^* = 0.201$$

$$c^* = 0.320$$

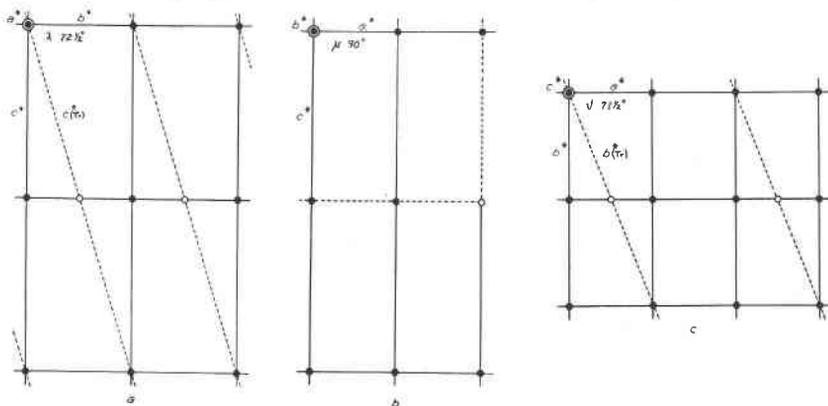


FIG. 4. Reciprocal lattice projections showing the relation of amblygonite to herderite. Solid lines represent the reciprocal cell of herderite, the dotted lines that of amblygonite. Figure 4a is projected on the  $c^*-b^*$  plane; figure 4b on the  $a^*-c^*$  plane; figure 4c on the  $a^*-b^*$  plane.

Figures 4 a, b, c indicate approximately the axial relationships. It will be noted that  $\mu$  is assumed to be  $90^\circ$  whereas the actual value is  $82^\circ 33'$ . There is also poor agreement between the two  $b^*$  values.

The unit cell formula is  $2[(\text{Li,Na})\text{AlPO}_4(\text{F,OH})]$  with  $\text{F}:\text{OH}=1:1$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
$\text{Al}_2\text{O}_3$	33.90	34.25	0.336	Al 0.672	1.85	2
$\text{Li}_2\text{O}$	9.24	9.34	0.312	Li 0.624	1.72	2
$\text{Na}_2\text{O}$	0.66	0.66	0.011	Na 0.022	0.61	
$\text{P}_2\text{O}_5$	47.44	47.90	0.337	P 0.674	1.86	2
$\text{H}_2\text{O}$	5.05	5.11	0.284	H 0.568	1.57	2
F	5.45	5.51	0.289	F 0.287	0.79	
				O 3.039	8.31	10
	101.74	102.77				
Less O	2.73	2.77				
	99.91	100.00				

Specific gravity: measured 3.032; calculated 3.18.

Analysis of amblygonite from Hebron, Maine; analyst Penfield (1879).

*Amblygonite Series.* Amblygonite is a name applied to a series covering a wide range of chemical variations. These variations are sufficiently systematic to enable one to form a series of very definite compounds, all of which have similar structures as shown by identical powder photographs.

In this series there is a double exchange of cations and elements of the hydroxyl radical. The general formula  $(Li,Na)AlPO_4(F,OH)$  expresses this interchange wherein *Li* and *Na*, *F* and *OH* replace each other statistically. From fifteen analyses of amblygonite in Doelter (1918), three from Quensel (1937) and one from Schaller (1912), the molecular ratios of *Li* and *Na* vary from 100:1 to 1:1; the *F* and *OH* vary from 25:1 to 1:8.

Three names have been given by various writers to certain of the intermediate members of the series: amblygonite, containing a low percentage of  $Na_2O$  and  $H_2O$ ; montebrasite, containing a low percentage of  $Na_2O$  but a large percentage of  $H_2O$ ; fremontite, containing a high percentage of  $Na_2O$  and approximately equal amounts of *F* and  $H_2O$ .

Quensel (1937) proposes to limit amblygonite to a compound with *F* content varying from 8–13%, with  $H_2O$  less than 3% and a specific gravity of 3.06; montebrasite to be used for a mineral with *F* less than 8%, with water more than 3% and the specific gravity less than 3.06. The writer is in accord with this division since it represents a well-defined partition in the series and also corresponds to the original separation proposed by Descloizeaux (1872). Therefore the three minerals may be designated by the following names and formulae:

amblygonite (Li, Na)  $AlPO_4$  (F, OH)  
 montebrasite (Li, Na)  $AlPO_4$  (OH, F)  
 fremontite (Na, Li)  $AlPO_4$  (F=OH)

*Tarbuttite.* The reorientation, lattice constants and space group were previously published by the writer (1938) and are repeated below:

$$\begin{array}{ll} a_0 = 8.097 & a_0 : b_0 : c_0 = 0.6271 : 1 : 0.5957 \\ b_0 = 12.91 & a : b : c = 0.6296 : 1 : 0.5971 \\ c_0 = 7.688 & \alpha = 89^\circ 34\frac{1}{2}', \beta = 91^\circ 37\frac{1}{2}', \gamma = 107^\circ 47' \\ & \alpha = 89^\circ 37\frac{1}{2}', \beta = 91^\circ 28\frac{1}{2}', \gamma = 107^\circ 41' \text{ (morphology)} \end{array}$$

Space group  $C_1^1 - P\bar{1}$ .

Tarbuttite appears to be related to the libethenite group. A reciprocal lattice projection of the zero-layer line of average values for the libethenite group indicates the following relationship:

Tarbuttite	Libethenite Group
$a^* = .200$	$a^* = .190$
$b^* = .125$	$\frac{1}{2}[\frac{1}{2}01]^* = .130$
$c^* = .200$	$b^* = .181$

} 72°

The angles  $\lambda$ ,  $\mu$  are approximately  $90^\circ$  so that the axial directions  $a$  and  $c$  of tarbuttite may be assumed to nearly coincide with the axial directions  $a$  and  $b$  of the libethenite group.

The unit cell formula is  $8[\text{Zn}_2\text{PO}_4(\text{OH})]$  derived from the following table:

	Analysis		Proportions		No. of atoms per unit cell	
	Reported	Calculated to 100%	Molecular	Atomic	Actual	Theory
ZnO	66.6	66.9	0.822	Zn 0.822	15.81	16
P <sub>2</sub> O <sub>5</sub>	29.2	29.3	0.205	P 0.410	7.89	8
H <sub>2</sub> O	3.8	3.8	0.212	H 0.424	8.14	8
				O 2.059	39.50	40
	99.6	100.0				

Specific gravity: measured 4.15; calculated 4.37.

Analysis of tarbuttite, Broken Hill mines, H. W. Rhodesia; analyst L. J. Spencer (1908).

A summary of the chemical and physical properties of amblygonite and tarbuttite is given in Table 7.

TABLE 7. SUMMARY OF THE CHEMICAL AND PHYSICAL PROPERTIES OF THE TRICLINIC MINERALS

<i>Mineral</i>	<i>Amblygonite</i>	<i>Tarbuttite</i>		
<i>Comp.</i>	(Li, Na) AlPO <sub>4</sub> (F, OH)	Zn <sub>2</sub> PO <sub>4</sub> (OH)		
$a_0$	4.92	8.097		
$b_0$	7.05	12.91		
$c_0$	4.93	7.688		
$a_0:b_0:c_0$	0.698:1:0.699	0.6271:1:0.5957		
$\alpha$	107°22'	89°34½'		
$\beta$	97°27'	91°37½'		
$\gamma$	109°50'	107°47'		
$V_0$	151	765		
No. of Mol.	2	8		
Space Group	$C_2^1-PI$	$C_2^1-PI$		
H	6	3.7		
D	3.01-3.09	4.15		
Opt. Orient.		$\phi$	$\rho$	
X	1.603	7°	58°	1.660
Y	1.613	159	25	1.705
Z	1.626	-86	80	1.713
Sign	Positive	Negative		

### III. MINERALS PREVIOUSLY CLASSIFIED WITH MEMBERS OF THIS TYPE

The writer has not examined the following minerals by  $x$ -ray methods, but from the data available he tentatively places them in their proper relation to minerals of this or other types.

*Cornetite*. A mineral described by Groth and Mieleitner (1921) from Katanga, Belgian Congo, is said to be isomorphous with libethenite with a formula  $(Cu,Co)CuPO_4(OH)$ . Schoep (1921) showed that the *Co* was due to admixed heterogenite. Carefully selected material was analyzed by Hutchinson and MacGregor (1921), leading to the composition  $13 CuO \cdot 2P_2O_5 \cdot 7H_2O$ . This mineral does not conform to the type formula, is therefore not isomorphous with libethenite and cannot be considered a mineral of the chemical type.

*Araoxen*. An analysis by Bergemann (1857) gives the weight percentage of  $V_2O_5$  and  $As_2O_5$  as essentially equal. The formula derived from this analysis is  $ZnPb(V,As)O_4(OH)$ . Analyses of descloizite give percentages of  $As_2O_5$  varying from 0.20–4.78 per cent. Araoxen may, therefore, be considered as an arsenian variety of the descloizite series.

*Brackebuschite*. A comparison of the analyses by Doering (1880) with that of pyrobelonite indicates that brackebuschite  $(Pb,Mn)_2VO_4(OH)$  with  $Pb:Mn=2:1$  and pyrobelonite  $(Mn,Pb)_2VO_4(OH)$  with  $Mn:Pb=3:2$  form a series.

*Spodiosite*. Tiborg (1885), Sjögren (1885), and Nordenskjöld (1893) give various formulae for this mineral. It is likely that spodiosite is related to wagnerite with *Mg* replaced by *Ca*, although no new work has been done to verify this conclusion.

*Calciovolborthite* (tangeite). No adequate material was available for x-ray determination. From the analysis by Nenadkewitsch and Wolkow (1926) the composition is  $2CaO \cdot 2CuO \cdot V_2O_5 \cdot H_2O$  or  $2CaCuVO_4(OH)$ . This mineral belongs in the adelite group and is closely related to higginite  $CaCuAsO_4(OH)$ .

*Pseudotriplite*. A comparison of the analysis by Delffs (1894) with that of triplite indicates that pseudotriplite is an iron-rich triplite and a member of that series.

*Allauaudite*. The analysis by Damour (1848) indicates that allauaudite is a member of the triphylite series and, therefore, does not conform to the type.

*Sarcopside*. The analysis by Holden (1920) indicates that sarcopside  $(Fe,Mn,Ca)_2PO_4(F)$  is closely related to triplite  $(Fe,Mn)_2PO_4(F)$  differing only in essential amounts of *Ca*. It may, therefore, be considered as a member of the triplite series.

*Xanthoarsenite*. An analysis by Igelström (1884) indicates this mineral contains *Sb*, but his analysis groups together the percentages of  $As_2O_5$  and  $Sb_2O_5$ . Analyses of sarkinite show per cents of  $Sb_2O_5$  up to 1.37%. Since no definite amount of  $Sb_2O_5$  is given, xanthoarsenite  $Mn_2(As,Sb)O_4(OH)$  must be considered a doubtful species and, if retained, should be classed as an antimonian variety of sarkinite.

*Melanchlor*. This alteration product of triplite, described by Fuchs (1839), is essentially an hydrous phosphate of ferric iron with no definite formula.

*Morinite and Soumansite*. These are alteration products of amblygonite forming hydrous compounds of complex composition but do not belong to the type.

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